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Instytut Chemii i Elektrochemii Technicznej
Zakład Elektrochemii Stosowanej

Elektrochemiczna redukcja tlenu w elektrolitach: wodnym i na bazie mieszanin DMSO-woda

Katarzyna Jolanta Szwabińska

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Promotor: prof. dr hab. inż. Grzegorz Lota

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"I have built this house (...) not to have a magnificent building for my residence, but in order to make something beautiful."

- J. C. Jacobsen, twórca browaru Carlsberg, o swojej posiadłości, której honorowym rezydentem w latach 1931-1962 był Niels Bohr

Niniejszą rozprawę doktorską dedykuję moim Dziadkom:

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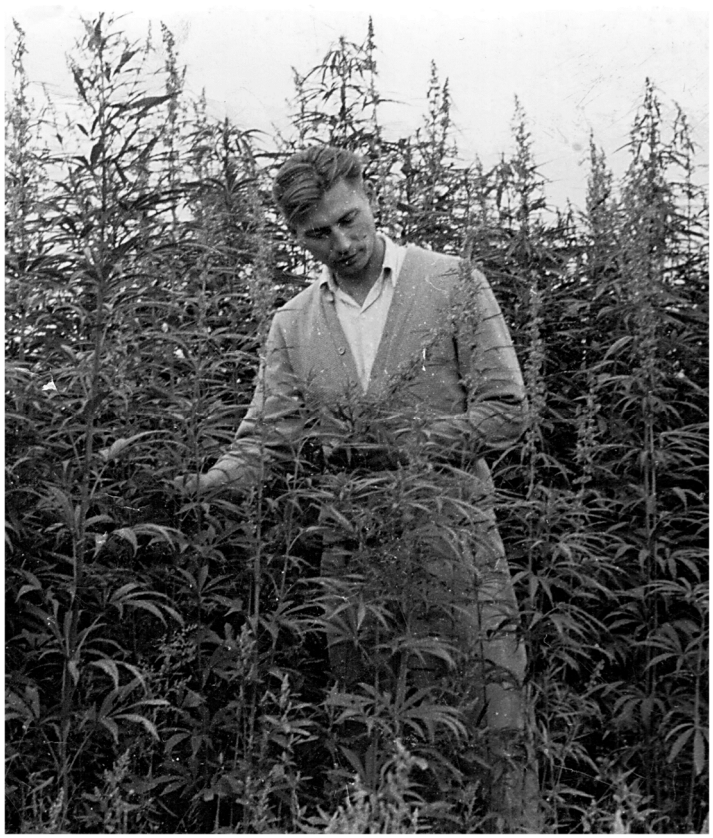


Streszczenie

Niniejsza praca podejmuje tematykę procesu elektrochemicznej redukcji tlenu, który stanowi podstawę funkcjonowania ogniw paliwowych oraz ogniw metal-powietrze.

Część literaturowa pracy (Rozdziały 1 i 2) przedstawia aktualny stan wiedzy na temat zagadnień związanych z rozprawą doktorską.

W Rozdziale 1 zamieszczono podstawowe informacje na temat procesu elektroredukcji tlenu oraz omówiono możliwe mechanizmy tego procesu w elektrolitach wodnych i w elektrolitach niewodnych (aprotycznych lub w obecności donora protonu). Opisano także elektrochemiczną redukcję tlenu na różnych materiałach węglowych, ukazując wpływ struktury materiału na przebieg tego procesu.

Rozdział 2 dotyczy podstawowych technik stosowanych podczas badań nad elektroredukcją tlenu, którymi są metoda wirującej elektrody dyskowej oraz metoda wirującej elektrody dyskowo-pierścieniowej. Poza zasadą działania obu tych technik, omówiono także ich podstawowe założenia oraz ograniczenia w ich stosowaniu.

Część doświadczalna pracy (Rozdziały 3 i 4) dotyczy elektrochemicznej redukcji tlenu przebiegającej na węglu szklistym w elektrolicie alkalicznym wodnym oraz elektrolitach alkalicznych powstałych na bazie mieszanin dwuskładnikowych dimetylosulfotlenek-woda.

W Rozdziale 3 zaprezentowano jaki wpływ na wyniki badań nad redukcją tlenu uzyskiwane przy zastosowaniu wirującej elektrody dyskowo-pierścieniowej wywiera kinetyka reakcji utleniania nadtlenku wodoru. Potwierdzono, że w elektrolicie alkalicznym wodnym utlenianie H_2O_2 na pierścieniu platynowym pokrytym tlenkami przebiega w warunkach mieszanej kontroli dyfuzyjno-kinetycznej, podczas gdy teoria metody wirującej elektrody dyskowo-pierścieniowej wymaga, aby reakcja na elektrodzie pierścieniowej była kontrolowana czysto dyfuzyjnie. Udowodniono, że stosunek mierzonego natężenia prądu na elektrodzie pierścieniowej do natężenia prądu, które byłoby obserwowane w warunkach całkowitej kontroli dyfuzyjnej zmienia się monotonicznie wraz ze zmianą szybkości wirowania elektrody. Zaprezentowano, że dla potencjału równego 1,2 V_{RHE} stosunek ten wynosi odpowiednio 79,9% i 61,4% dla częstotliwości 400 rpm oraz 2500 rpm. Wykazano, że takie odchylenia prowadzą do zawyżonych wartości liczby elektronów wymienianych podczas procesu elektroredukcji tlenu oraz uniemożliwiają poprawne określenie mechanizmu tego procesu. Aby wyeliminować błąd wynikający z niepełnej kontroli dyfuzyjnej reakcji na pierścieniu zaproponowano nową procedurę opartą o metodę Koutecký'ego-Levicha, która to procedura nie była nigdy dotąd stosowana ani opisywana w literaturze.

Rozdział 4 poświęcono elektrochemicznej redukcji tlenu w elektrolitach na bazie mieszanin dwuskładnikowych DMSO-woda, które zawierały od 0,0 do 93,3 obj.% DMSO. Stosując metodę wirującej elektrody dyskowej, zaprezentowano, że liczba elektronów wymienianych podczas elektroredukcji tlenu stopniowo wzrasta, gdy udział DMSO rośnie od 0,0 do 50,0 obj.%. Wykazano, że bez dodatku dimetylosulfotlenku redukcja O_2 przy potencjale -1,5 V vs. Hg/HgO przebiega głównie jako proces dwuelektronowy (n = 2,28

dla 400 rpm, n = 2,21 dla 2500 rpm), natomiast w obecności 50 obj.% DMSO zaobserwowano zmianę charakteru procesu w kierunku pełnej czteroelektronowej redukcji (n = 3,70 dla 400 rpm, n = 2,78 dla 2500 rpm). Nietypowy przebieg elektroredukcji tlenu w elektrolitach na bazie mieszanin DMSO-woda powiązano z obecnością w tego typu elektrolitach kompleksów międzycząsteczkowych ($DMSO{\cdot}2H_2O$) charakteryzujących się dużym momentem dipolowym.

Abstract

This thesis concerns the oxygen reduction reaction (ORR), which is the fundamental process for the operation of fuel cells and metal-air batteries.

The first part of the work (Chapters 1 and 2) is the literature review presenting the current state of knowledge for dissertation-related issues.

In Chapter 1 elementary information on oxygen electroreduction is provided as well as possible mechanisms of this process in aqueous and non-aqueous electrolytes (aprotic or with the addition of proton donor) are discussed. Electrochemical oxygen reduction on various carbon materials is also described, showing the relation between the structure of the material and the course of the process.

Chapter 2 is devoted to the basic techniques applied for research on oxygen electroreduction, which are the rotating disk electrode method and rotating ring-disk electrode method. Apart from working principles of these techniques, their underlying assumptions and limitation in their use are also presented.

The experimental part of the work (Chapters 3 and 4) concerns the electrochemical oxygen reduction on glassy carbon electrode both in alkaline aqueous electrolyte and in alkaline electrolytes based on dimethyl sulfoxide-water binary mixtures.

In Chapter 3 the impact of hydrogen peroxide oxidation kinetics on the results of oxygen electroreduction studies performed using rotating ring-disk electrode is presented. It has been confirmed that in alkaline aqueous electrolyte H_2O_2 oxidation on oxide-covered Pt ring undergoes under mixed diffusion-kinetic control, whereas the theory of the rotating ring-disk electrode method requires the ring reaction to be purely controlled by diffusion. It has been proved that the ratio of the empirical ring current to corresponding ring current under pure diffusion control varies monotonically with rotation rate of the electrode. It has been demonstrated that at 1.2 V_{RHE}, the ratio is equal to 79.9% and 61.4% at 400 rpm and 2500 rpm, respectively. Such deviations have been proved to prevent the correct diagnosis of ORR mechanism and lead to overestimated electron transfer number values. To eliminate the error in RRDE measurements, novel procedure based on the Koutecký-Levich method has been proposed, which has not been reported yet.

Chapter 4 is devoted to electrochemical oxygen reduction in electrolytes based on DMSO-water binary mixtures of various compositions ranging from 0.0 to 93.3 vol.% DMSO. Using rotating disk electrode method, it has been demonstrated that electron transfer number for oxygen electroreduction process gradually increases when DMSO content is raised from 0.0 to 50.0 vol.%. As has been shown, in the absence of dimethyl sulfoxide, the oxygen electroreduction at -1.5 V vs. Hg/HgO proceeds mainly as a two-electron process (n = 2.28 at 400 rpm, n = 2.21 at 2500 rpm), whereas when DMSO constitutes 50 vol.% of the binary mixture, the shift towards complete four-electron reduction has been observed (n = 3.70 at 400 rpm, n = 2.78 at 2500 rpm). The abnormal course of oxygen electroreduction in electrolytes based on DMSO-water mixtures has been

related to the fact that intermolecular complexes ($DMSO{\cdot}2H_2O$) of high dipole moment value are present in these electrolytes.

Spis treści

Wykaz symboli i skrótów

AC	węgiel aktywny (ang. *activated carbon*)
at. %	stężenie procentowe atomowe
c	stężenie substancji elektroaktywnej w głębi elektrolitu (ang. *bulk concentration*)
$c_{H_2O_2}$	stężenie nadtlenku wodoru
c_{O_2}	stężenie tlenu
CNTs	nanorurki węglowe (ang. *carbon nanotubes*)
c^0	stężenie substancji elektroaktywnej przy powierzchni elektrody
D	współczynnik dyfuzji substancji elektroaktywnej
DFT	teoria funkcjonału gęstości (ang. *density functional theory*)
DMSO	dimetylosulfotlenek
D_{O_2}	współczynnik dyfuzji tlenu
E_D	potencjał elektrody dyskowej (ang. *disk potential*)
$E_{Hg/HgO}$	potencjał względem tlenkowo-rtęciowej elektrody odniesienia
$E^{\circ}_{Hg/HgO}$	standardowy potencjał tlenkowo-rtęciowej elektrody odniesienia
E_R	potencjał elektrody pierścieniowej (ang. *ring potential*)
E_{RHE}	potencjał względem odwracalnej elektrody wodorowej
f	częstotliwość wirowania elektrody
F	stała Faradaya
HMRDE	wirująca elektroda dyskowa dotykająca jedynie menisku elektrolitu (ang. *hanging meniscus rotating disk electrode*)
HOPG	wysoce zorientowany grafit pirolityczny (ang. *highly oriented pyrolytic graphite*)
i	natężenie prądu
i_D	natężenie prądu na elektrodzie dyskowej (ang. *disk current*)
$i_{D,k}$	natężenie prądu na elektrodzie dyskowej w warunkach całkowitej kontroli kinetycznej
$i_{D,l,c}$	natężenie prądu na elektrodzie dyskowej w warunkach całkowitej kontroli dyfuzyjnej
i_k	natężenie prądu kinetycznego (ang. *kinetic current*)
i_R	natężenie prądu na elektrodzie pierścieniowej (ang. *ring current*)
$i_{R,k}$	natężenie prądu na elektrodzie pierścieniowej w warunkach całkowitej kontroli kinetycznej
$i_{R,l,c}$	natężenie prądu na elektrodzie pierścieniowej w warunkach całkowitej kontroli dyfuzyjnej
izoterma BET	izoterma Brunauera, Emmetta i Tellera
j	gęstość natężenia prądu

j_D	gęstość natężenia prądu na elektrodzie dyskowej (ang. *disk current density*)
$j_{D,k}$	gęstość natężenia prądu na elektrodzie dyskowej w warunkach całkowitej kontroli kinetycznej
$j_{D,l,c}$	gęstość natężenia prądu na elektrodzie dyskowej w warunkach całkowitej kontroli dyfuzyjnej
j_k	gęstość natężenia prądu kinetycznego (ang. *kinetic current density*)
j_R	gęstość natężenia prądu na elektrodzie pierścieniowej (ang. *ring current density*)
$j_{R,k}$	gęstość natężenia prądu na elektrodzie pierścieniowej w warunkach całkowitej kontroli kinetycznej
$j_{R,l,c}$	gęstość natężenia prądu na elektrodzie pierścieniowej w warunkach całkowitej kontroli dyfuzyjnej
k	stała szybkości reakcji
K	stała równowagi
K_a	stała dysocjacji kwasu
k_s	standardowa stała szybkości reakcji
LSV	woltamperometria z liniowo zmieniającym się potencjałem (ang. *linear sweep voltammetry*)
mas. %	stężenie procentowe masowe
mol. %	stężenie procentowe molowe
n	liczba wymienianych elektronów (ang. *electron transfer number*)
N	współczynnik efektywności zbierania (ang. *collection efficiency*)
NAD^+	forma utleniona dinukleotydu nikotynoamidoadeninowego (ang. *nicotinamide adenine dinucleotide*)
N-GNS	nanopłatki grafenu domieszkowane azotem (ang. *nitrogen-doped graphene nanosheets*)
n_{RRDE}	liczba wymienianych elektronów wyznaczona za pomocą RRDE
n_∞	liczba wymienianych elektronów dla $\omega \rightarrow \infty$
obj. %	stężenie procentowe objętościowe
OCP	potencjał obwodu otwartego (ang. *open circuit potential*)
ORR	elektroredukcja tlenu (ang. *oxygen reduction reaction*)
Ox	utleniacz
p_{O_2}	ciśnienie parcjalne tlenu
R	całkowity promień elektrody wirującej (z uwzględnieniem obecności izolatora wokół przewodzącego dysku lub pierścienia)
Red	reduktor
RDE	wirująca elektroda dyskowa (ang. *rotating disk electrode*)
Re	liczba Reynoldsa
Re_{kr}	krytyczna liczba Reynoldsa
RHE	odwracalna elektroda wodorowa (ang. *reversible hydrogen electrode)*

rpm	liczba obrotów na minutę (ang. *revolutions per minute)*
RRDE	wirująca elektroda dyskowo-pierścieniowa (ang. *rotating ring disk electrode*)
r_1	promień elektrody dyskowej
r_2	wewnętrzny promień elektrody pierścieniowej
r_3	zewnętrzny promień elektrody pierścieniowej
R^2	współczynnik determinacji
t	czas
TBAP	nadchloran tetrabutyloamoniowy (ang. *tetrabutylammonium perchlorate*)
UV	ultrafiolet
XPS	spektroskopia fotoelektronów w zakresie promieniowania X (ang. *X-ray photoelectron spectroscopy*)
α	współczynnik symetrii reakcji elektrodowej
δ	grubość warstwy dyfuzyjnej
ε_r	stała dielektryczna
η	lepkość dynamiczna
ν	lepkość kinematyczna
ρ	gęstość
ω	częstość kołowa obrotu elektrody

Wprowadzenie

Wysoki efekt energetyczny związany z przyłączeniem elektronów do cząsteczkowego tlenu oraz powszechność jego występowania są powodem, dla którego redukcja tlenu jest wykorzystywana przez człowieka do konwersji energii chemicznej w bardziej użyteczną dla niego energię elektryczną. Do przekształcenia takiego dochodzi w ogniwach metal-powietrze, a także w ogniwach paliwowych, gdzie jako donor elektronów przyłączanych do cząsteczki O_2 wykorzystuje się np. wodór bądź metanol.

Chociaż ogniwa paliwowe są powszechnie kojarzone z nowoczesnymi technologiami i innowacyjnością, to tak naprawdę zostały wynalezione już ponad 150 lat temu. Największą przeszkodą dla ich szerokiego wykorzystania jest konieczność stosowania drogich katalizatorów (bazujących przede wszystkim na platynie), które wymagane są do zwiększenia szybkości, z natury powolnego, procesu elektroredukcji tlenu (ORR – ang. *oxygen reduction reaction*) przebiegającego na katodzie.

Proces elektroredukcji tlenu limituje działanie całego ogniwa paliwowego. Stąd olbrzymi wysiłek został dotychczas poświęcony poszukiwaniu nowych, stosunkowo tanich katalizatorów procesu ORR. Według ostatnich doniesień zamiennikami katalizatorów opartych na platynie mogą stać się materiały węglowe.

Głównym problemem związanym z materiałami węglowymi stosowanymi jako katalizatory procesu ORR jest fakt, że przeważnie nie zapewniają one całkowitej redukcji tlenu, co negatywnie wpływa na wydajność elektrochemicznej konwersji energii. Aby rozwiązać ten problem, zaproponowano wiele metod modyfikacji materiałów węglowych, takich jak zwiększanie liczby defektów obecnych w materiale węglowym oraz wprowadzanie do jego struktury heteroatomów. Dla porównania, niewielką uwagą przywiązuje się do elektrolitu, pomimo tego, że powszechnie wiadomym jest, iż zarówno materiał elektrodowy, jak i skład elektrolitu warunkują proces ORR przebiegający na granicy faz elektroda/elektrolit.

W ramach niniejszej pracy jako media dla procesu ORR przebiegającego na elektrodzie z węgla szklistego przetestowane zostały elektrolity na bazie mieszanin dwuskładnikowych dimetylosulfotlenek-woda. Elektrolity takie mogą oferować nowe możliwości w porównaniu do konwencjonalnych elektrolitów wodnych, z uwagi na obecność międzycząsteczkowych kompleksów $DMSO{\cdot}2H_2O$ o dużym momentem dipolowym.

Niniejsza praca dotyczy także metodologii badań nad elektroredukcją tlenu przy zastosowaniu wirującej elektrody dyskowo-pierścieniowej. Matematyczny opis metody owej metody został wyprowadzony przy szeregu założeń. Jednym z nich jest wymóg, aby reakcja na elektrodzie pierścieniowej przebiegała w warunkach pełnej kontroli dyfuzyjnej

Wraz z rosnącym zainteresowaniem technologią ogniw paliwowych, metoda wirującej elektrody dyskowo-pierścieniowej stała się wiodącą metodą oceny aktywności elektrokatalitycznej różnego rodzaju katalizatorów elektroredukcji tlenu, zarówno katalizatorów bazujących na platynie i innych metalach szlachetnych, jak również tlenków

metali przejściowych, kompleksów metaloorganicznych oraz materiałów węglowych. Niestety najczęściej spotykanym podejściem jest stosowanie metody wirującej elektrody dyskowo-pierścieniowej do badań nad procesem ORR bez żadnej weryfikacji, czy reakcja na elektrodzie pierścieniowej jest faktycznie całkowicie kontrolowana przez dyfuzję. W ramach niniejszej pracy przeanalizowano jak fakt, że takie założenie nie jest spełnione wpływa na wyniki badań nad procesem ORR uzyskiwane za pomocą tej metody.

I

Część literaturowa

1. Elektrochemiczna redukcja tlenu

1.1 Potencjał redukcji tlenu

Elektrochemiczna redukcja tlenu jest procesem uprzywilejowanym termodynamicznie. Potencjał standardowy dla całkowitej redukcji tlenu w środowisku kwaśnym równy jest 1,23 V. Wartość taka sugeruje, że tlen cząsteczkowy charakteryzuje się silnymi właściwościami utleniającymi, a także wskazuje, że stanowi on atrakcyjny substrat reakcji katodowej w ogniwie, w którym energia chemiczna przekształcana jest w energię elektryczną, szczególnie jeżeli wziąć pod uwagę, że całkowita redukcja O_2 wiąże się z przyłączeniem aż czterech elektronów [1].

Dla porównania absolutny potencjał standardowy dla całkowitej redukcji tlenu w środowisku kwaśnym wynosi aż 5,67 V [2]. Innymi słowy, przyłączenie czterech elektronów do cząsteczki O_2 związane jest z efektem energetycznym -2188 kJ/mol O_2. Należy jednak mieć na uwadze, że koncept absolutnego potencjału standardowego zakłada, że przyłączane elektrony występują w stanie wolnym (są zawieszone w próżni). W rzeczywistości, aby móc przyłączyć elektrony do cząsteczki O_2 trzeba je wcześniej odłączyć od innych cząsteczek lub indywiduów chemicznych, co związane jest z pracą. Dlatego też wypadkowy efekt energetyczny uzależniony jest od wyboru donora elektronów i może znacznie odbiegać od wartości wyznaczonej na podstawie absolutnego potencjału standardowego.

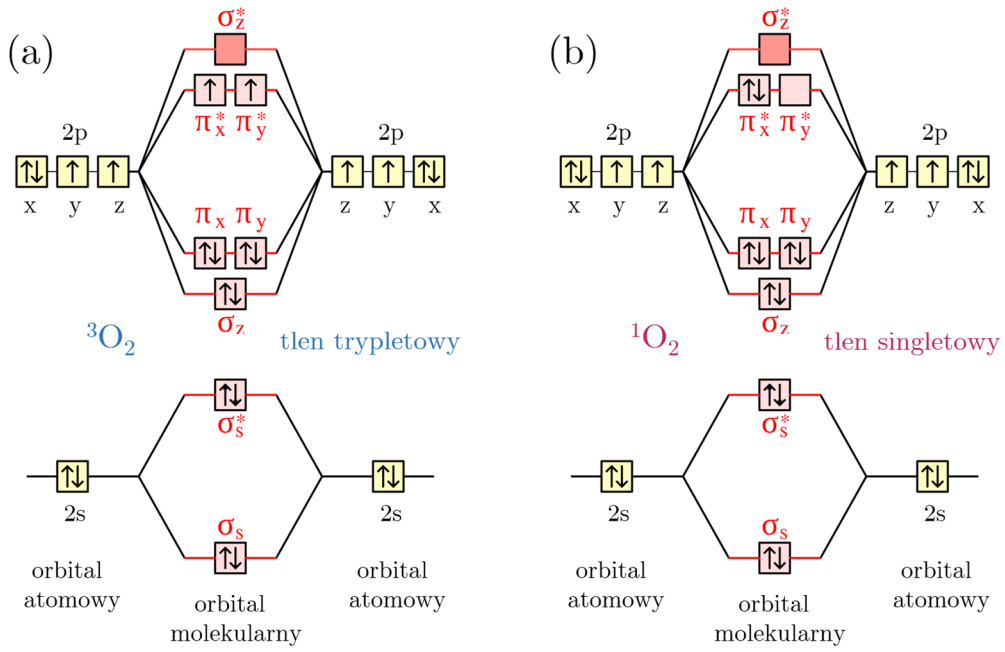
Wartości potencjału standardowego (skala względna) oraz absolutnego potencjału standardowego (skala bezwzględna) redukcji tlenu dotyczą termodynamiki tego procesu, czyli określają położenie stanu równowagi. Jednak o szybkości, z jaką układ dąży do stanu równowagi decyduje kinetyka, która w przypadku elektroredukcji tlenu nie jest korzystna [3].

1.2 Stan trypletowy i singletowy tlenu a jego właściwości utleniające

Jak przedstawiono na Rysunku 1, cząsteczka tlenu w stanie podstawowym posiada dwa niesparowane elektrony, które znajdują się na podwójnie zdegenerowanym poziomie energetycznym antywiążących orbitali π^* [4]. Dwa niesparowane elektrony oznaczają, iż tlen cząsteczkowy w stanie podstawowym występuję w stanie trypletowym, odwrotnie niż dla większości znanych indywiduów chemicznych, dla których stanem o najniższej energii jest stan singletowy, czyli stan bez niesparowanych elektronów [4].

Nawet częściowa redukcja tlenu do nadtlenku wodoru wymaga, aby do cząsteczki O_2 zostały przyłączone dwa elektrony pochodzące od cząsteczki (lub innego indywiduum) ulegającego utlenieniu. Co istotne, konieczne jest, aby te dwa elektrony posiadały równoległe

spiny, skierowane przeciwnie do spinów dwóch niesparowanych elektronów obecnych w cząsteczce tlenu na orbitalach antywiążących π*. Zatem, aby doszło do przeniesienia elektronów między tlenem cząsteczkowym a cząsteczką utlenianą, konieczne jest wcześniejsze odwrócenie spinu jednego z elektronów cząsteczki utlenianej, czyli jej wzbudzenie ze stanu podstawowego (singletowego) do stanu trypletowego [5].



Rysunek 1. Orbitale molekularne w cząsteczce tlenu (a) w stanie podstawowym (tlen trypletowy) oraz (b) w stanie wzbudzonym (tlen singletowy) [6].

Konieczność występowanie substancji utlenianej w stanie trypletowym sprawia, że tlen cząsteczkowy w stanie podstawowym nie jest tak skłonny do ulegania wieloelektronowej redukcji jak sugeruje to wartość potencjału standardowego. Z kolei stosunkowo łatwo cząsteczka O_2 w stanie trypletowym przyłącza jeden elektron, w wyniku czego powstaje anionorodnik ponadtlenkowy $O_2^{\bullet -}$ (ang. *superoxide anion radical*), charakteryzujący się właściwościami paramagnetycznymi [7].

Cząsteczka tlenu w stanie podstawowym (trypletowym) może zostać wzbudzona do stanu singletowego m.in. na skutek ekspozycji na wysokoenergetyczne promieniowanie elektromagnetyczne (np. promieniowanie UV) lub w wyniku dostarczenia energii cieplnej podczas procesu spalania. Pojedyncza cząsteczka O_2 w stanie singletowym reagując z paliwem inicjuje reakcję łańcuchową, w której wydzielona energia umożliwia przeniesienie kolejnych cząsteczek O_2 na wyższy poziom energetyczny, a takie wzbudzone cząsteczki są zdolne do przereagowania z kolejnymi cząsteczkami paliwa [7].

Należy podkreślić, że ograniczenia związane z wieloelektronową redukcją tlenu w stanie trypletowym wynikające z mechaniki kwantowej obowiązują jedynie w sytuacji, gdy tlen redukowany jest na drodze chemicznej [7]. Kiedy cząsteczka O_2 ulega redukcji elektrochemicznej z wytworzeniem nadtlenku wodoru jako produktu, dochodzi

do przyłączenia dwóch niezależnych elektronów, które mogą utworzyć pary z elektronami na antywiążących orbitalach π* cząsteczki O_2 znajdującej się w stanie podstawowym (trypletowym). Dlatego też, elektrochemiczna redukcja tlenu, inaczej niż redukcja na drodze chemicznej, nie wymaga wcześniejszego wzbudzenia tlenu ze stanu podstawowego do tlenu singletowego [7]. Warto także dodać, że wątpliwe jest, aby tlen w stanie singletowym w ogóle ulegał elektroredukcji w elektrolitach wodnych z uwagi na krótki średni czas życia (~10^{-6} s) cząsteczki tlenu singletowego w takim środowisku [3].

1.3 Elektrochemiczna redukcja tlenu w elektrolitach wodnych

1.3.1 Mechanizm elektrochemicznej redukcji tlenu w elektrolitach wodnych

Elektrochemiczna redukcja tlenu (ORR - ang. *oxygen reduction reaction*) w środowisku wodnym może przebiegać na dwa sposoby, poprzez przyłączenie do cząsteczki O_2 czterech elektronów, czyli bezpośrednią redukcję do wody lub anionu wodorotlenkowego, bądź z wytworzeniem nadtlenku wodoru lub anionu wodoronadtlenkowego HO_2^- (ang. *perhydroxyl ion*), kiedy cząsteczka tlenu jest akceptorem jedynie dwóch elektronów. Wydzielony podczas elektroredukcji tlenu nadtlenek wodoru lub anion HO_2^- mogą stanowić zarówno produkt końcowy, jak i produkt pośredni, który ulega dalszym przemianom chemicznym lub elektrochemicznym [8].

Na przebieg elektrochemicznej redukcji tlenu silny wpływ wywiera odczyn elektrolitu. W elektrolitach kwaśnych w wyniku całkowitej czteroelektronowej redukcji tworzy się woda (1.1).

$$O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O \tag{1.1}$$

Z kolei przyłączenie tylko dwóch elektronów prowadzi w takich warunkach do powstania nadtlenku wodoru (1.2),

$$O_2 + 2e^- + 2H^+ \longrightarrow H_2O_2 \tag{1.2}$$

który może zostać następnie zredukowany do wody (1.3)

$$H_2O_2 + 2e^- + 2H^+ \longrightarrow 2H_2O \tag{1.3}$$

bądź może ulegać reakcji dysproporcjonowania, w wyniku której odtwarzany jest cząsteczkowy tlen (1.4) [8].

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \tag{1.4}$$

W elektrolitach alkalicznych natomiast produktem całkowitej redukcji tlenu są aniony wodorotlenkowe (1.5)

$$O_2 + 4e^- + 2H_2O \longrightarrow 4OH^- \tag{1.5}$$

a w wyniku częściowej dwuelektronowej redukcji tworzy się anion wodoronadtlenkowy (1.6)

$$O_2 + 2e^- + H_2O \longrightarrow HO_2^- + OH^- \quad (1.6)$$

który, analogicznie do nadtlenku wodoru, może ulegać zarówno dalszej redukcji (1.7)

$$HO_2^- + 2e^- + H_2O \longrightarrow 3OH^- \quad (1.7)$$

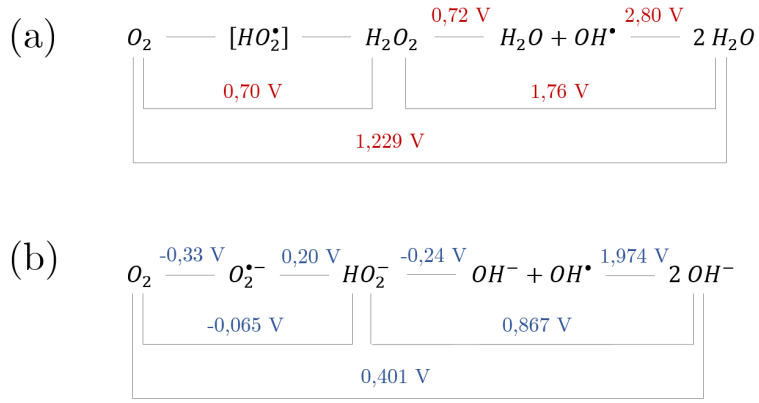
jak i rozpadowi z wydzieleniem cząsteczkowego tlenu (1.8) [8].

$$2HO_2^- \longrightarrow 2OH^- + O_2 \quad (1.8)$$

Wartości potencjałów standardowych dla przedstawionych powyżej reakcji zamieszczono w Tabeli 1, a także na diagramach Latimera (Rysunek 2).

Tabela 1. Standardowe potencjały redukcji O_2 oraz H_2O_2 i HO_2^- w elektrolitach kwaśnych i zasadowych [1].

Reakcja połówkowa	**Opis**	**E° vs. SHE**	**Uwagi**
$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$	całkowita redukcja O_2	+1,229 V	środowisko
$O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O_2$	częściowa redukcja O_2	+0,70 V	kwaśne
$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O$	redukcja H_2O_2	+1,76 V	(pH=0)
$O_2 + 2H_2O + 4e^- \rightleftarrows 4OH^-$	całkowita redukcja O_2	+0,401 V	środowisko
$O_2 + H_2O + 2e^- \rightleftarrows HO_2^- + OH^-$	częściowa redukcja O_2	-0,065 V	zasadowe
$HO_2^- + H_2O + 2e^- \rightleftarrows 3\,OH^-$	redukcja HO_2^-	+0,867 V	(pH=14)

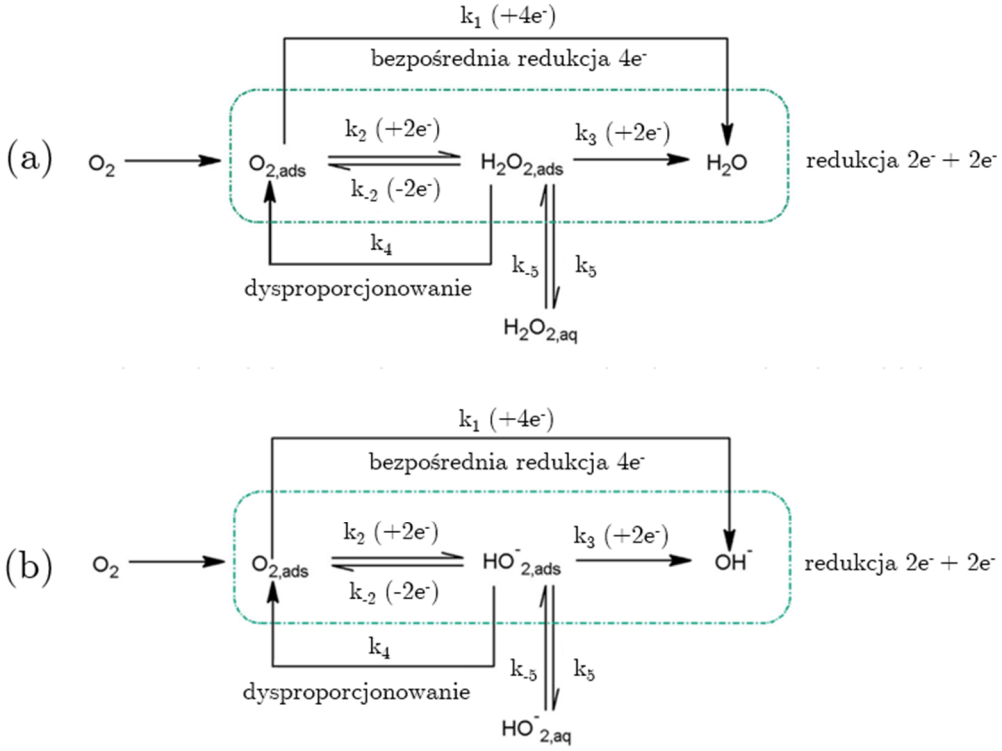


Rysunek 2. Diagram Latimera dla redukcji O_2 w środowisku (a) kwaśnym (pH=0) i (b) zasadowym (pH=14) [1,9,10].

Bezpośrednia czteroelektronowa redukcja tlenu wymaga zerwania wiązania O=O, którego energia dysocjacji jest znaczna i wynosi 494 kJ mol^{-1}. Z tego powodu na większości materiałów elektrodowych całkowita redukcja tlenu przebiega przez produkt pośredni, którym jest, zależnie od odczynu elektrolitu, nadtlenek wodoru bądź anion wodoronadtlenkowy HO_2^-. Energia dysocjacji wiązania O-O jest wówczas dużo niższa i wynosi jedynie 146 kJ mol^{-1} [11].

Całkowita czteroelektronowa redukcja O_2 nie musi zatem koniecznie być procesem jednoetapowym, ale równie dobrze może bazować na reakcjach następczych, w wyniku

których dochodzi sumarycznie do wymiany czterech elektronów. Różnicę między bezpośrednią redukcją czteroelektronową a redukcją ($2e^-$+$2e^-$) przedstawiono na Rysunku 3.



Rysunek 3. Uproszczony mechanizm elektroredukcji tlenu w środowisku (a) kwaśnym i (b) alkalicznym. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [11].

Przyczyną, dla której niektóre materiały elektrodowe zapewniają jedynie dwuelektronową redukcję tlenu są słabe oddziaływania pomiędzy tymi materiałami a produktami niepełnej redukcji tlenu. Nadtlenek wodoru oraz jon HO_2^- nie mogą ulegać dalszej redukcji w sytuacji, gdy desorbują się z powierzchni elektrody [8].

Jak pokazano na Rysunku 4, cząsteczka O_2 może sorbować się na powierzchni materiału węglowego w dwóch różnych orientacjach. Do adsorpcji zgodnej z modelem Yeagera dochodzi, gdy chemisorbowana cząsteczka przyjmuje orientację równoległą do powierzchni elektrody (ang. *side-on adsorption*). Drugim możliwością jest adsorpcja zgodnie z modelem Paulinga, kiedy to cząsteczka tlenu przyjmuje orientację prostopadłą do podłoża (ang. *end-on adsorption*). To w jaki sposób cząsteczka O_2 oddziaływuje z powierzchnią elektrody warunkuje przebieg procesu redukcji. Adsorpcja w orientacji *side-on* sprzyja całkowitej redukcji tlenu, a w przypadku orientacji *end-on* bardziej prawdopodobne jest, że proces zakończy się na wymianie jedynie dwóch elektronów [12,13].

Rysunek 4. Schematyczna prezentacja adsorpcji cząsteczki tlenu na powierzchni materiału elektrodowego w orientacji *end-on* oraz *side-on*. Przedruk za zgodą (po modyfikacjach) z [12].

Klasyfikacja materiałów elektrodowych według ich zdolności do przeprowadzania pełnej redukcji tlenu została przedstawiona w Tabeli 2.

Tabela 2. Materiały elektrodowe stosowane do elektrochemicznej redukcji O_2 w środowisku wodnym [8].

Klasa I	**Materiały elektrodowe, na których zachodzi głownie dwuelektronowa redukcja tlenu**
	- grafit, większość materiałów węglowych - metale: złoto, rtęć, większość metali, których powierzchnia pokryta jest tlenkami (np. Ni, Co) - tlenki: większość tlenków metali przejściowych (np. NiO, spinele) - większość makrocyklicznych związków metali przejściowych
Klasa II	**Materiały elektrodowe umożliwiające czteroelektronową lub dwuelektronową redukcję tlenu**
	- platyna, stopy platyny, platynowce - inne metale: srebro, pallad - tlenki: niektóre perowskity - niektóre makrocykliczne związki metali przejściowych

1.3.2 Elektrochemiczna redukcja tlenu na materiałach węglowych w elektrolitach wodnych

1.3.2.1 Informacje podstawowe

Materiały węglowe znajdują zastosowanie głównie do elektrochemicznej redukcji O_2 w elektrolitach alkalicznych. W środowisku kwaśnym większość materiałów węglowych charakteryzuje się słabymi właściwościami elektrokatalitycznymi względem procesu ORR. Dodatkowo powierzchnia materiałów węglowych w elektrolitach kwaśnych może utleniać się do dwutlenku węgla (1.9) [8].

$$C + H_2O \longrightarrow CO_2 + 4H^+ + 4e^- \quad (1.9)$$

Standardowy potencjał reakcji (1.9) jest równy 0,207 V vs. SHE. Natomiast w ogniwie galwanicznym z elektrolitem kwaśnym potencjał katody, na której zachodzi elektroredukcja O_2 jest dużo wyższy [1].

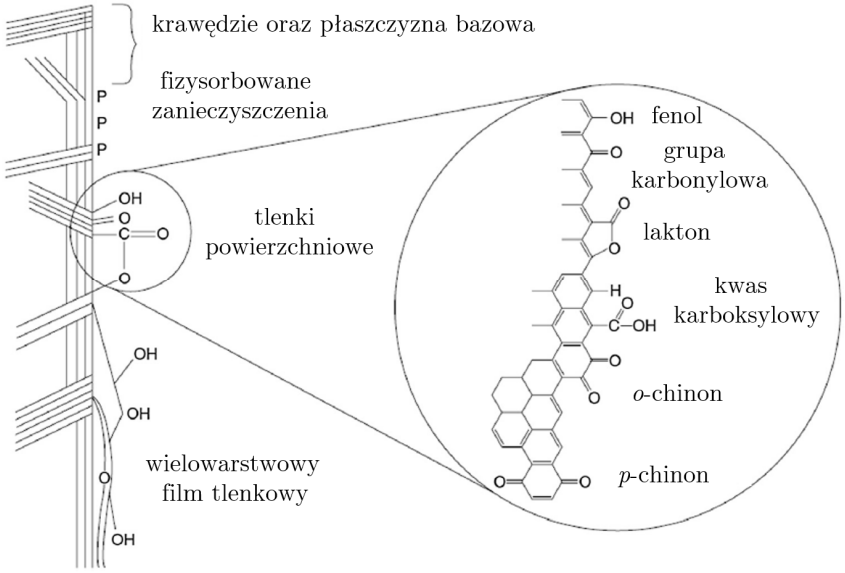
Materiały węglowe zapewniają przede wszystkim dwuelektronową redukcję tlenu do nadtlenku wodoru lub sprzężonej z nim zasady HO_2^-. W przypadku nielicznych materiałów węglowych, zwłaszcza tych o wysokiej zawartości popiołu oraz rozwiniętej powierzchni właściwej, możliwe są dalsze przemiany utworzonego anionu HO_2^- na drodze chemicznej (1.10) lub elektrochemicznej (1.11).

$$2HO_2^- \longrightarrow 2OH^- + O_2 \quad (1.10)$$

$$HO_2^- + 2e^- + H_2O \longrightarrow 3OH^- \quad (1.11)$$

Jednak, aby rozkład jonu HO_2^- przebiegał z wystarczającą szybkością, konieczne jest osadzenie na materiale węglowym dodatkowego elektrokatalizatora [8].

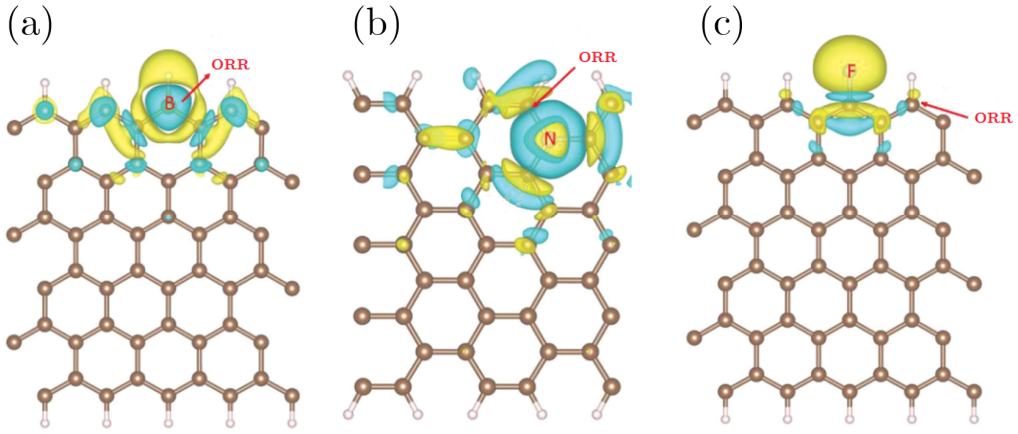
Właściwości elektrokatalityczne materiału węglowego są w dużej mierze określone przez właściwości fizykochemiczne jego powierzchni. Redukcja tlenu jest ułatwiona, gdy na powierzchni materiału występują ugrupowania zapewniające silnie oddziaływania z cząsteczkami O_2 [1], takie jak na przykład tlenowe grupy funkcyjne przedstawione na Rysunku 5.



Rysunek 5. Tlenowe grupy funkcyjne, których obecność na powierzchni materiału węglowego ma istotne znaczenie dla przebiegu elektrochemicznej redukcji tlenu. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [1].

W celu poprawy właściwości elektrokatalitycznych materiałów węglowych można do ich struktury wprowadzać także heteroatomy inne niż tlen, takie jak N, B, S, P [12] bądź Se [14]. Domieszkowanie materiału węglowego atomami o elektroujemności odbiegającej od elektroujemności atomów C skutkuje zmianą rozkładu gęstości ładunku, co wpływa

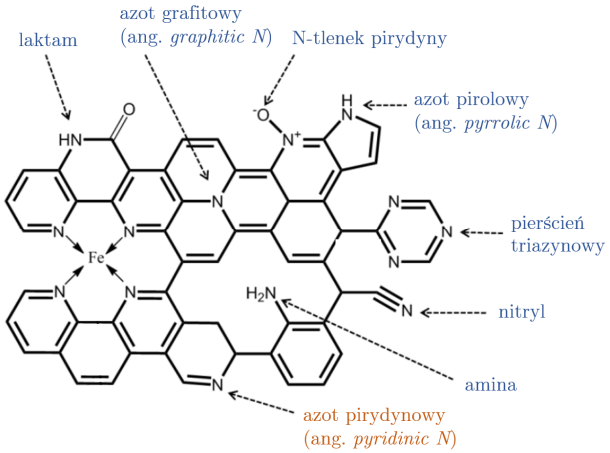
na adsorpcję cząsteczkowego tlenu na tymże materiale. Rozkład ładunku w płaszczyznach grafenowych po wprowadzeniu atomów boru, azotu i fluoru przedstawiono na Rysunku 6.



Rysunek 6. Rozkład ładunku w płaszczyznach grafenowych domieszkowanych atomami (a) boru, (b) azotu oraz (c) fluoru. Strzałkami zaznaczono miejsca stanowiące centra aktywne dla redukcji O_2. Przedruk za zgodą (po modyfikacjach) z [15].

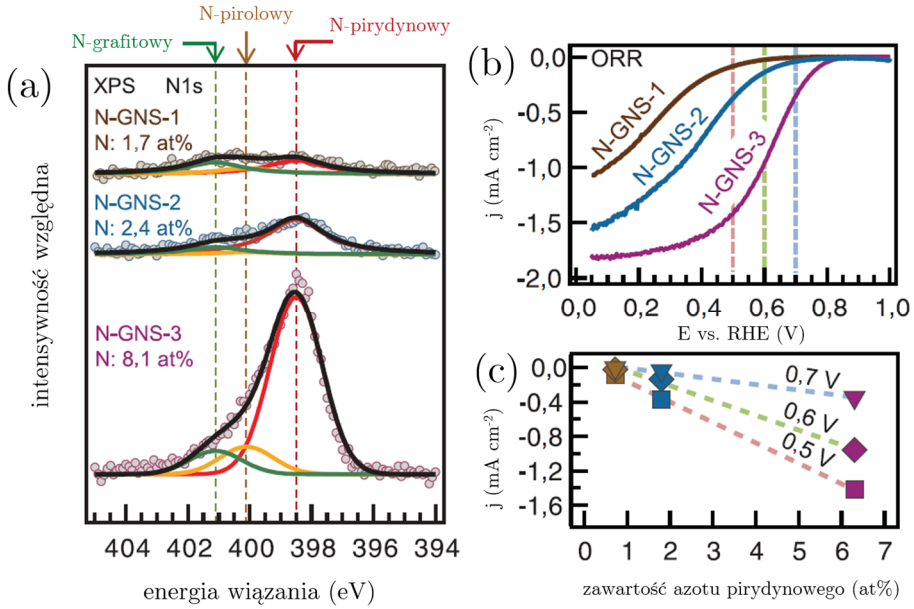
W przypadku materiałów węglowych domieszkowanych azotem, atomy węgla znajdujące się w jego bezpośrednim sąsiedztwie uzyskują częściowy ładunek dodatni, co sprawia, że ułatwiona jest adsorpcja O_2 w orientacji *side-on*, prowadząca do całkowitej czteroelektronowej redukcji tlenu [12].

Na właściwości elektryczne i elektrokatalityczne materiału węglowego wpływ ma, poza rodzajem i ilością wprowadzanych heteroatomów, także typ grup funkcyjnych utworzonych w wyniku procesu domieszkowania. Jak przedstawiono na Rysunku 7, wprowadzane atomy azotu mogą występować w postaci pierścienia pirydynowego, pierścienia pirolowego, a także jako azot grafitowy, amina, nitryl, laktam bądź tlenek pirydyny [16].



Rysunek 7. Grupy funkcyjne, które mogą powstać na skutek domieszkowania materiału węglowego azotem. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [16].

Spośród wielu możliwych grup funkcyjnych zawierających azot najlepsze parametry kinetyczne redukcji tlenu uzyskuje się w sytuacji, kiedy wprowadzony azot występuje w postaci pierścienia pirydynowego (ang. *pyridinic N*) [17], o czym świadczą wyniki badań zaprezentowane na Rysunku 8.



Rysunek 8. (a) Widma spektroskopii fotoelektronów w zakresie promieniowania X (XPS - ang. *X-ray photoelectron spectroscopy*) dla trzech typów nanopłatków grafenowych domieszkowanych azotem (N-GNS - ang. *nitrogen-doped graphene nanosheets*). (b) Krzywe woltamperometryczne dla redukcji tlenu na tych materiałach oraz (b) zależność gęstości natężenia prądu dla procesu ORR od zawartości azotu pirydynowego. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [17].

W grupie materiałów węglowych domieszkowanych azotem szczególną aktywność wobec procesu ORR wykazują nanorurki węglowe oraz materiały na bazie grafenu. Szybkość elektrochemicznej redukcji O_2 na tych materiałach w elektrolitach alkalicznych jest porównywalna z szybkością uzyskiwaną, gdy stosowane są katalizatory na bazie platyny [18].

Poza domieszkowaniem heteroatomami, modyfikacja właściwości elektrycznych materiałów węglowych może być dokonywana również poprzez zwiększanie liczby defektów geometrycznych (krawędzi, zniekształceń sieci krystalicznej itp.) występujących w tych materiałach. Niemniej jednak, aktywność elektrokatalityczna tak zdefektowanych materiałów pozostaje ciągle dużo niższa niż na przykład aktywność nanorurek węglowych domieszkowanych atomami azotu [12].

1.3.2.2 Elektroredukcja tlenu na graficie

Dla redukcji O_2 na graficie zaproponowano dwa różne mechanizmy, jednak żaden nie został ostatecznie udowodniony. Pierwszy z sugerowanych mechanizmów obejmuje utworzenie anionorodnika ponadtlenkowego $O_2^{\bullet-}$ (ang. *superoxide anion radical*) (1.12), który ulega rozpadowi do anionu wodorotlenkowego oraz indywiduum $(O_2H)_{ads}$ (1.13), które z kolei ulega dalszej redukcji do HO_2^- (1.14) [1].

$$O_{2\,(ads)} + e^- \longrightarrow [O_{2\,(ads)}]^{\bullet-} \tag{1.12}$$

$$[O_{2\,(ads)}]^{\bullet-} + H_2O \longrightarrow O_2H_{(ads)} + OH^- \tag{1.13}$$

$$O_2H_{(ads)} + e^- \longrightarrow [O_2H_{(ads)}]^- \tag{1.14}$$

$$[O_2H_{(ads)}]^- \longrightarrow HO_2^- \tag{1.15}$$

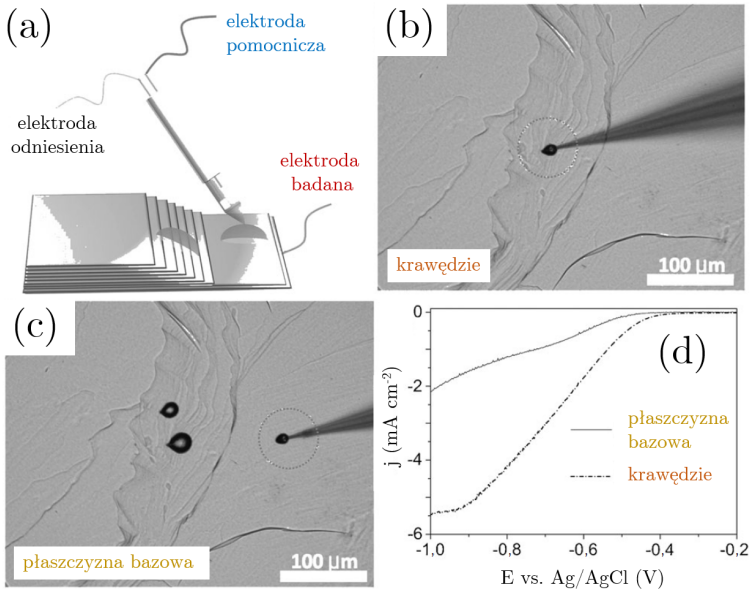
Według drugiego z proponowanych mechanizmów początkowo również tworzy się anionorodnik ponadtlenkowy (1.16), który jednak następnie ulega wieloetapowej przemianie do HO_2^- z wydzieleniem cząsteczkowego tlenu (1.17) [1].

$$O_{2\,(ads)} + e^- \longrightarrow [O_{2\,(ads)}]^{\bullet-} \tag{1.16}$$

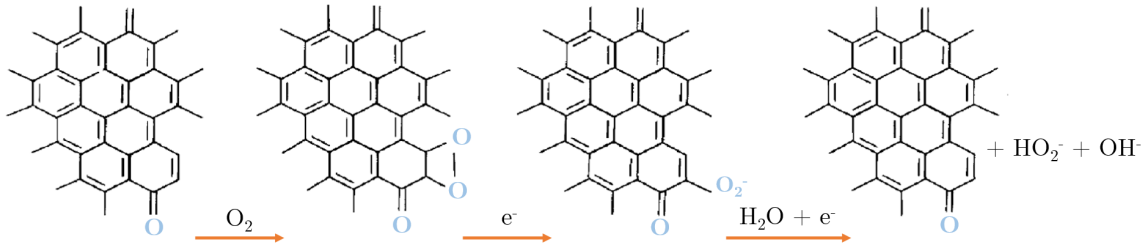
$$2\,[O_{2\,(ads)}]^{\bullet-} + H_2O \longrightarrow O_2 + HO_2^- + OH^- \tag{1.17}$$

Podstawowa różnica między dwoma zaprezentowanymi mechanizmami polega na tym, że w pierwszym przypadku konieczne jest zerwanie wiązania O-O w cząsteczce tlenu ulegającej redukcji, natomiast drugi mechanizm umożliwia przekształcenie cząsteczki O_2 w anion HO_2^- bez rozrywania tego wiązania [1].

Wykazano, że w przypadku elektroredukcji tlenu aktywność grafitu jest silnie zależna od miejsca, w którym dochodzi do reakcji elektrodowej. Jak pokazano na Rysunku 9, uzyskiwana gęstość natężenia prądu jest niższa, jeżeli proces ORR prowadzony jest na płaszczyźnie bazowej grafitu (ang. *basal plane*), którą stanowi płaszczyzna grafenowa niż wówczas, gdy elektroredukcja przebiega na krawędziach (ang. *edge plane*) [19,20]. Sugeruje się, że możliwą przyczyną takich różnic w aktywności elektrokatalitycznej jest występowanie na krawędziach większej liczby grup funkcyjnych, szczególnie tych zawierających tlen [1]. Rysunek 10 przedstawia proponowany przebieg procesu ORR, kiedy na krawędziach grafitu obecne są ugrupowania chinonowe.

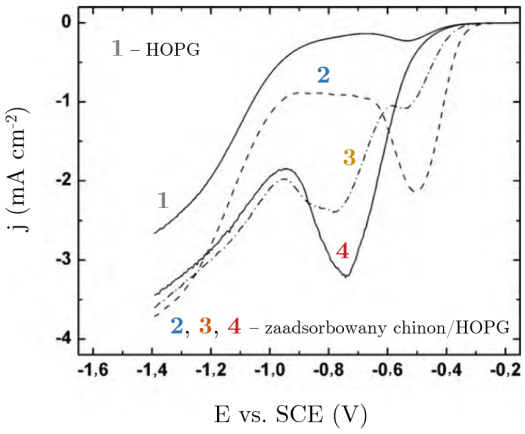


Rysunek 9. (a) Mikroaparat do badań nad elektroredukcją tlenu na powierzchni wysoce zorientowanego grafitu pirolitycznego (HOPG - ang. *highly oriented pyrolytic graphite*). Kropla elektrolitu nasyconego powietrzem naniesiona na (b) krawędzie oraz (c) płaszczyznę bazową HOPG. (d) Krzywe woltamperometryczne dla elektroredukcji tlenu na HOPG. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [19].



Rysunek 10. Dwuelektronowa redukcja tlenu katalizowana przez ugrupowanie chinonowe. Przedruk za zgodą (po modyfikacjach) z [8].

Aby zwiększyć ilość grup funkcyjnych występujących w graficie można zastosować prostą technikę, którą jest adsorpcja odpowiednich związków z roztworu. Wykazano, że w ten sposób można osadzić na powierzchni wysoce zorientowanego grafitu pirolitycznego różne chinony, których obecność zwiększa aktywność materiału wobec procesu ORR, jak to zaprezentowano na Rysunku 11 [21]. Do adsorpcji chinonów na graficie dochodzi głównie na krawędziach płaszczyzn grafenowych oraz w ich sąsiedztwie [22].



Rysunek 11. Elektroredukcja O_2 w 0,1 M KOH nasyconym tlenem na wirującej elektrodzie dyskowej z wysoce zorientowanego grafitu pirolitycznego (HOPG): (1) niemodyfikowany HOPG oraz HOPG, na powierzchni którego zaadsorbowano (2) 9,10-fenantrenochinon, (3) 9,10-antrachinon oraz (4) 1,4-difluoro-9,10-antrachinon. Szybkość skanowania: 10 mV s^{-1}. Częstotliwość wirowania elektrody: 3100 rpm. Przedruk (po modyfikacjach i tłumaczeniu) z [21].

1.3.2.3 Elektroredukcja tlenu na węglu szklistym

Proces elektrochemicznej redukcji tlenu na węglu szklistym jest prawdopodobnie bardziej złożony niż w przypadku grafitu [8]. Proponowany mechanizm obejmuje przyłączenie jednego elektronu do chemisorbowanego tlenu, w wyniku czego powstaje anionorodnik ponadtlenkowy $O_2^{\bullet -}$ (1.18). Na powierzchni węgla szklistego ów anionorodnik prawdopodobnie występuje w dwóch różnych formach (1.19), przy czym tylko jedna z nich może wejść w reakcję z wodą, co prowadzi do utworzenia rodnika wodoronadtlenkowego $HO_2^{\bullet}$ (1.20). Przyjmuje się, że w wyniku przyłączenia kolejnego elektronu, rodnik $HO_2^{\bullet}$ może zostać przekształcony w anion wodoronadtlenkowy HO_2^- (1.21).

$$O_{2\,(ads)} + e^- \longrightarrow [O_{2\,(ads)}]^{\bullet -} \tag{1.18}$$

$$[O_{2\,(ads)}]^{\bullet -} \longrightarrow \{O_{2\,(ads)}\}^{\bullet -} \tag{1.19}$$

$$\{O_{2\,(ads)}\}^{\bullet -} + H_2O \longrightarrow HO^{\bullet}_{2\,(ads)} + OH^- \tag{1.20}$$

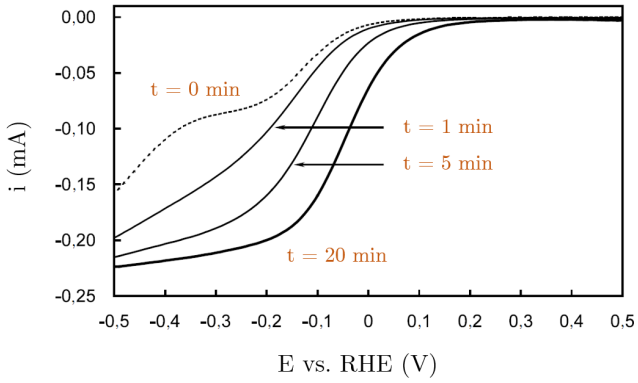
$$HO^{\bullet}_{2\,(ads)} + e^- \longrightarrow HO^-_{2\,(ads)} \tag{1.21}$$

$$HO^-_{2\,(ads)} \longrightarrow HO^-_2 \tag{1.22}$$

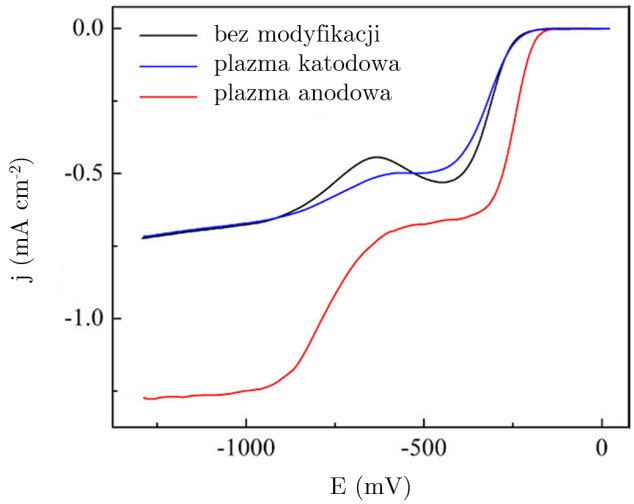
Szybkość redukcji O_2 na węglu szklistym jest prawdopodobnie kontrolowana przez reakcję anionorodnika $O_2^{\bullet -}$ z wodą (1.20) [8].

Podobnie jak w przypadku grafitu, przebieg redukcji O_2 na węglu szklistym uzależniony jest od obecności tlenowych grup funkcyjnych. Na powierzchni niemodyfikowanego węgla szklistego występują przede wszystkim ugrupowania fenolowe, układy chinon/hydrochinon oraz reszty karboksylowe [23]. Ilość tlenowych grup funkcyjnych można zwiększyć poprzez utlenianie elektrochemiczne [24] bądź plazmowe utlenianie

elektrolityczne [25]. Wpływ takich modyfikacji węgla szklistego na przebieg procesu elektroredukcji tlenu został przedstawiony odpowiednio na Rysunku 12 oraz na Rysunku 13.



Rysunek 12. Redukcja O_2 na wirującej elektrodzie dyskowej z węgla szklistego w środowisku kwaśnym (0,5 M H_2SO_4). Szybkość skanowania: 10 mV s^{-1}. Częstotliwość wirowania elektrody: 2000 rpm. Przed elektroredukcją tlenu węgiel szklisty poddawany był elektrochemicznemu utlenianiu przy potencjale 2,0 V_{RHE} przez okres odpowiednio 0, 1, 5 lub 20 minut. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [24].

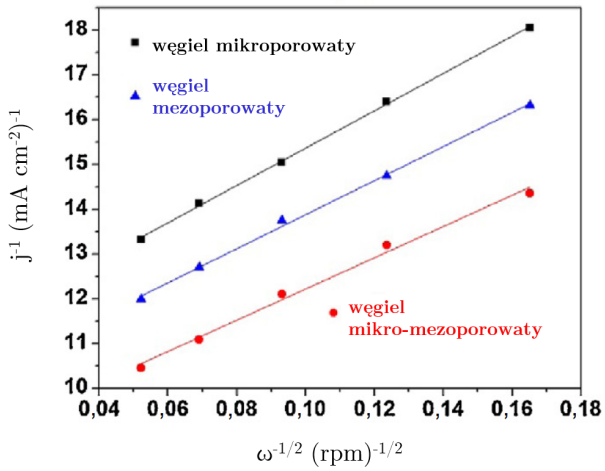


Rysunek 13. Redukcja tlenu na wirującej elektrodzie dyskowej z węgla szklistego przed i po modyfikacji plazmą. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [25].

1.3.2.4 Elektroredukcja tlenu na węglach aktywnych

W przypadku węgli aktywnych ich aktywność elektrochemiczna jest ściśle powiązana z parametrami fizykochemicznymi takimi jak powierzchnia właściwa oraz rozkład objętości mikro- i mezoporów. Wykazano, że mezopory są kluczowe dla transportu cząsteczkowego

tlenu, podczas gdy centra aktywne umożliwiające redukcję tlenu występują głównie w mikroporach. Dlatego też dla elektrochemicznej redukcji O_2 optymalnym typem węgla aktywnego jest węgiel mikro-mezoporowaty [26], co obrazuje Rysunek 14.



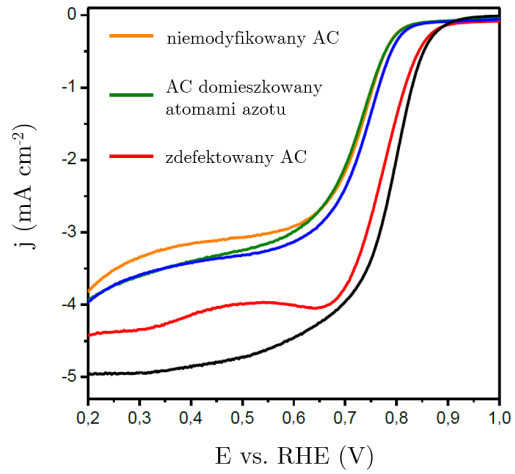
Rysunek 14. Redukcja tlenu w środowisku zasadowym (0,1 M KOH) na węglach aktywnych o różnym typie struktury porowatej. Szybkość skanowania: 5 mV s^{-1}. Potencjał: -0,8 V vs. Ag/AgCl. Częstotliwość wirowania elektrody: 350-3500 rpm. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [26].

Właściwości elektrokatalityczne węgla aktywnego zależne są także od obecności na jego powierzchni heteroatomów takich jak tlen i azot. Tlenowe grupy funkcyjne zwiększają zdolności adsorpcyjne węgla aktywnego oraz nadają powierzchni charakter kwasowy, jako że wiele ugrupowań tlenowych (np. -COOH oraz -C_6H_5OH) może dysocjować z wydzieleniem jonu wodorowego [18].

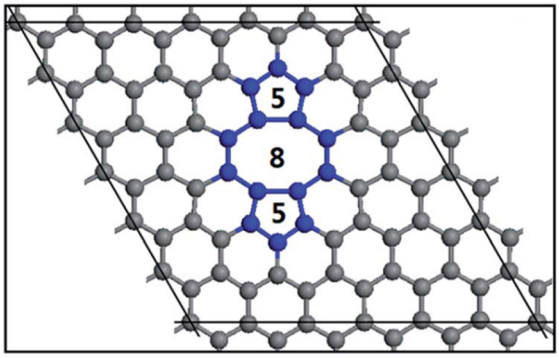
Zawartość tlenowych grup funkcyjnych na węglu aktywnym można zwiększyć poprzez jego utlenianie. Jeżeli proces ten prowadzony jest w fazie ciekłej, to powstają głównie grupy karboksylowe oraz fenolowe grupy hydroksylowe. Natomiast utlenianie w fazie gazowej prowadzi do utworzenia przede wszystkim grup karbonylowych i hydroksylowych [18].

Aby wprowadzić do struktury węgla aktywnego atomy azotu, przeprowadza się reakcję z amoniakiem bądź aminami. Węgiel aktywny w wyniku takiej modyfikacji uzyskuje właściwości zasadowe [18].

Jak zaprezentowano na Rysunku 15, szczególnie wysoką aktywnością wobec procesu ORR cechuje się zdefektowany węgiel aktywny (ang. *defective activated carbon*). Materiał ten powstał w wyniku domieszkowania węgla atomami azotu, które następnie zostały usunięte wskutek termicznej obróbki (1050°C, 2 h) w atmosferze gazu obojętnego [27]. Postuluje się, że za wysoką aktywność elektrokatalityczną zdefektowanego węgla odpowiadać mogą defekty typu 585 [28], które przedstawiono schematycznie na Rysunku 16.



Rysunek 15. Redukcja tlenu na węglach aktywnych w środowisku zasadowym (0,1 M KOH). Częstotliwość wirowanie elektrody: 1600 rpm. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [27].



Rysunek 16. Defekt typu 585 w warstwie grafenowej. Przedruk za zgodą (po modyfikacjach) z [28].

1.3.2.5 Elektroredukcja tlenu na nanorurkach węglowych

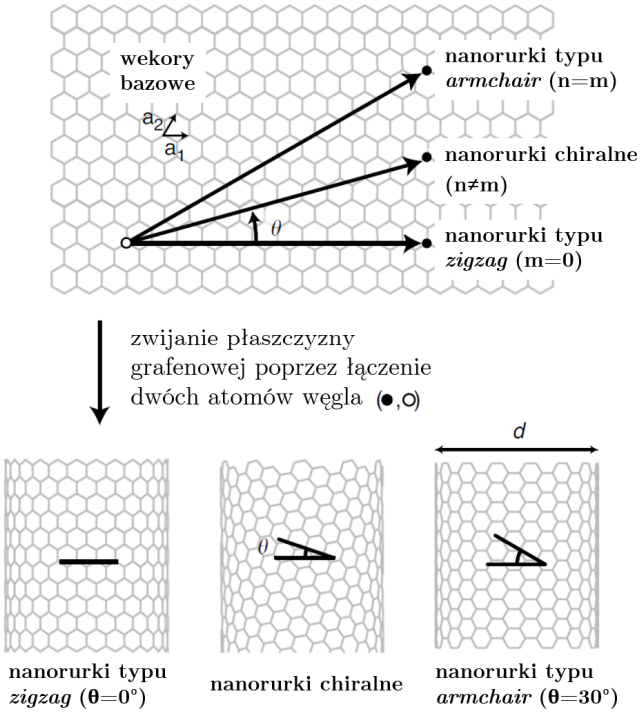
Aby na nanorurkach węglowych mogła zachodzić elektrochemiczna redukcja tlenu, muszą one posiadać odpowiednią strukturę, która zapewnia przewodnictwo metaliczne [18].

Struktura nanorurek węglowych określana jest przez wektor zwijania (n,m) (ang. *wrapping vector*), który opisuje kierunek i odległość na jaką zwijana jest płaszczyzna grafenowa. Jak pokazano na Rysunku 17, nanorurki opisywane wektorami (n,n) oraz (n,0) posiadają płaszczyznę symetrii (są achiralne), a pozostałe nanorurki są optycznie czynne.

Aby nanorurki węglowe wykazywały przewodnictwo metaliczne, wektor zwijania płaszczyzny grafenowej musi spełniać warunek dany równaniem (1.23).

$$n - m = 3l \quad (l = 0,1,2,3 \ldots) \tag{1.23}$$

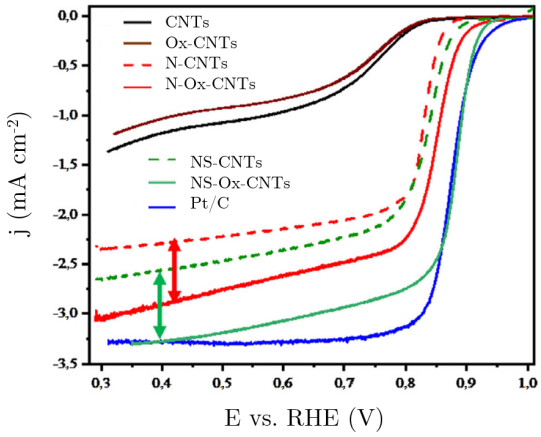
W przeciwnym przypadku nanorurki charakteryzują się właściwościami półprzewodnikowymi [18].



Rysunek 17. Klasyfikacja jednościennych nanorurek węglowych na podstawie wektora zwijania (n,m) (ang. *wrapping vector*) płaszczyzny grafenowej [29].

Na niemodyfikowanych nanorurkach węglowych zachodzi głównie dwuelektronowa redukcja tlenu, podczas gdy na nanorurkach domieszkowanych atomami azotu liczba elektronów wymienianych podczas procesu ORR wynosi nawet 4,0 [12]. Przykładowe krzywe woltamperometryczne dla redukcji O_2 na nanorurkach węglowych domieszkowanych heteroatomami przedstawiono na Rysunku 18.

Należy jednak mieć na uwadze, że w przypadku nanorurek węglowych duży wpływ na ich aktywność w procesie ORR mogą mieć zanieczyszczenia metalami przejściowymi (Fe, Co, Ni, Mo) i ich tlenkami, które katalizują rozkład nadtlenku wodoru [30]. Obecność takich zanieczyszczeń jest konsekwencją stosowania katalizatorów na etapie syntezy nanorurek węglowych, a całkowite usunięcie zanieczyszczeń z gotowego materiału węglowego nie jest możliwe, nawet w przypadku wielokrotnego wymywania kwasem [31].



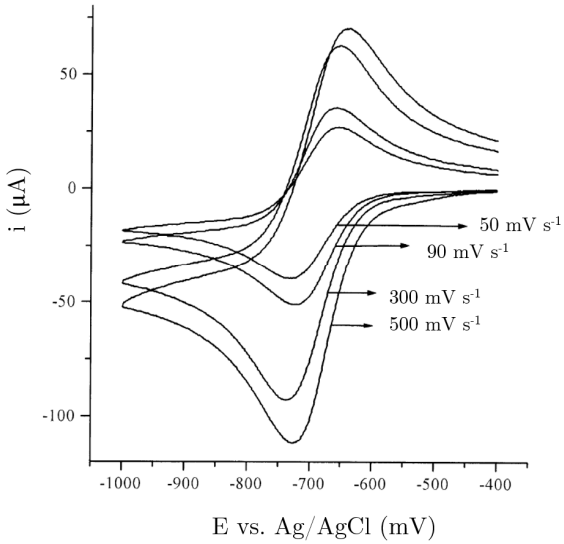
Rysunek 18. Redukcja tlenu w środowisku zasadowym (1 M NaOH) na nanorurkach węglowych (CNTs - ang. *carbon nanotubes*) utlenianych (Ox), domieszkowanych heteroatomami (N, NS) oraz niepoddanych żadnej modyfikacji. Częstotliwość wirowania elektrody: 1600 rpm. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [32].

1.4 Elektrochemiczna redukcja tlenu w elektrolitach niewodnych na bazie dimetylosulfotlenku

W przypadku aprotycznych elektrolitów niewodnych możliwa jest jedynie jednoelektronowa redukcja O_2 z utworzeniem anionorodnika ponadtlenkowego (1.24) [1].

$$O_{2\,(ads)} + e^- \longrightarrow [O_{2\,(ads)}]^{\bullet -} \qquad (1.24)$$

Proces ten, jak pokazano na Rysunku 19, ma charakter odwracalny bądź *quasi*-odwracalny [33].



Rysunek 19. Woltamperogramy dla układu $O_2/O_2^{\bullet -}$ uzyskane przy zastosowaniu elektrody z węgla szklistego. Elektrolit: 0,1 M TBAP w DMSO. Przedruk za zgodą (po modyfikacjach) z [33].

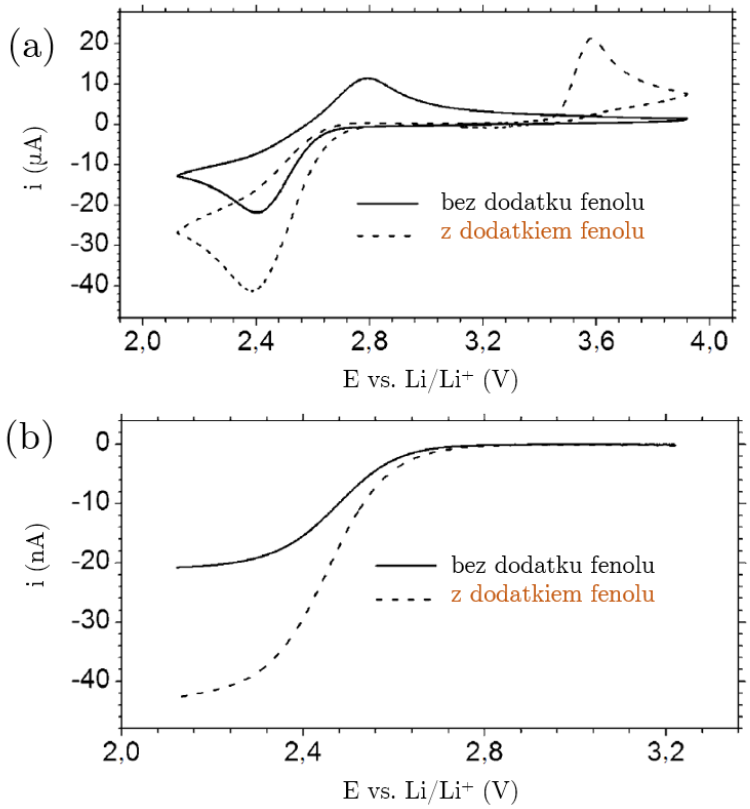
W sytuacji, gdy w elektrolicie niewodnym obecne będą związki protyczne (stanowiące potencjalny donor protonu) utworzony anionorodnik ponadtlenkowy przekształca się w rodnik $HO_2^{\bullet}$ (1.25), który następnie może ulegać przemianie na drodze chemicznej (1.26) lub elektrochemicznej (1.27) w nadtlenek wodoru lub sprzężoną z nim zasadę HO_2^- [34].

$$[O_{2\,(ads)}]^{\bullet -} + HA \longrightarrow HO^{\bullet}_{2\,(ads)} + A^- \tag{1.25}$$

$$HO^{\bullet}_{2\,(ads)} + [O_{2\,(ads)}]^{\bullet -} \longrightarrow HO^{-}_{2\,(ads)} + O_2 \tag{1.26}$$

$$HO^{\bullet}_{2\,(ads)} + e^- + HA \longrightarrow H_2O_2 + A^- \tag{1.27}$$

Jako donory protonu w procesie ORR wykorzystywane mogą być związki takie jak fenol i jego pochodne, nitrometan [35], jak również nizoldypina [36]. Przebieg elektrochemicznej redukcji tlenu na elektrodzie złotej w elektrolicie niewodnym z i bez dodatku donora protonu został zaprezentowany na Rysunku 20.



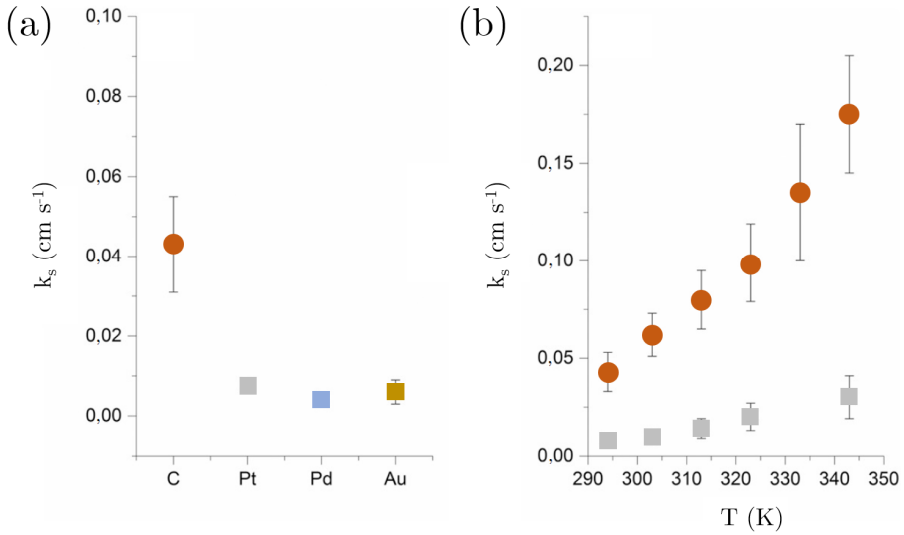
Rysunek 20. Wpływ dodatku 20 mM fenolu na przebieg redukcji tlenu na elektrodzie złotej o średnicy (a) 2 mm oraz (b) 25 μm. Elektrolit: 0,1 M $TBAClO_4$ w DMSO. Szybkość skanowania: (a) 100 mV s^{-1} oraz (b) 5 mV s^{-1} [34]. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [34].

W Tabeli 3 zebrano standardowe stałe szybkości redukcji tlenu do anionorodnika $O_2^{\bullet -}$ dla różnych materiałów elektrodowych. Co ciekawe, w elektrolitach aprotycznych materiały węglowe charakteryzują się znacznie wyższymi wartościami stałych szybkości reakcji k_s niż metale szlachetne.

Tabela 3. Standardowe stałe szybkości reakcji redukcji O_2 do anionorodnika ponadtlenkowego w elektrolicie aprotycznym na bazie dimetylosulfotlenku (0,1 M TBAP w DMSO).

Materiał elektrodowy	**k_s (cm s^{-1})**
węgiel szklisty	$3{,}20 \cdot 10^{-2}$ [37]
węgiel szklisty	$9{,}3 \cdot 10^{-2}$ [33]
grafit	$2{,}77 \cdot 10^{-2}$ [37]
włókno węglowe	$4{,}3 \cdot 10^{-2}$ [38]
platyna	$7{,}5 \cdot 10^{-3}$ [38]
pallad	$4{,}0 \cdot 10^{-3}$ [38]
złoto	$6{,}0 \cdot 10^{-3}$ [38]

Jak pokazano na Rysunku 21, tendencja taka jest zachowana także wówczas, gdy proces ORR prowadzony jest w podwyższonych temperaturach.



Rysunek 21. (a) Stała szybkości redukcji tlenu w dimetylosulfotlenku z dodatkiem 0,1 M TBAP dla różnych materiałów elektrodowych w temperaturze 293 K oraz (b) wpływ temperatury na wartość stałej szybkości tej reakcji dla platyny i włókna węglowego [38].

Podejrzewa się, że względnie niskie wartości k_s dla redukcji O_2 na metalach szlachetnych wynikają z adsorpcji DMSO na powierzchni takich elektrod, w wyniku czego zwiększeniu ulega odległość na jaką cząsteczki tlenu mogą zbliżyć się do elektrody [38].

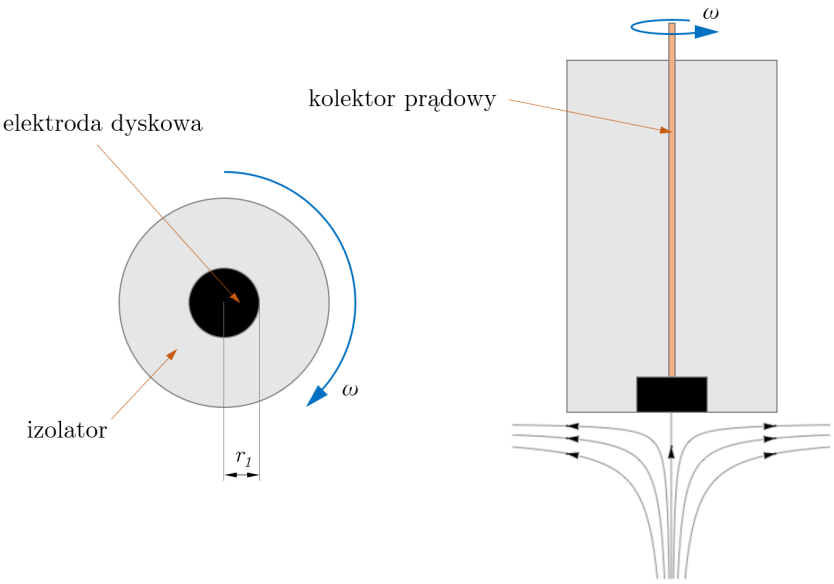
2. Procesy elektrochemiczne w układach hydrodynamicznych z wymuszoną konwekcją

2.1 Wirująca elektroda dyskowa

2.1.1 Budowa i zasada działania

Badania elektrochemiczne w układach hydrodynamicznych realizowane są przy wymuszonym przepływie elektrolitu względem powierzchni elektrody, co może być osiągnięte na dwa sposoby. Pierwszy sposób polega na umieszczeniu nieruchomej elektrody w mieszanym lub przepływającym elektrolicie. Przykładem może być mikroelektroda, na powierzchnię której elektrolit jest dostarczany za pomocą dyszy (ang. *microjet electrode*) [39]. Natomiast drugim rozwiązaniem jest wprawienie w ruch samej elektrody, jak dzieje się to w przypadku wirującej elektrody dyskowej (RDE – ang. *rotating disk electrode*) lub wirującej elektrody dyskowo-pierścieniowej (RRDE – ang. *rotating ring disk electrode*). Przepływ elektrolitu względem powierzchni elektrody skutkuje tym, że poza transportem dyfuzyjnym substancji elektroaktywnej, występuje także jej transport na drodze konwekcji [40].

Główną zaletą wirującej elektrody dyskowej jest prostota jej konstrukcji. Przewodzący dysk osadzony jest w wale wykonanym z izolatora (najczęściej z teflonu [41]), jak pokazano to na Rysunku 22.



Rysunek 22. Schemat wirującej elektrody dyskowej [42].

Wał obracany jest wokół własnej osi z zadaną częstotliwością, wyrażaną najczęściej jako liczba obrotów na minutę (rpm – ang. *revolutions per minute*). Kontakt elektryczny między wirującym dyskiem, od którego odchodzi kolektor miedziany, a potencjostatem zapewniają szczotki węglowe [43,44]. Dysk elektrody wirującej może być wykonany z różnego rodzaju metali (Au, Pt, Cu, Ni, Al, Ta, Ti, W [45]), a także z węgla szklistego bądź pasty węglowej, którą wypełnia się wgłębienie wycięte w walcu teflonowym i następnie odpowiednio wygładza [40].

W przypadku wirującej elektrody dyskowej, możliwa jest regulacja szybkości transportu substancji elektroaktywnej do powierzchni elektrody poprzez zmianę częstotliwości wirowania elektrody. Wymuszona konwekcja wpływa na transport dyfuzyjny, decyduje bowiem ona o grubości warstwy dyfuzyjnej, która określa w jakiej odległości od powierzchni elektrody stężenie substancji elektroaktywnej jest równe stężeniu w głębi elektrolitu [40]. Transport masy do powierzchni elektrody wirującej odbywa się zatem dzięki dyfuzji konwekcyjnej [46-48]. W niniejszej pracy nazywana ona będzie skrótowo dyfuzją, podobnie jak przyjęło się to robić w publikacjach [49-53] i książkach [54] dotyczących wirującej elektrody dyskowej oraz wirującej elektrody dyskowo-pierścieniowej. Wpływ transportu migracyjnego na szybkość dostarczania substancji elektroaktywnej do elektrody dyskowej może natomiast zostać pominięty, gdyż jest on zaniedbywalnie mały, o ile stosowany jest elektrolit podstawowy o dostatecznie wysokim stężeniu [43].

Zaletą metod hydrodynamicznych, do których należy metoda wirującej elektrody dyskowej jest szybkość z jaką dyfuzja osiąga stan ustalony, czyli dla danego potencjału i częstotliwości obrotu elektrody staje się niezależna od czasu [41]. Przykładowo, czas potrzebny do osiągnięcia stanu ustalonego dla elektrody wirującej z częstotliwością 1000 rpm w elektrolicie o przeciętnych wartościach lepkości oraz współczynnika dyfuzji wynosi około 0,2 s [43].

Aby natężenia prądu rejestrowane dla wirującej elektrody dyskowej były odtwarzalne, przepływ elektrolitu do powierzchni elektrody musi mieć charakter laminarny [55]. Maksymalną dozwoloną częstotliwość wirowania elektrody określa krytyczna liczba Reynoldsa, po przekroczeniu której przepływ laminarny przechodzi w przepływ turbulentny. Krytyczna liczba Reynoldsa Re_{kr} wynosi $2 \cdot 10^5$ [43], chociaż w literaturze pojawiają się także wartości o rząd wielkości niższe ($1\text{-}2 \cdot 10^4$ [56]).

Dla wirującej elektrody dyskowej liczbę Reynoldsa definiuje równanie (2.1) [57]

$$\mathrm{Re} = \frac{\omega R^2}{\nu} \tag{2.1}$$

w którym ω oznacza częstość kołową obrotu elektrody *($\omega = 2\pi f$)*, R – całkowity promień elektrody (z uwzględnieniem obecności izolatora wokół przewodzącego dysku), a ν - lepkość kinematyczną elektrolitu.

Przepływ laminarny dla $\mathrm{Re} < 2 \cdot 10^5$ dotyczy gładkiej i dobrze wycentrowanej elektrody [40]. Występowanie drgań dysku w płaszczyźnie poziomej, przepuszczanie gazu przez elektrolit bądź wydzielanie się gazowych produktów podczas reakcji elektrodowej skutkuje dodatkowym mieszaniem elektrolitu i obniżeniem krytycznej liczby Reynoldsa [58].

Podobny efekt mogą wywierać nieregularności obecne na powierzchni elektrody, w tym także porowate warstwy katalizatora naniesione na elektrodę dyskową w celu jej modyfikacji [31].

Dla większości wirujących elektrod dyskowych użyteczny zakres częstotliwości to 100-10 000 rpm. Górna granica podyktowana jest właśnie wymogiem zachowania przepływu laminarnego, natomiast dolna granica wynika z konieczności spełnienia warunku, iż grubość warstwy dyfuzyjnej musi być niewielka względem rozmiarów elektrody dyskowej [57]. Teoria wirującej elektrody dyskowej opiera się bowiem na założeniu, że średnica przewodzącego dysku jest nieskończenie wielka w porównaniu do grubości warstwy dyfuzyjnej. W praktyce stosuje elektrody o średnicy niemniejszej niż 1 mm, mając na uwadze, że grubość warstwy dyfuzyjnej jest rzędu około 10^{-3} cm [40].

2.1.2 Kontrola dyfuzyjna i kinetyczna procesu elektrodowego

Szybkość reakcji elektrodowej wyrażona jako natężenie prądu na dysku i_D zależna jest od grubości warstwy dyfuzyjnej δ zgodnie z równaniem (2.2).

$$i_D = \frac{nF\pi r_1^2 D(c - c^0)}{\delta} \tag{2.2}$$

Symbole w równaniu (2.2) oznaczają kolejno:

- n - liczbę elektronów wymienianych podczas reakcji elektrodowej
- F - stałą Faradaya
- r_1 - promień elektrody dyskowej (bez izolatora)
- D - współczynnik dyfuzji substancji elektroaktywnej
- c^0 - stężenie substancji elektroaktywnej przy powierzchni elektrody
- c - stężenie substancji elektroaktywnej w głębi elektrolitu (ang. *bulk concentration*)

Grubość warstwy dyfuzyjnej δ powiązana jest natomiast z częstością kołową obrotu elektrody ω równaniem (2.3) [40].

$$\delta = \frac{1{,}62\, D^{1/3}\nu^{1/6}}{\omega^{1/2}} \tag{2.3}$$

W wyniku podstawienia wyrażenia na grubość warstwy dyfuzyjnej do równania (2.2) otrzymuje się zależność natężenia prądu i_D na elektrodzie dyskowej od częstości kołowej ω obrotu elektrody określoną równaniem (2.4).

$$i_D = 0{,}62\, nF\pi r_1^2\, D^{2/3}\, \nu^{-1/6}\, \omega^{1/2}\, (c - c^0) \tag{2.4}$$

Stężenie substancji elektroaktywnej przy powierzchni elektrody c^0 występujące w równaniu (2.4) może przyjmować wartości z przedziału <0,c>. W przypadku, kiedy stężenie substancji elektroaktywnej przy powierzchni elektrody jest równe zeru ($c^0 = 0$), o szybkości reakcji elektrodowej decyduje proces dyfuzji. Natomiast, gdy stężenie substancji elektroaktywnej przy powierzchni elektrody jest równe stężeniu w głębi elektrolitu ($c^0 = c$), to szybkość reakcji elektrodowej zależy wyłącznie od kinetyki wymiany ładunku na granicy faz elektroda-elektrolit.

Dla nieodwracalnej reakcji pierwszego rzędu natężenie prądu na wirującej elektrodzie dyskowej i_D dane jest równaniem Koutecký'ego-Levicha (2.5) [54].

$$\frac{1}{i_D} = \frac{1}{i_{D,k}} + \frac{1}{i_{D,l,c}} = \frac{1}{nF\pi r_1^2 kc} + \frac{1}{0{,}62nF\pi r_1^2 D^{2/3}\omega^{1/2}\nu^{-1/6}c} \tag{2.5}$$

W równaniu (2.5) $i_{D,k}$ oznacza natężenie prądu na dysku w warunkach pełnej kontroli kinetycznej, tj. natężenie prądu, które byłoby obserwowane, jeżeli transport masy byłby w stanie zapewnić stężenie substancji elektroaktywnej przy powierzchni elektrody równe stężeniu w głębi elektrolitu mimo przebiegającej reakcji elektrodowej [43]. Z kolei $i_{D,l,c}$ odpowiada natężeniu prądu na dysku w sytuacji, kiedy reakcja elektrodowa jest całkowicie kontrolowana przez dyfuzję konwekcyjną (w niniejszej pracy nazywaną po prostu dyfuzją) substancji elektroaktywnej do powierzchni elektrody.

Stosując matematyczny opis powyższych warunków, dla $i_{D,l,c}$ dążącego do nieskończoności występuje pełna kontrola kinetyczna, a i_D jest równe $i_{D,k}$ (2.6).

$$\lim_{i_{D,l,c}\to\infty}\left(\frac{1}{i_D}\right) = \lim_{i_{D,l,c}\to\infty}\left(\frac{1}{i_{D,k}} + \frac{1}{i_{D,l,c}}\right) = \frac{1}{i_{D,k}} \tag{2.6}$$

Natomiast dla $i_{D,k}$ dążącego do nieskończoności reakcja przebiega przy pełnej kontroli dyfuzyjnej, a i_D staje się równe $i_{D,l,c}$ (2.7).

$$\lim_{i_{D,k}\to\infty}\left(\frac{1}{i_D}\right) = \lim_{i_{D,k}\to\infty}\left(\frac{1}{i_{D,k}} + \frac{1}{i_{D,l,c}}\right) = \frac{1}{i_{D,l,c}} \tag{2.7}$$

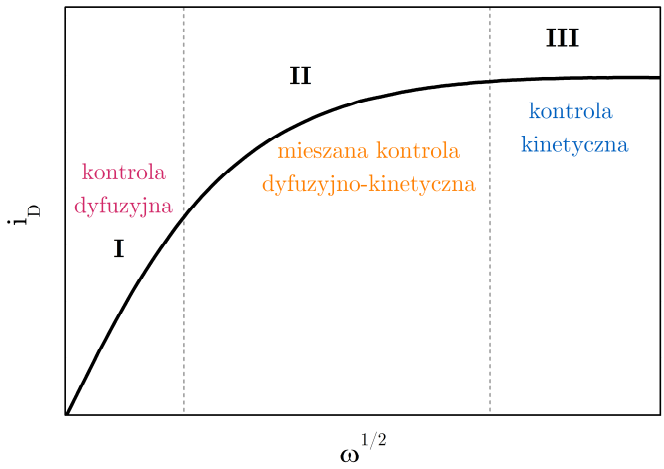
W takim przypadku równanie Koutecký'ego-Levicha (2.5) upraszcza się do równania Levicha (2.8).

$$i_D = i_{D,l,c} = 0{,}62nF\pi r_1^2 D^{2/3}\omega^{1/2}\nu^{-1/6}c \tag{2.8}$$

Jak wynika z równania Levicha (2.8), dla procesu elektrodowego kontrolowanego jedynie szybkością transportu substancji elektroaktywnej do powierzchni elektrody natężenie prądu i_D jest wprost proporcjonalne do pierwiastka kwadratowego z częstości kołowej $\omega^{1/2}$. Z kolei przy występowaniu pełnej kontroli kinetycznej, natężenie prądu i_D staje się niezależne od szybkości wirowania elektrody, jak przedstawiono to na Rysunku 23 [40].

W praktyce reakcja elektrodowa jest klasyfikowana jako kontrolowana dyfuzyjnie lub kinetycznie, jeżeli szybkość transportu masy znacząco różni się od szybkości przeniesienia ładunku. Jeżeli szybkości obu tych procesów są porównywalne, to reakcja przebiega w warunkach mieszanej kontroli dyfuzyjno-kinetycznej [54].

Niemniej jednak należy mieć na uwadze, że obie wielkości $i_{D,k}$ oraz $i_{D,l,c}$ mają wpływ na wypadkowe natężenie prądu na dysku i_D, chyba że stosunek tych dwóch wielkości jest odpowiednio wysoki. Na podstawie równania Koutecký'ego-Levicha można stwierdzić, że aby uzyskać natężenie prądu na dysku i_D nie odbiegające bardziej niż o 5% od teoretycznej wartości w warunkach pełnej kontroli dyfuzyjnej $i_{D,l,c}$, to stosunek $i_{D,k}$ do $i_{D,l,c}$ nie może być niższy niż 19. Aby zmniejszyć ten błąd do 1%, stosunek ten musi wynosić 99.



Rysunek 23. Zależność natężenia prądu i_D od pierwiastka kwadratowego szybkości kątowej elektrody dyskowej. Obszar I – reakcja kontrolowana dyfuzją, obszar II – reakcja podlegająca mieszanej kontroli dyfuzyjno-kinetycznej, obszar III – reakcja kontrolowaną kinetyką wymiany ładunku [40].

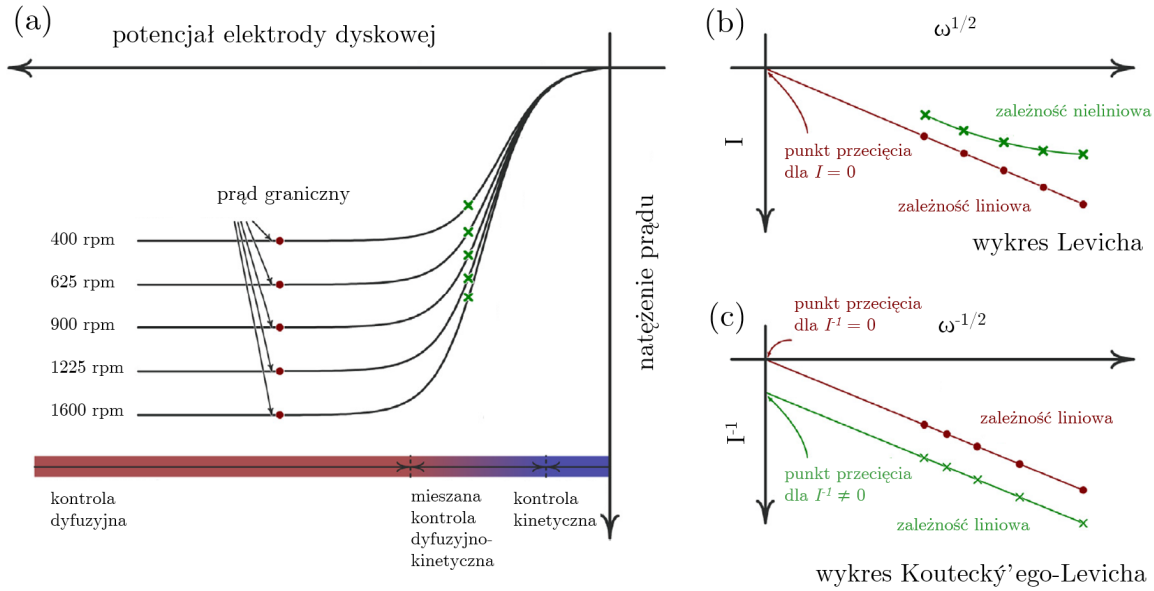
Ponadto, jeżeli $i_{D,k}$ jest tylko nieznacznie większe niż $i_{D,l,c}$, to wypadkowe natężenie prądu i_D różni się nawet o kilkadziesiąt procent od teoretycznej wartości $i_{D,l,c}$. Na przykład, jeżeli $i_{D,k}$ jest równe 1,5 $i_{D,l,c}$, to różnica ta sięga 40%. Stąd, warunek $i_{D,k} > i_{D,l,c}$ jest konieczny, ale niewystarczający, aby uznać, że reakcja elektrochemiczna jest kontrolowana dyfuzyjnie.

2.1.3 Stosowanie metody wirującej elektrody dyskowej

Badania elektrochemiczne z udziałem wirującej elektrody dyskowej przeprowadza się najczęściej stosując woltamperometrię z liniowo zmieniającym się potencjałem bądź woltamperometrię cykliczną. Rzadziej stosowanymi technikami są chronoamperometria [59,60] oraz elektrochemiczna spektroskopia impedancyjna [61-63]. W przypadku metod woltamperometrycznych szybkość skanowania musi być na tyle niska, aby możliwe było ustalenie się warunków dyfuzji stacjonarnej [40]. Pomiar zależności natężenia prądu od potencjału wykonywany jest przy kilku różnych wartościach częstotliwości wirowania elektrody, a uzyskiwane krzywe woltamperometryczne mają kształt fal, jak na Rysunku 24a. Plateau pojawiające się przy odpowiednio silnej polaryzacji świadczy o występowaniu prądu granicznego, kiedy to szybkość procesu elektrodowego limitowana jest transportem substancji elektroaktywnej do powierzchni elektrody dyskowej. Natężenie prądu granicznego jest wprost proporcjonalne do pierwiastka kwadratowego z szybkości kątowej wirowania elektrody (Rysunek 24b), co wynika z równania Levicha (2.8).

Podstawowym obszarem wykorzystania metody wirującej elektrody dyskowej są badania mechanizmu i kinetyki umiarkowanie szybkich reakcji elektrodowych. W celu wyznaczenia na podstawie uzyskanych krzywych woltamperometrycznych parametrów

takich jak współczynnik symetrii α i standardowa stała szybkości reakcji elektrodowej k_s, które determinują natężenie prądu kinetycznego i_k, konstruuje się wykresy odwrotności natężenia prądu i_D od odwrotności pierwiastka kwadratowego z szybkości kątowej wirowania elektrody ω dla różnych wartości potencjału [55]. Przykładowy taki wykres, nazywany wykresem Koutecký'ego-Levicha, przedstawiono na Rysunku 24c.



Rysunek 24. (a) Krzywe woltamperometryczne dla substancji elektroaktywnej ulegającej redukcji na wirującej elektrodzie dyskowej. Na podstawie wybranych wartości natężenia prądu (zaznaczonych czerwonymi kropkami oraz zielonymi krzyżykami) wykreślono wykres Levicha (b) oraz wykres Koutecký'ego-Levicha (c). Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [64].

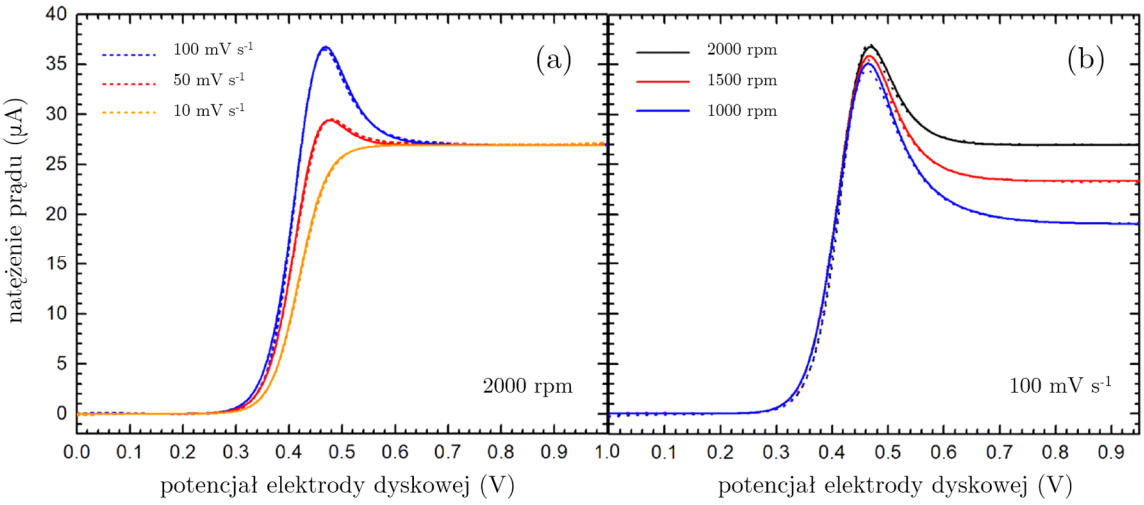
Dla różnych wartości potencjału uzyskuje się na wykresie Koutecký'ego-Levicha szereg prostych równoległych, których punkty przecięcia z osią rzędnych odpowiadają odwrotnościom natężenia prądu kinetycznego i_k. Na podstawie współczynnika nachylenia prostych wyznaczyć można natomiast liczbę elektronów wymienianych podczas procesu elektrodowego, współczynnik dyfuzji substancji elektroaktywnej lub powierzchnię aktywną elektrochemicznie [55].

Aby zależność między natężeniem prądu a częstotliwością wirowania elektrody spełniała równanie Koutecký'ego-Levicha (2.5), szybkość wirowania elektrody nie może być zupełnie dowolna, lecz poza ograniczeniami wynikającymi z konieczności zachowania przepływu laminarnego, musi być dostosowana do szybkości zmiany potencjału elektrody [40].

Jeżeli szybkość skanowania jest zbyt wysoka względem stosowanej częstotliwości wirowania elektrody, to niemożliwe jest ustalenie się dyfuzji stacjonarnej. W rezultacie na woltamperogramach pojawiają się piki, podobne do pików opisywanych równaniem Randlesa-Sevčika dla elektrody stacjonarnej. Wysokość pików otrzymywanych przy zastosowaniu wirującej elektrody dyskowej jest proporcjonalna do pierwiastka

kwadratowego ilorazu szybkości skanowania i częstotliwości wirowania elektrody [65]. Wpływ obu tych parametrów na kształt krzywej woltamperometrycznej ilustruje Rysunek 25.

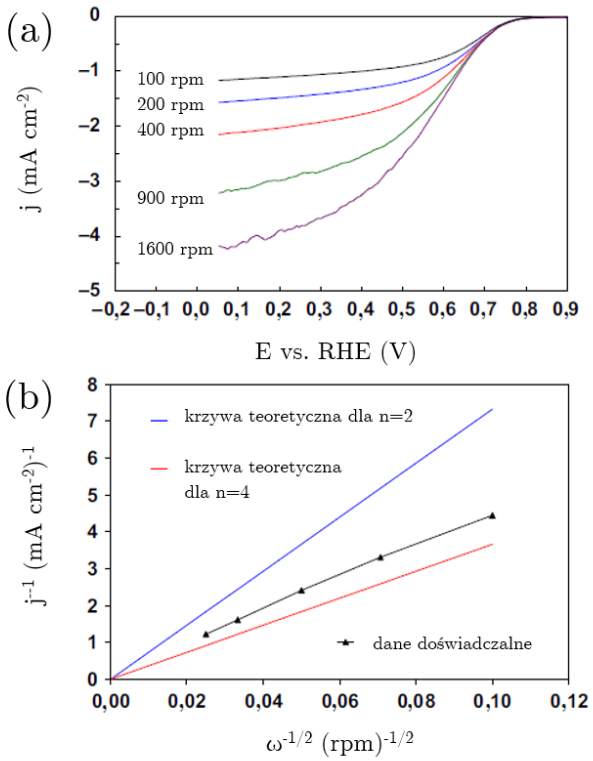
Podobieństwo pików uzyskiwanych za pomocą elektrody wirującej i elektrody stacjonarnej nie powinno dziwić, jeżeli rozważyć fakt, że woltamperogram dla elektrody stacjonarnej nie powinien znacząco odbiegać od woltamperogramu uzyskanego dla elektrody wirującej, której częstotliwość obrotów jest bliska zeru. Jeżeli względem takiej elektrody chcieć stosować równanie Koutecký'ego-Levicha (2.5), to okazuje się, że dla szybkości wirowania dążącej do zera, także natężenie prądu powinno dążyć do zera, czego się w rzeczywistości jednak nie obserwuje. Z tego względu częstotliwość wirowania elektrody nie może być dowolnie niska, aby odchylenia od równania Koutecký'ego-Levicha (2.5) pozostawały niewielkie [40].



Rysunek 25. Utlenianie ferrocenu na wirującej elektrodzie dyskowej. Liniami ciągłymi oznaczono krzywe woltamperometryczne otrzymane doświadczalnie, natomiast liniami przerywanym – krzywe uzyskane za pomocą symulacji. Wykresy (a) i (b) przedstawiają wpływ odpowiednio szybkości skanowania oraz częstotliwości wirowania elektrody na kształt krzywej. Piki świadczą o stosowaniu zbyt wysokiej szybkości skanowania w stosunku do częstotliwości wirowania elektrody [66].

2.1.4 Wirująca elektroda dyskowa w kontekście badań nad elektroredukcją tlenu

Metoda wirującej elektrody dyskowej jest podstawową techniką stosowaną w badaniach nad procesem ORR. Powszechną, aczkolwiek budzącą wątpliwości [67] praktyką jest wyznaczanie liczby elektronów wymienianych podczas elektroredukcji tlenu na podstawie współczynnika nachylenia wykresu Koutecký'ego-Levicha, jak zostało to przedstawione na Rysunku 26.



Rysunek 26. (a) Krzywe woltamperometryczne dla redukcja tlenu w środowisku kwasowym (0,5 M H_2SO_4) na elektrodzie z węgla szklistego z naniesioną warstwą kompleksu kobaltu (Co-TPTZ) oraz powstały na bazie tychże krzywych (b) wykres Koutecký'ego-Levicha dla potencjału 0,1 V_{RHE}. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [68].

Zhou i współpracownicy dowiedli, że niestety analiza Koutecký'ego-Levicha nie jest odpowiednia do wyznaczania liczby n dla procesu ORR, zarówno pod względem teoretycznym, jak i praktycznym [67]. Liczba wymienianych elektronów wyznaczona w ten sposób może być pozornie nawet wyższa niż wynika to z teoretycznych przewidywań [67]. Na przykład Kim i Gewirth [69] stosując metodę Koutecký'ego-Levicha, uzyskali dla elektroredukcji tlenu na elektrodzie złotej liczbę wymienianych elektronów równą 4,5. Z kolei Cheng i Scott [70], dla innego złożonego procesu jakim jest utlenianie borowodorku, otrzymali wartości n przekraczające 9, podczas gdy maksymalne liczba elektronów biorących udział w tej reakcji wynosi 8.

2.2 Wirująca elektroda pierścieniowa

Wirująca elektroda pierścieniowa polecana jest zamiast wirującej elektrody dyskowej do badania reakcji, w których powstają produkty gazowe. Podyktowane jest to faktem, że pęcherze gazu są efektywniej usuwane z powierzchni pierścienia niż z dysku [71].

Równanie Koutecký'ego-Levicha (2.5) podaje natężenie prądu na elektrodzie dyskowej i_D jako funkcję warunków zachodzenia reakcji (ω, c), parametrów kinetycznych (n, k) oraz właściwości fizykochemicznych (D, ν). Jeżeli wszystkie te wielkości pozostają

stałe, a elektroda dyskowa zastępowana jest przez elektrodę pierścieniową, to natężenie prądu i_R obserwowane na takiej elektrodzie pierścieniowej jest wprost proporcjonalne do natężenia prądu na dysku i_D (2.9) [43].

$$i_R = i_D \left(\frac{r_3^3}{r_1^3} - \frac{r_2^3}{r_1^3} \right)^{2/3} \tag{2.9}$$

Równanie wiążące i_R oraz i_D (2.9) obowiązuje niezależnie od warunków, w których przebiega proces elektrodowy (kontrola dyfuzyjna, kinetyczna lub mieszana), a współczynnik proporcjonalności między wielkościami i_R oraz i_D jest zależny jedynie od wymiarów elektrody dyskowej (r_1) i pierścieniowej (r_2, r_3). Stąd natężenie prądu i_R na wirującej elektrodzie pierścieniowej dane jest równaniem (2.10), analogicznym do równania Koutecký'ego-Levicha dla elektrody dyskowej.

$$\frac{1}{i_R} = \frac{1}{i_{R,k}} + \frac{1}{i_{R,l,c}} = \frac{1}{nF\pi(r_3^3 - r_2^3)^{2/3}kc} + \frac{1}{0{,}62nF\pi(r_3^3 - r_2^3)^{2/3}D^{2/3}\omega^{1/2}\nu^{-1/6}c} \tag{2.10}$$

Mnożąc obie strony równania (2.10) przez stężenie substancji elektroaktywnej c oraz wprowadzając zmienne $a = \left(0{,}62nF\pi(r_3^3 - r_2^3)^{2/3}D^{2/3}\nu^{-1/6}\right)^{-1}$ oraz $b = \left(nF\pi(r_3^3 - r_2^3)^{2/3}k\right)^{-1}$, równanie przyjmuje uproszczoną formę (2.11), która jasno pokazuje linową zależność pomiędzy c/i_R a $\omega^{-1/2}$.

$$\frac{c}{i_R} = \frac{c}{i_{R,k}} + \frac{c}{i_{R,l,c}} = b + a\omega^{-1/2} \tag{2.11}$$

Jeżeli reakcja przebiegająca na wirującej elektrodzie pierścieniowej jest całkowicie kontrolowana przez dyfuzję, tj. $i_{R,k}$ dąży do nieskończoności i b jest równe zeru, to natężenie prądu na pierścieniu jest wprost proporcjonalne do $\omega^{1/2}$ (2.12).

$$i_R = i_{R,l,c} = \frac{c}{a}\omega^{1/2} \tag{2.12}$$

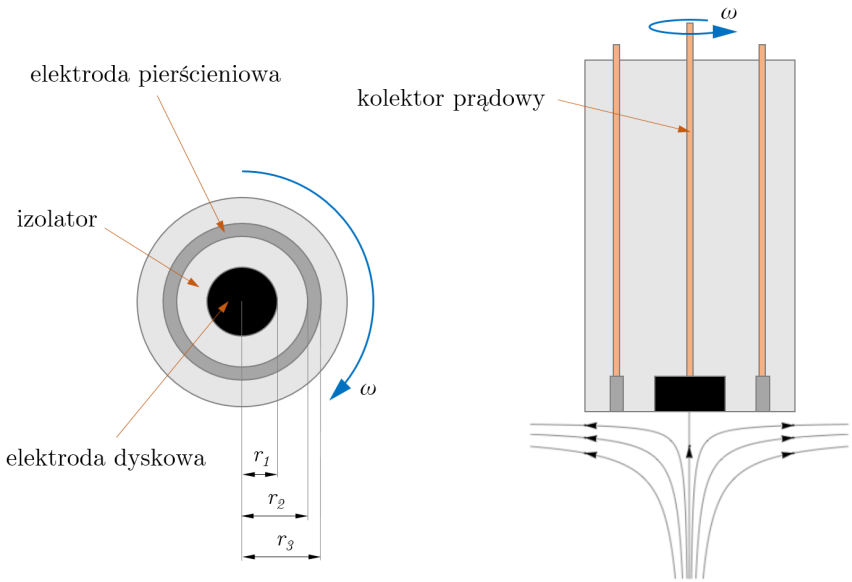
Podobnie jak w przypadku wirującej elektrody dyskowej, warunek $i_{R,k} > i_{R,l,c}$ nie jest wystarczający, aby stwierdzić, że reakcja podlega całkowitej kontroli dyfuzyjnej. Stosunek mierzonego natężenia prądu na pierścieniu i_R do teoretycznego natężenia prądu w warunkach pełnej kontroli dyfuzyjnej $i_{R,l,c}$ zmienia się wraz z szybkością wirowania elektrody zgodnie z równaniem (2.13).

$$\frac{i_R}{i_{R,l,c}} = \frac{1}{\frac{b}{a}\omega^{1/2} + 1} \tag{2.13}$$

2.3 Wirująca elektroda dyskowo-pierścieniowa

2.3.1 Budowa i zasada działania

Chociaż elektroda pierścieniowa może stanowić jedyną elektrodę badaną w układzie pomiarowym [72], to jest ona przeważnie stosowana razem z elektrodą dyskową jako wirująca elektroda dyskowo-pierścieniowa. Schemat takiej elektrody przedstawiono na Rysunku 27. Elektrodę taką można stosować do wykrywania i badania nietrwałych produktów procesu elektrodowego przebiegającego na wewnętrznej elektrodzie dyskowej. Na skutek wirowania elektrody produkty reakcji elektrodowej są w sposób ciągły usuwane z powierzchni elektrody [43]. Pierścień otaczający wewnętrzną elektrodę dyskową może wykryć produkty generowane na dysku, o ile odległość między tymi dwiema elektrodami jest niewielka, a potencjały obu elektrod są odpowiednio różne. Na przykład, jeżeli na wewnętrznej elektrodzie dyskowej zachodzi proces redukcji, to potencjał elektrody pierścieniowej musi być tak dobrany, aby umożliwić utlenianie substancji elektroaktywnej pochodzącej z elektrody dyskowej [40]. W takim układzie elektroda pierścieniowa pełni rolę detektora produktów generowanych na elektrodzie wewnętrznej, sama nie wpływając na przebieg procesu elektrodowego na dysku [41].

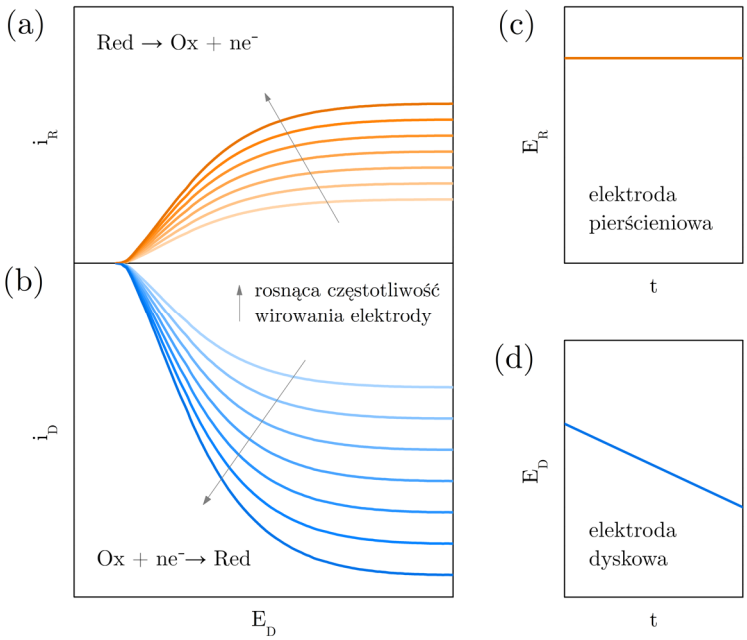


Rysunek 27. Schemat wirującej elektrody dyskowo-pierścieniowej [40].

2.3.2 Stosowanie metody wirującej elektrody dyskowo-pierścieniowej

Przeważnie na wewnętrzną elektrodę dyskową nakłada się potencjał zmieniający się liniowo w czasie, natomiast potencjał elektrody pierścieniowej pozostaje stały i ma taką wartość, aby dochodziło do utleniania bądź redukcji produktów generowanych na dysku [40] (Rysunek 28). Sporadycznie badania z wykorzystaniem wirującej elektrody dyskowo-pierścieniowej prowadzi się w taki sposób, że jednocześnie zmieniają się potencjały obu elektrod [73]. Możliwe jest także sprzężenie metody wirującej elektrody dyskowo-pierścieniowej z technikami impedancyjnymi. Kiedy prąd przemienny przepływa przez elektrodę dyskową, na elektrodzie pierścieniowej rejestrowany jest prąd przemienny przesunięty w fazie i o mniejszej amplitudzie [74,75].

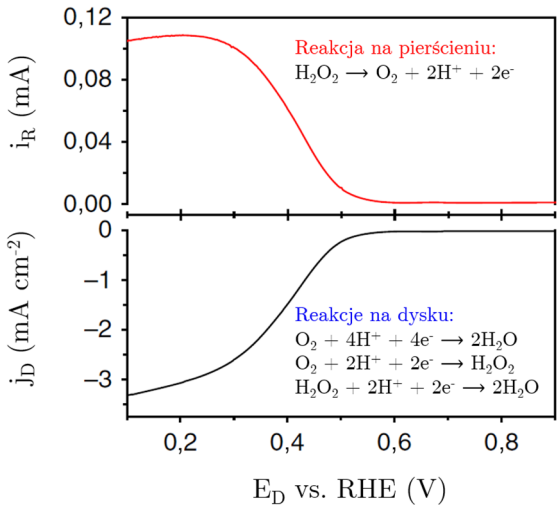
Metoda wirującej elektrody dyskowo-pierścieniowej jest szczególnie przydatna podczas badań reakcji równoległych bądź procesów elektrodowych zachodzących w kilku etapach. Znajduje ona zastosowanie w badaniach nad elektroredukcją tlenu [76-78], korozją [79,80], osadzaniem metali [81,82], a także elektroredukcją CO_2 [83,84], reakcjami polisiarczków [85] oraz utlenianiem borowodorków [86-88].



Rysunek 28. Reakcja redukcji badana za pomocą wirującej elektrody dyskowo-pierścieniowej. (a-b) Krzywe natężenia prądu od potencjału elektrody dyskowej. (c-d) Zależność potencjału elektrod od czasu.

2.3.3 Wirująca elektroda dyskowo-pierścieniowa w kontekście badań nad elektroredukcją tlenu

W przypadku badań nad elektroredukcją tlenu, pierścień ma za zadanie wykryć nadtlenek wodoru generowany w wyniku redukcji tlenu przebiegającej na elektrodzie dyskowej (Rysunek 29).



Rysunek 29. Reakcje przebiegające na elektrodzie pierścieniowej oraz elektrodzie dyskowej podczas badań nad elektroredukcją tlenu [89].

Na podstawie stosunku między natężeniem prądu na pierścieniu i_R oraz natężeniem prądu na dysku i_D wyznaczyć można liczbę wymienianych elektronów n_{RRDE}, jak to opisuje równanie (2.14) [67].

$$n_{RRDE} = \frac{4N}{N + (i_R/i_D)} \tag{2.14}$$

N występujące w równaniu (2.14) oznacza współczynnik efektywności zbierania (ang. *collection efficiency*), który jest parametrem zależnym jedynie od wymiarów elektrody dyskowej i pierścieniowej [43]. Współczynnik ten określa jaka część produktu generowanego na elektrodzie dyskowej jest wykrywana na elektrodzie pierścieniowej, zakładając, że produkt ten jest chemicznie stabilny, a reakcja na elektrodzie pierścieniowej jest kontrolowana całkowicie przez dyfuzję [1].

Współczynnik efektywności zbierania N pozostaje stały, gdy zmienia się szybkość wirowania elektrody, chyba że na elektrodzie dyskowej osadzona jest stosunkowo gruba warstwa katalizatora, która zaburza geometrię elektrody [67]. W takim przypadku N maleje wraz ze wzrostem częstotliwości wirowania elektrody i powinno być wyznaczane doświadczalnie [67].

Warto podkreślić, że podstawianie do równania (2.14) stałej wartości N w sytuacji, gdy na dysk naniesiona jest warstwa katalizatora skutkuje otrzymaniem zawyżonych wartości n_{RRDE}. Co więcej, różnica między wyznaczonymi a rzeczywistymi wartościami n_{RRDE}

rośnie wraz ze wzrostem szybkości wirowania elektrody. W efekcie można otrzymać wartości n_{RRDE}, które pozornie zależą od szybkości wirowania elektrody, nawet jeżeli w rzeczywistości pozostają one stałe.

Liczba wymienianych elektronów n_{RRDE} wskazuje na wydajność elektrochemicznej konwersji tlenu [90]. Nie dostarcza ona jednak szczegółowych informacji na temat reakcji, którym tlen ulega. Podczas elektroredukcji tlenu powstawać mogą zarówno H_2O, jak i H_2O_2, co wymaga wymiany odpowiednio czterech oraz dwóch elektronów, jak wynika to z reakcji (2.15) i (2.16).

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{2.15}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2.16}$$

Dodatkowo, nadtlenek wodoru, który może stanowić produkt końcowy redukcji tlenu, może także być produktem przejściowym i ulegać dalszej redukcji elektrochemicznej zgodnie z reakcją (2.17).

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{2.17}$$

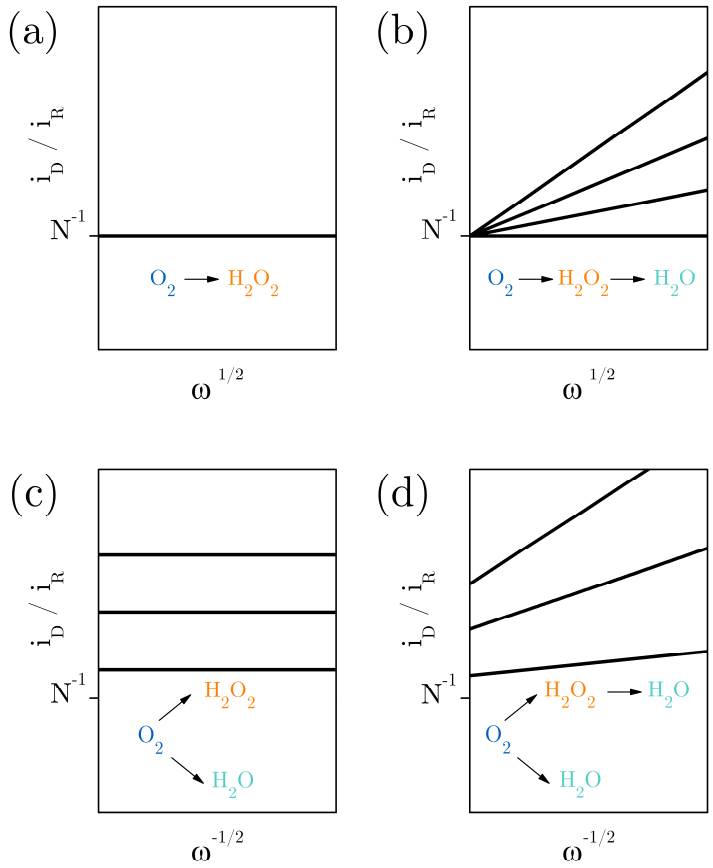
Warto zaznaczyć, że reakcje (2.15) i (2.16) nie wykluczają się wzajemnie i mogą przebiegać równolegle. Stąd elektroredukcja tlenu powinna być domyślnie traktowana jako złożony proces obejmujący zarówno reakcje równoległe, jak i następcze, chyba że istnieją jakieś dowody na to, że któraś spośród reakcji (2.15-2.17) faktycznie nie zachodzi. Co za tym idzie, niepoprawnym jest wyznaczanie parametrów kinetycznych dla redukcji tlenu biorąc pod uwagę przykładowo jedynie reakcje (2.16) i (2.17), nie prezentując żadnego uzasadnienia dla pominięcia reakcji (2.15) [91].

Zgodnie z teoretyczną analizą wykonaną przez Damjanovica i współpracowników [91], metoda wirującej elektrody dyskowo-pierścieniowej pozwala określić, które spośród reakcji (2.15-2.17) faktycznie zachodzą podczas elektroredukcji tlenu. Ponieważ reakcja (2.17) nie może przebiegać bez reakcji (2.16), trzy reakcje (2.15-2.17) dają jedynie pięć możliwych kombinacji. Jedna z tych kombinacji odpowiada sytuacji, kiedy reakcja (2.15) jest jedyną reakcją i wówczas nadtlenek wodoru nie jest w ogólne wykrywany na elektrodzie pierścieniowej (i_R=0). W przypadku pozostałych czterech kombinacji, przebieg zależności i_D/i_R vs. $\omega^{-1/2}$ zmienia się wraz ze zmianą potencjału elektrody dyskowej, jak to przedstawiono na Rysunku 30.

Podstawą koncepcji metody wirującej elektrody dyskowo-pierścieniowej jest możliwość badania procesu elektrodowego przebiegającego na dysku przy zastosowaniu elektrody pierścieniowej jako selektywnego detektora. Kiedy na dysku przebiega złożony proces i generowanych jest kilka produktów, elektroda pierścieniowa powinna dawać odpowiedź tylko na jeden z nich. W przypadku elektroredukcji tlenu, na pierścieniu selektywnie wykrywany jest nadtlenek wodoru. Teoria metody wirującej elektrody dyskowo-pierścieniowej została wyprowadzona przy założeniu, że wykrywany produkt ulega reakcji elektrochemicznej na elektrodzie pierścieniowej natychmiast po tym jak zostaje dostarczony do powierzchni tej elektrody [54]. Innymi słowy, zakłada się, że reakcja na elektrodzie pierścieniowej jest kontrolowana całkowicie przez dyfuzję. Istotnym jest, aby zrozumieć,

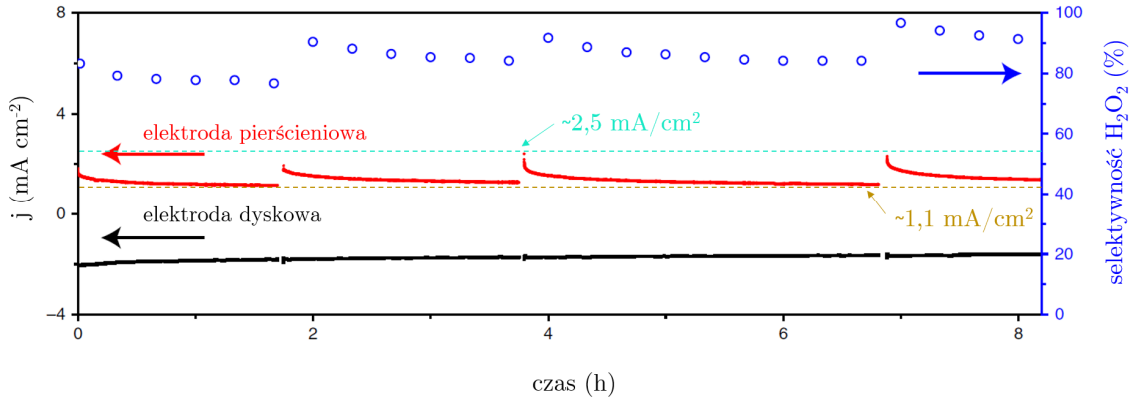
że wyniki pomiarów uzyskanych za pomocą wirującej elektrody dyskowo-pierścieniowej mogą być podstawą do określenia mechanizmu oraz wyznaczenia parametrów kinetycznych reakcji elektrodowej tylko w przypadku, kiedy powyższe założenie jest spełnione.

W rezultacie, aby wyznaczyć liczbę wymienianych elektronów n_{RRDE} podczas elektroredukcji tlenu, natężenie prądu na pierścieniu i_R podstawiane do równania (2.14) musi być natężeniem prądu w warunkach pełnej kontroli dyfuzyjnej $i_{R,l,c}$. Podobnie wykresy zależności i_D/i_R vs. $\omega^{-1/2}$ na Rysunku 30 obowiązują jedynie wówczas, gdy i_R jest równe $i_{R,l,c}$.



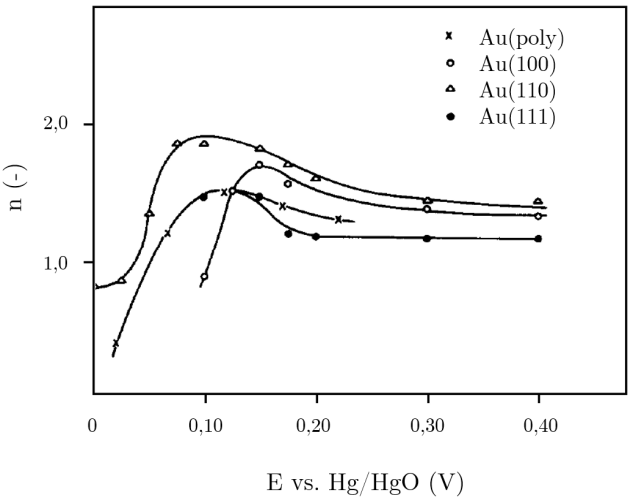
Rysunek 30. Schematyczne zależności i_D/i_R vs. $\omega^{-1/2}$ dla różnych wartości potencjału elektrody dyskowej E_D, gdy (a) reakcja (2.16) jest jedyną reakcją; (b) po reakcji (2.16) następuje reakcja (2.17); (c) reakcje (2.15) oraz (2.16) zachodzą równolegle; (d) reakcja (2.16), po której następuje reakcja (2.17), przebiega równolegle z reakcją (2.15) [91].

Wirująca elektroda dyskowo-pierścieniowa jest powszechnie wykorzystywana w badaniach nad elektroredukcją tlenu. W celu wykrycia H_2O_2 generowanego na skutek redukcji O_2, elektroda pierścieniowa jest najczęściej polaryzowana do potencjału 1,2 V_{RHE}. Przy takiej wartości potencjału na pierścieniu wykonanym z platyny tworzy się powierzchniowa warstwa tlenkowa, która wpływa na kinetykę utleniania nadtlenku wodoru. W efekcie rejestrowane natężenie prądu na elektrodzie pierścieniowej spada (nie jest już limitowane dyfuzyjnie), jak zostało to przedstawione na Rysunku 31.



Rysunek 31. Redukcja tlenu na Fe-CNT (nanorurkach węglowych domieszkowanych atomami Fe) w 0,1 M KOH. Potencjał elektrody dyskowej wynosił 0,71 V_{RHE}. Elektroda pierścieniowa była cyklicznie polaryzowana katodowo, aby usunąć warstwę PtO_x [89].

Aby uniknąć zmiany odpowiedzi pierścienia na skutek tworzenia się na nim warstwy tlenkowej, zamiast powszechnie stosowanych pierścieni platynowych proponuje się pierścienie wykonane ze złota. Jednak jak można wywnioskować z Rysunku 32, pierścienie złote również nie zapewniają kontroli dyfuzyjnej procesu utleniania H_2O_2, czyli nawet przy ich zastosowaniu podstawowe założenie metody wirującej elektrody dyskowo-pierścieniowej nadal nie jest spełnione.



Rysunek 32. Liczba elektronów wymienianych podczas utleniania HO_2^- na elektrodach złotych. Przedruk za zgodą (po modyfikacjach i tłumaczeniu) z [92].

II

Cel pracy oraz hipotezy badawcze

Głównym celem niniejszej pracy było określenie przebiegu procesu elektroredukcji tlenu na elektrodzie węglowej w elektrolitach alkalicznych na bazie mieszanin dwuskładnikowych dimetylosulfotlenek-woda.

Postawiono hipotezę, iż elektrolity tego typu mogą oferować nowe możliwości w porównaniu do konwencjonalnych elektrolitów wodnych. Charakterystyczną cechą mieszanin dwuskładnikowych dimetylosulfotlenek-woda jest fakt, że właściwości takiej mieszaniny nie są średnią właściwości jej składników. Wynika to z silnych oddziaływań między cząsteczkami dimetylosulfotlenku a cząsteczkami wody. Woda jest donorem wiązania wodorowego, natomiast dimetylosulfotlenek, będący polarnym rozpuszczalnikiem aprotycznym, jest jego akceptorem. W rezultacie w tego typu elektrolitach obecne są międzycząsteczkowe kompleksy DMSO-woda cechujące się dużym momentem dipolowym. Dodatkową motywacją, by przetestować wspomniane elektrolity jako media do procesu elektrochemicznej redukcji tlenu były doniesienia literaturowe, według których w elektrolitach bezwodnych na bazie dimetylosulfotlenku materiały węglowe charakteryzują się znacznie wyższymi wartościami stałych szybkości redukcji tlenu niż metale szlachetne.

Celem pobocznym pracy, sformułowanym na podstawie wyników badań wstępnych, było określenie jaki wpływ na wyniki badań nad redukcją tlenu uzyskiwane przy zastosowaniu wirującej elektrody dyskowo-pierścieniowej wywiera kinetyka reakcji utleniania nadtlenku wodoru.

Metoda wirującej elektrody dyskowo-pierścieniowej jest powszechnie wykorzystywana w badaniach nad elektroredukcją tlenu, bowiem nadtlenek wodoru generowany na elektrodzie dyskowej jako produkt pośredni lub produkt uboczny może zostać wykryty na niezależnej, położonej koncentrycznie elektrodzie pierścieniowej. W celu wykrycia nadtlenku wodoru pierścień platynowy polaryzowany jest do potencjału równego 1,2 V_{RHE}, czyli do potencjału, przy którym platyna pokrywa się warstwą tlenkową. Teoria metody wirującej elektrody dyskowo-pierścieniowej została wyprowadzona przy założeniu, że reakcja przebiegająca na elektrodzie pierścieniowej zachodzi w warunkach pełnej kontroli dyfuzyjnej. Postawiono hipotezę, iż warstwa tlenkowa może zmniejszać szybkość utleniania nadtlenku wodoru i tym samym sprawiać, że założenie odnośnie reakcji na elektrodzie pierścieniowej kontrolowanej wyłącznie przez dyfuzję nie będzie już spełnione.

III

Część doświadczalna

3. Kinetyka utleniania H_2O_2 a badania nad elektroredukcją tlenu przy zastosowaniu wirującej elektrody dyskowo-pierścieniowej

3.1 Aparatura, odczynniki oraz układ pomiarowy

Wszystkie pomiary elektrochemiczne prowadzono przy zastosowaniu elektrody wirującej z dyskiem z węgla szklistego (r_1=2 mm) oraz pierścieniem platynowym (r_2=2,5 mm, r_3=3,5 mm) (ALS, Japonia) przyłączonej do aparatu RRDE-3A (ALS, Japonia). Doświadczenia przeprowadzano w dwóch różnych konfiguracjach, tj. w układzie czteroelektrodowym, w którym zarówno dysk, jak i pierścień stanowiły elektrody badane, oraz w układzie trójelektrodowym, w którym elektroda pierścieniowa stanowiła jedyną elektrodę badaną, a dysk pozostawał niepodłączony. W obu konfiguracjach elektrodę odniesienia stanowiła elektroda tlenkowo-rtęciowa Hg/HgO/6 M KOH (RE-61AP, ALS, Japonia), a mierzony potencjał przeliczany był na potencjał względem odwracalnej elektrody wodorowej (RHE – ang. *reversible hydrogen electrode*) zgodnie z równaniem Nernsta (3.1).

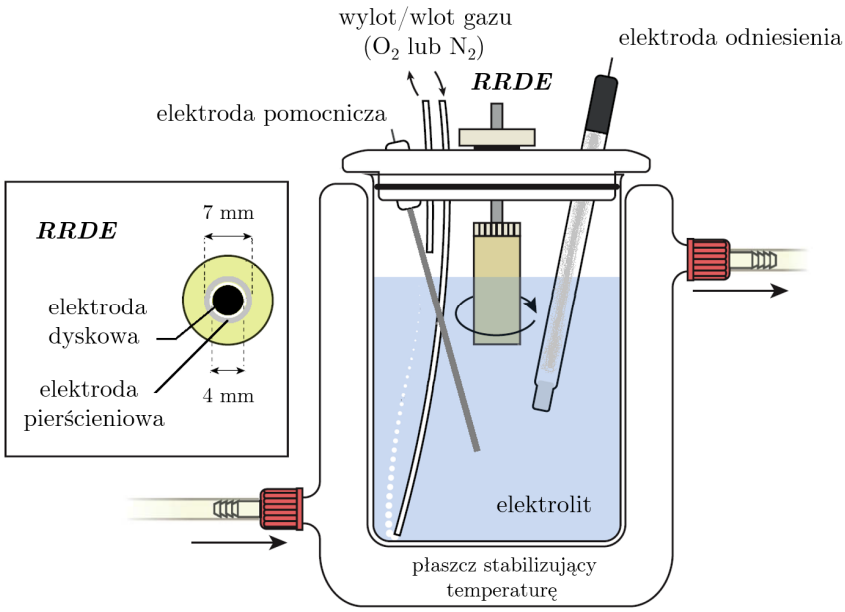
$$E_{RHE} = E_{Hg/HgO} + E^{\circ}_{Hg/HgO} + 0{,}059\ pH \tag{3.1}$$

E_{RHE} to potencjał względem odwracalnej elektrody wodorowej, $E_{Hg/HgO}$ to potencjał mierzony względem tlenkowo-rtęciowej elektrody odniesienia, natomiast $E^{\circ}_{Hg/HgO}$ to standardowy potencjał elektrody Hg/HgO/6 M KOH równy 0,098 V [93]. Ponieważ wszystkie pomiary elektrochemiczne były wykonywane w środowisku 0,1 M KOH (pH 13), równanie (3.1) upraszcza się do postaci (3.2).

$$E_{RHE} = E_{Hg/HgO} + 0{,}865\ V \tag{3.2}$$

Skręcony spiralnie drut platynowy (ALS, Japonia) pełnił rolę elektrody pomocniczej podczas wszystkich eksperymentów za wyjątkiem badań nad elektroredukcją tlenu na węglu szklistym oraz kondycjonowania elektrody pierścieniowej przed tego typu badaniami. W tych przypadkach zamiast drutu platynowego jako elektrodę pomocniczą stosowano pręt grafitowy, aby uniknąć możliwego zanieczyszczenia powierzchni węgla szklistego w wyniku osadzenia cząstek platyny [94,95].

Schemat układu pomiarowego przedstawiono na Rysunku 33. Wszystkie elektrody umieszczone były w naczyniu termostatowanym (T-GL 250, Schott Duran, Niemcy), zawierającym ok. 225 mL elektrolitu. W zależności od potrzeb, elektrolitem był czysty 0,1 M KOH lub roztwór nadtlenku wodoru w tym medium. Badania elektrochemiczne przeprowadzano przy użyciu potencjostatu/galwanostatu VMP3 (BioLogic, Francja). Stałą temperaturę podczas wszystkich pomiarów (25±0,1°C) zapewniał termostat cyrkulacyjny (CC-K6 with Pilot ONE, Huber, Niemcy).



Rysunek 33. Schemat układu pomiarowego [96].

Elektrolity zostały przygotowane przy użyciu wody dejonizowanej oraz następujących odczynników o klasie czystości cz.d.a.: wodorotlenek potasu (POCH, Polska) oraz nadtlenek wodoru (30% roztwór wodny, Sigma Aldrich, Niemcy). Przygotowanie roztworów nadtlenku wodoru w 0,1 M KOH odbywało się bezpośrednio przed pomiarami elektrochemicznymi, aby uniknąć możliwej zmiany stężenia nadtlenku wodoru na skutek jego rozkładu w alkaliach [97].

Elektroda wirująca z dyskiem z węgla szklistego oraz pierścieniem platynowym przed każdą serią pomiarów elektrochemicznych była starannie polerowana za pomocą proszku diamentowego (1 μm) oraz aluminy (0,05 μm) (PK-3 polishing kit, ALS, Japonia). W celu usunięcia pozostałości past polerskich elektroda była spłukiwana etanolem oraz wodą dejonizowaną, a następnie była umieszczana w łaźni ultradźwiękowej wypełnionej wodą dejonizowaną na okres 5 minut. Bezpośrednio potem platynowa elektroda pierścieniowa była kondycjonowana w 0,1 M KOH za pomocą woltamperometrii cyklicznej. Potencjał elektrody pierścieniowej był zmieniany z szybkością 100 mV s^{-1} w zakresie od +0,865 V do +1,215 V vs. RHE. W powyższym zakresie potencjałów wykonywano 50 cykli, przy czym cykl pierwszy rozpoczynał się od wartości potencjału obwodu otwartego (OCP – ang. *open circuit potential*), a ostatni cykl kończył się przy potencjale +1,215 V vs. RHE.

3.2 Metodyka badań

3.2.1 Utlenianie nadtlenku wodoru na platynowej elektrodzie pierścieniowej pokrytej tlenkami

Utlenianie H_2O_2 było prowadzone w układzie trójelektrodowym poprzez zmianę potencjału platynowej elektrody pierścieniowej w zakresie od +0,865 V to +1,215 V vs. RHE z szybkością 10 mV s^{-1}. Pomiary były wykonywane dla roztworów o czterech różnych stężeniach (0,05, 0,1, 0,5 oraz 1 mM) nadtlenku wodoru w 0,1 M KOH. Ponadto, czysty 0,1 M KOH (bez dodatku H_2O_2) był stosowany do wyznaczenia natężenia prądu tła (ang. *background current*), inaczej zwanego prądem szczątkowym, który wynika z pojemności warstwy podwójnej na granicy faz elektroda-elektrolit [40]. Utlenianie nadtlenku wodoru było prowadzone dla szybkości wirowania elektrody równych 400, 625, 900, 1225, 1600, 2025 oraz 2500 rpm. Dodatkowe pomiary w szerszym zakresie potencjałów (od +0,865 V do +1,865 V vs. RHE) były wykonywane jedynie dla szybkości wirowania równej 2500 rpm, przy czym pozostałe warunki pozostawały niezmienione.

3.2.2 Utlenianie oraz redukcja H_2O_2 na pierścieniu platynowym pozbawionym tlenków

Podczas badań nad redukcją oraz utlenianiem H_2O_2 na pierścieniu platynowym pozbawionym tlenków potencjał zmieniany był w zakresie od +0,050 V_{RHE} do +1,215 V_{RHE} z szybkością 10 mV s^{-1}. Pomiary prowadzone były przy częstotliwości wirowania elektrody równej 2500 rpm, a jako elektrolit stosowano odtleniony 0,1 M KOH z dodatkiem 1 mM H_2O_2. Ponadto czysty 0,1 M KOH (bez dodatku H_2O_2) pozbawiony tlenu wykorzystywany był do wyznaczenia natężenia prądu tła dla elektrody pierścieniowej. Przed badaniami dotyczącymi redukcji i utleniania H_2O_2 pierścień platynowy poddawany był dwuetapowemu procesowi redukcji w celu usunięcia powierzchniowej warstwy tlenków na elektrodzie. W pierwszym etapie elektroda pierścieniowa polaryzowana były do potencjału +0,050 V_{RHE} przez okres 20 minut, a w etapie drugim (również trwającym 20 minut) potencjał elektrody pierścieniowej wynosił –0,335 V_{RHE}. Dwuetapowy proces redukcji był przeprowadzany w odtlenionym 0,1 M KOH, w warunkach stacjonarnych (szybkość wirowania elektrody wynosiła 0 rpm).

3.2.3 Wyznaczanie współczynnika efektywności zbierania dla wirującej elektrody dyskowo-pierścieniowej

W celu wyznaczenia współczynnika efektywności zbierania N został użyty elektrolit alkaliczny zawierający $K_3[Fe(CN)_6]$. Badania prowadzone były w układzie

czteroelektrodowym, przy czym potencjał elektrody dyskowej z węgla szklistego zmieniany był z szybkością 10 mV s^{-1} w zakresie od +1,365 V_{RHE} do 0,000 V_{RHE}, a potencjał elektrody pierścieniowej był stały i wynosił 1,5 V_{RHE}. Pomiarów dokonywano przy częstotliwości wirowania elektrody równych 400, 625, 900, 1225, 1600, 2025 oraz 2500 rpm, a jako elektrolit stosowano odtleniony 0,1 M KOH zawierający 0,010 M $K_3[Fe(CN)_6]$. Ponadto, czysty 0,1 M KOH (bez dodatku jonów heksacyjanożelazianowych(III)) pozbawiony tlenu wykorzystywany był do wyznaczenia natężenia prądu tła dla elektrody dyskowej i pierścieniowej. Jony heksacyjanożelazianowe(III) ulegały redukcji na elektrodzie dyskowej do jonów heksacyjanożelazianowych(II) zgodnie z reakcją (3.3), a powstałe w ten sposób jony heksacyjanożelazianowe(II) były częściowo utleniane na elektrodzie pierścieniowej z powrotem do jonów heksacyjanożelazianowych(III), jak opisuje to reakcja (3.4).

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-} \tag{3.3}$$

$$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^- \tag{3.4}$$

Roztwory $K_3[Fe(CN)_6]$ w alkaliach są powszechnie wykorzystywane [98-115] do wyznaczania współczynnika efektywności zbierania N dla wirującej elektrody dyskowo-pierścieniowej, co wynika za stabilności układu $Fe(CN)_6^{4-}$/ $Fe(CN)_6^{3-}$ w tym środowisku. Jedyną publikacją opisującą rozkład jonów $Fe(CN)_6^{4-/3-}$ w medium alkalicznym do jonów CN^- jest publikacja Luo i współpracowników [116], która ukazała się w 2017 roku w *Nano Energy*. Niemniej jednak tezy przedstawione w tejże publikacji obalili w 2020 roku Páez i współpracownicy [117] w artykule na łamach *Journal of Power Sources*.

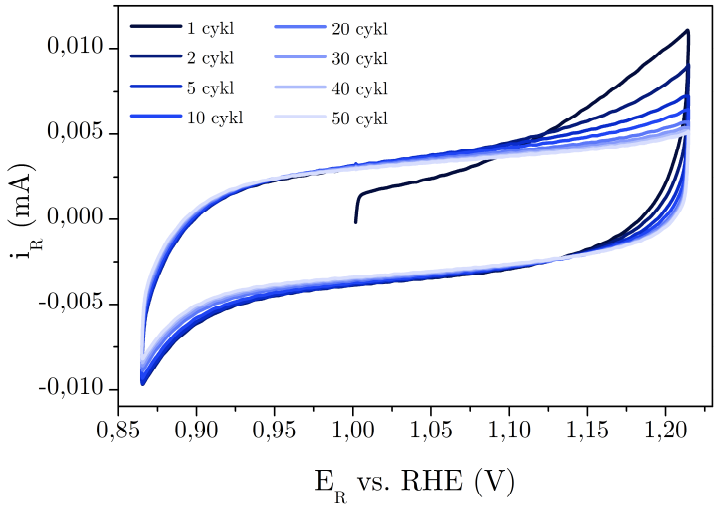
3.2.4 Elektroredukcja tlenu na elektrodzie dyskowej z węgla szklistego

Redukcja tlenu na dysku z węgla szklistego była prowadzona w układzie czteroelektrodowym poprzez zmianę potencjału elektrody dyskowej w zakresie od +1,050 V do -0,650 V vs. RHE z szybkością 10 mV s^{-1}, podczas gdy potencjał elektrody pierścieniowej był stały i równy +1,200 V vs. RHE. Pomiary wykonywane były w 0,1 M KOH nasyconym tlenem pod ciśnieniem 1 atm, dla szybkości wirowania elektrody równych 400, 625, 900, 1225, 1600, 2025 oraz 2500 rpm. W celu wyznaczenia natężenia prądu tła dla elektrody dyskowej i pierścieniowej przeprowadzono także pomiary w 0,1 M KOH pozbawionym tlenu. Elektrolit nasycony tlenem oraz elektrolit odtleniony uzyskiwano poprzez przepuszczanie przez roztwór 0,1 M KOH odpowiednio tlenu (99,5%, Air Products, Polska) lub azotu (99,9992%, Air Products, Polska) przez okres 20 min bezpośrednio przed pomiarami. W trakcie pomiarów elektrochemicznych strumień odpowiedniego gazu kierowany był powyżej lustra elektrolitu.

3.3 Wyniki badań i dyskusja

3.3.1 Utlenianie nadtlenku wodoru na platynowej elektrodzie pierścieniowej pokrytej tlenkami

Przed pomiarami dotyczącymi utleniania H_2O_2 (a także przed badaniami nad elektroredukcją tlenu) elektroda platynowa była kondycjonowana za pomocą woltamperometrii cyklicznej w 0,1 M KOH. Krzywe woltamperometryczne dla wybranych cykli zamieszczono na Rysunku 34.



Rysunek 34. Kondycjonowanie pierścienia platynowego przed dalszymi badaniami dotyczącymi utleniania H_2O_2 oraz redukcji O_2. Elektrolit: 0,1 M KOH. Szybkość skanowania: 100 mV s^{-1}.

Systematyczne pomiary utleniania nadtlenku wodoru w środowisku alkalicznym na pierścieniu platynowym pokrytym tlenkami zostały przeprowadzone, aby zweryfikować czy i w jakim stopniu proces ten odbiega od reakcji kontrolowanej całkowicie przez dyfuzję.

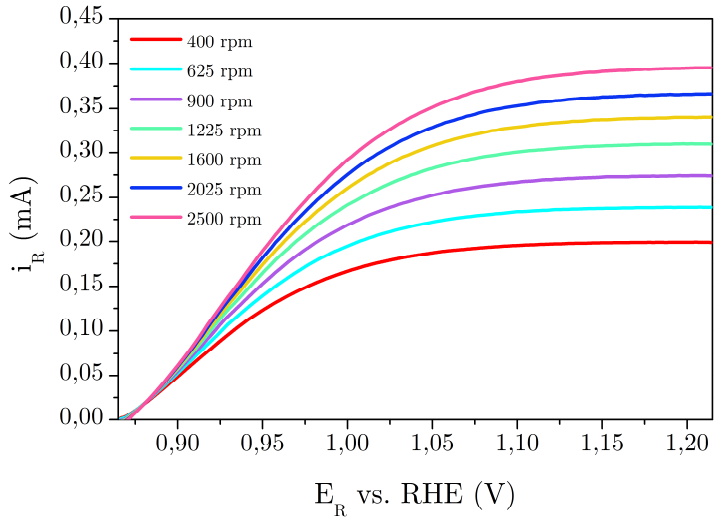
Odpowiedź pierścienia platynowego pokrytego tlenkami na nadtlenek wodoru była badana w zakresie potencjałów od +0,865 V do +1,215 V, dla roztworów o czterech różnych stężeniach H_2O_2 (0,05, 0,1, 0,5 oraz 1 mM w 0,1 M KOH). Dla każdego ze stężeń krzywa woltamperometryczna była rejestrowana dla szybkości wirowania elektrody 400, 625, 900, 1225, 1600, 2025 oraz 2500 rpm.

Nadtlenek wodoru w środowisku alkalicznym przekształca się niemal całkowicie (p_{K_a}=11,7 [118]) w anion wodoronadtlenkowy HO_2^- (ang. *perhydroxyl ion*) zgodnie z reakcją (3.5).

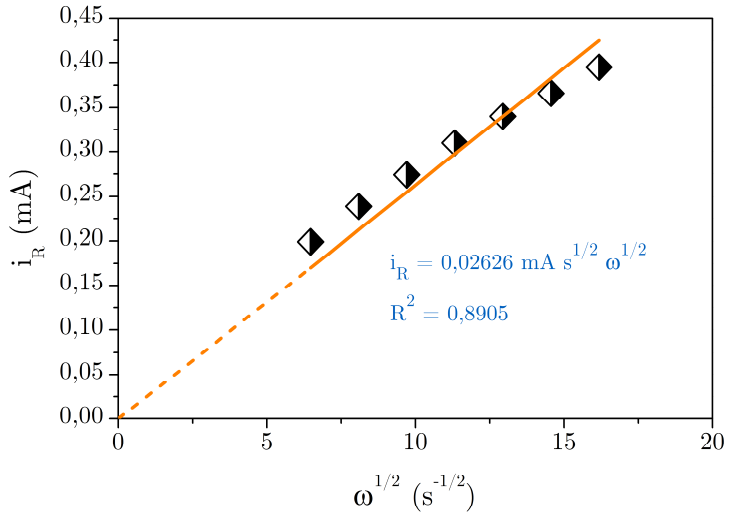
$$H_2O_2 + OH^- \rightleftarrows HO_2^- + H_2O \qquad (3.5)$$

Z tego względu utlenianie nadtlenku wodoru w środowisku alkalicznym dotyczy tak naprawdę utleniania anionu wodoronadtlenkowego.

Rysunek 35 przedstawia woltamperogramy dla pierścienia platynowego pokrytego tlenkami zarejestrowane w 0,1 M KOH z dodatkiem 1 mM H_2O_2. Jak można zauważyć, dobrze wykształcone fale z plateau powyżej 1,15 V rejestrowane są dla wszystkich stosowanych szybkości wirowania elektrody. Niemniej jednak wykres Levicha (zależność i_R vs. $\omega^{1/2}$) na Rysunku 36 dowodzi, że dla potencjału 1,2 V_{RHE} natężenie prądu i_R na pierścieniu platynowym nie jest proporcjonalne do $\omega^{1/2}$. Zatem, zgodnie z równaniem (2.8), utlenianie nadtlenku wodoru na platynie pokrytej tlenkami znacząco odbiega od reakcji elektrodowej przebiegającej przy całkowitej kontroli dyfuzyjnej. Analogiczne rezultaty, obejmujące krzywe woltamperometryczne oraz wykresy Levicha, uzyskano dla pozostałych stężeń H_2O_2 w KOH.

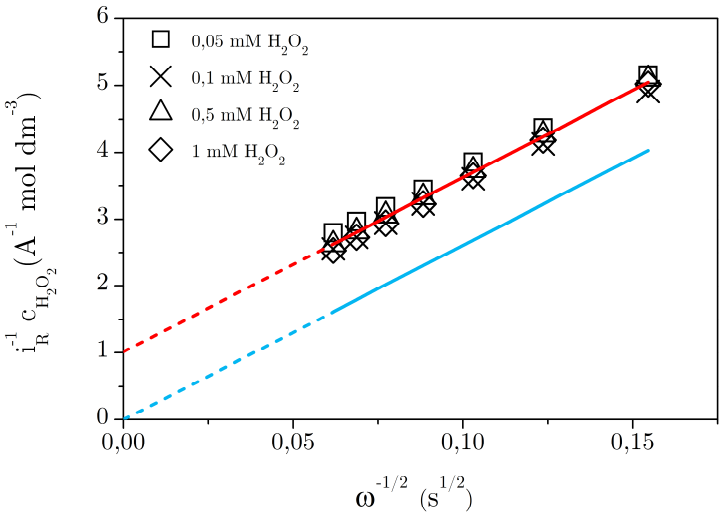


Rysunek 35. Krzywe woltamperometryczne (po korekcie uwzględniającej występowanie natężenia prądu tła) dla utleniania nadtlenku wodoru na pierścieniu platynowym pokrytym tlenkami. Elektrolit: 1 mM H_2O_2 w 0,1 M KOH.



Rysunek 36. Wykres Levicha dla utleniania nadtlenku wodoru na pierścieniu platynowym pokrytym tlenkami przy potencjale 1,2 V_{RHE}. Elektrolit: 1 mM H_2O_2 w 0,1 M KOH.

Dalsza analiza odpowiedzi pierścienia platynowego pokrytego tlenkami na nadtlenek wodoru przy potencjale 1,2 V_{RHE} została przeprowadzona przy zastosowaniu metody Koutecký'ego-Levicha (KL). Wykresy zależności $i_R^{-1} c_{H_2O_2}$ vs. $\omega^{-1/2}$ zostały wykonane zamiast konwencjonalnych wykresów KL (i^{-1} vs. $\omega^{-1/2}$), aby umożliwić porównanie wyników uzyskanych dla różnych stężeń H_2O_2. Jak można zauważyć na Rysunku 37, liniowa zależność między $i_R^{-1} c_{H_2O_2}$ a $\omega^{-1/2}$ z punktem przecięcia osi rzędnych dla ~1 A^{-1} mol dm^{-3} jest obserwowana dla wszystkich badanych stężeń H_2O_2.



Rysunek 37. Zmodyfikowany wykres Koutecký'ego-Levicha dla utleniania nadtlenku wodoru na pierścieniu platynowym pokrytym tlenkami przy potencjale 1,2 V_{RHE}. Linią czerwoną oznaczono przebieg zależności na podstawie uśrednionych danych eksperymentalnych, natomiast linią niebieską zaznaczono teoretyczny przebieg zależności dla utleniania H_2O_2 w warunkach pełnej kontroli dyfuzyjnej.

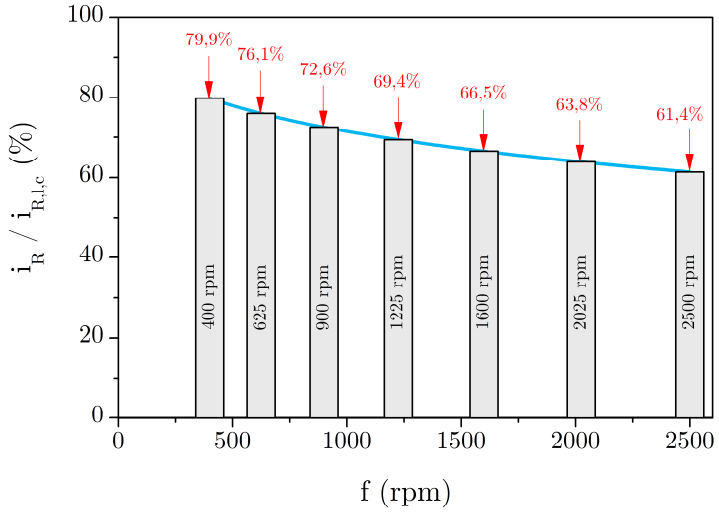
Wartości współczynników a i b w równaniu $i_R^{-1} c_{H_2O_2} = a\omega^{-1/2} + b$ wyznaczone za pomocą regresji liniowej zamieszczone zostały w Tabeli 4 razem z wartościami współczynników determinacji R^2. Współczynniki a i b przyjmują zbliżone wartości dla różnych stężeń H_2O_2, dlatego też ich średnie wartości (a=26,09 A^{-1} mol dm^{-3} $s^{-1/2}$ oraz b=1,016 A^{-1} mol dm^{-3}, R^2=0,9860) zostały wykorzystane do skonstruowania zmodyfikowanego wykresu KL obowiązującego dla zakresu stężeń H_2O_2 od 0,05 do 1 mM. Taka uśredniona zależność $i_R^{-1} c_{H_2O_2}$ od $\omega^{-1/2}$ została oznaczona na Rysunku 37 kolorem czerwonym.

Tabela 4. Wartości współczynników a, b oraz R^2 dla różnych stężeń H_2O_2.

$c_{H_2O_2}$ (mmol dm^{-3})	a (A^{-1} mol dm^{-3} $s^{-1/2}$)	b (A^{-1} mol dm^{-3})	R^2 (-)
0,05	25,56	1,209	0,9998
0,1	25,42	0,9853	1,000
0,5	26,56	0,9914	0,9999
1	26,82	0,8762	0,9999

Natomiast kolorem niebieskim zaznaczono na Rysunku 37 teoretyczny przebieg zmodyfikowanego wykresu KL, który byłby obserwowany w takich samych warunkach, gdyby utlenianie H_2O_2 było kontrolowane całkowicie przez dyfuzję. Teoretyczny wykres KL przedstawia zależność między $i_{R,l,c}^{-1} c_{H_2O_2}$ a $\omega^{-1/2}$. Współczynnik nachylenia dla teoretycznego wykresu KL jest taki sam jak współczynnik nachylenia wykresu KL dla danych eksperymentalnych, ponieważ kinetyka procesu elektrodowego nie wpływa na wartość współczynnika a $(a = \left(0{,}62nF\pi(r_3^3 - r_2^3)^{2/3}D^{2/3}\nu^{-1/6}\right)^{-1})$. Zgodnie z równaniem (2.8), teoretyczny wykres KL przechodzi przez początek układu współrzędnych.

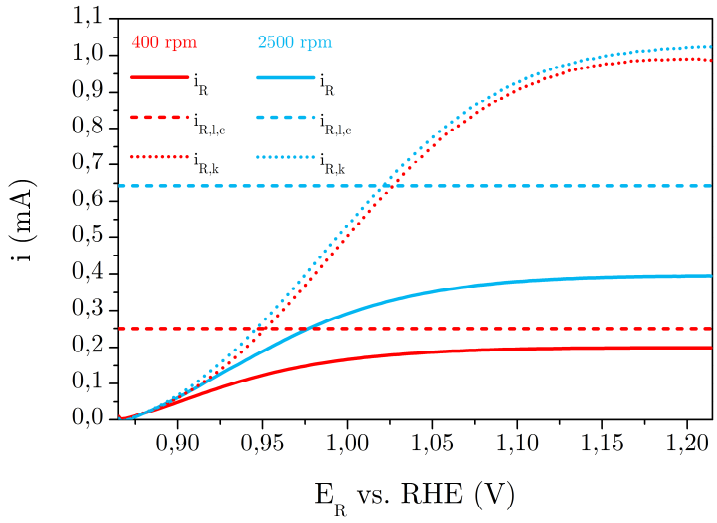
Stosunek mierzonego natężenia prądu na elektrodzie pierścieniowej i_R do teoretycznego natężenia prądu w warunkach pełnej kontroli dyfuzyjnej $i_{R,l,c}$ dany jest równaniem (2.13). Dla utleniania H_2O_2 w 0,1 M KOH na pierścieniu platynowym pokrytym tlenkami stosunek i_R do $i_{R,l,c}$ zmienia się monotonicznie od 79,9% dla 400 rpm do 61,4% dla 2500 rpm, jak zostało to pokazane na Rysunku 38. Fakt, że i_R różni się o kilkadziesiąt procent od $i_{R,l,c}$ wskazuje, że utlenianie H_2O_2 na platynie pokrytej tlenkami podlega mieszanej kontroli dyfuzyjno-kinetycznej. Z tego względu pierścień platynowy pokryty tlenkami nie powinien był stosowany do ilościowego oznaczania H_2O_2 w elektrolitach alkalicznych. Dotyczy to także badań nad elektroredukcją tlenu za pomocą wirującej elektrody dyskowo-pierścieniowej (RRDE), gdzie H_2O_2, początkowo nieobecny w elektrolicie, jest generowany na elektrodzie dyskowej.



Rysunek 38. Stosunek i_R do $i_{R,l,c}$ dla utleniania H_2O_2 w 0,1 M KOH na pierścieniu platynowym pokrytym tlenkami przy potencjale 1,2 V_{RHE}.

Istotnym jest, że stosunek i_R do $i_{R,l,c}$ dla platyny pokrytej tlenkami zależy od potencjału, a wartości pokazane na Rysunku 38 odnoszą się do potencjału równego 1,2 V_{RHE}. Niemniej jednak, wartości te są wystarczające, aby rozdzielić natężenie prądu na pierścieniu i_R na składowe $i_{R,l,c}$ oraz $i_{R,k}$ w szerokim zakresie potencjałów. Rysunek 39 stanowi ilustrację takiego podejścia. Linią ciągłą oznaczono krzywe woltamperometryczne $i_R(E_R)$ po korekcie uwzględniającej występowanie natężenia prądu tła. Natomiast linia

przerywana oraz linia kropkowana przedstawia odpowiednio zależności $i_{R,l,c}(E_R)$ oraz $i_{R,k}(E_R)$. Wartości $i_{R,l,c}$ są niezależne od potencjału i zostały wyznaczone na postawie znanych stosunków $i_R/i_{R,l,c}$ dla 1,2 V_{RHE}. Następnie na podstawie równania (2.10) i znanych wartości $i_R(E_R)$ oraz $i_{R,l,c}(E_R)$ wyznaczono zależności $i_{R,k}(E_R)$. Jak można zauważyć na Rysunku 39, zależność $i_{R,k}(E_R)$ dla 400 rpm oraz 2500 rpm jest prawie jednakowa. Potwierdza to poprawność proponowanego podejścia, gdyż można oczekiwać, że składowa $i_{R,k}$ jest niezależna od szybkości wirowania elektrody. Dodatkowo Rysunek 39 pokazuje, że dobrze wykształcone plateau na krzywej woltamperometrycznej może być obecne nawet jeżeli natężenie prądu na pierścieniu i_R odbiega o kilkadziesiąt procent od natężenia prądu w warunkach całkowitej kontroli dyfuzyjnej $i_{R,l,c}$.

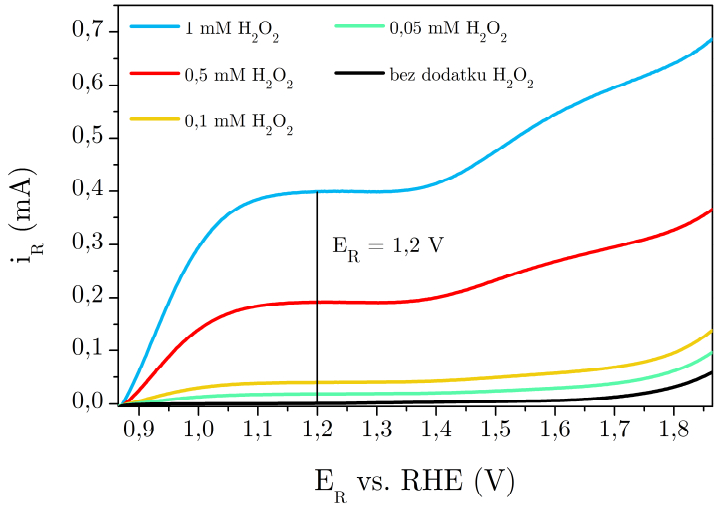


Rysunek 39. Krzywe woltamperometryczne (linie ciągłe), zależności $i_{R,l,c}$ od E_R (linie przerywane) oraz zależności $i_{R,k}$ od E_R (linie kropkowane) dla utleniania H_2O_2 na pierścieniu platynowym pokrytym tlenkami. Elektrolit: 1 mM H_2O_2 w 0,1 M KOH.

Aby określić, czy potencjał 1,2 V_{RHE} jest rzeczywiście optymalnym potencjałem dla utleniania H_2O_2 w środowisku alkalicznym, odpowiedź platyny pokrytej tlenkami na nadtlenek wodoru była badana w zakresie potencjałów od +0,865 V_{RHE} do +1,865 V_{RHE}. Jak można zauważyć na Rysunku 40, dobrze wykształcone plateau jest widoczne w zakresie potencjałów 1,15-1,35 V_{RHE} dla wszystkich badanych stężeń H_2O_2.

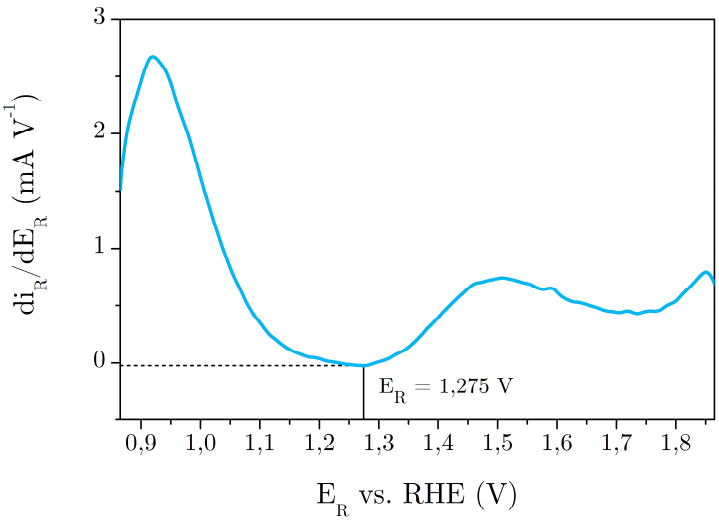
Co ciekawe, przy potencjale 1,35 V_{RHE} natężenie prądu przekracza wartości obserwowane w plateau i rośnie nieprzerwanie aż do potencjału +1,865 V_{RHE}. Szczegółowa analiza krzywej woltamperometrycznej uzyskanej w czystym 0,1 M KOH (bez dodatku H_2O_2) pozwala określić, że za znaczny wzrost natężenia prądu obserwowany powyżej 1,35 V_{RHE} w przypadku roztworów H_2O_2 w 0,1 M KOH nie może być odpowiedzialny proces dalszego tworzenia warstewki tlenkowej na powierzchni elektrody platynowej. Dla platyny pokrytej tlenkami w środowisku czystego 0,1 M KOH widoczny jest jedynie niewielki wzrost natężenia prądu po przekroczeniu potencjału 1,215 V_{RHE}, co wynika z wcześniejszego kondycjonowania elektrody w zakresie potencjałów od +0,865 V_{RHE} do +1,215 V_{RHE}. Wzrost

natężenia prądu obserwowany powyżej 1,35 V_{RHE} nie może być także przypisany utlenianiu jonów hydroksylowych, ponieważ w 0,1 M KOH dla platyny pokrytej tlenkami proces ten przebiega dopiero po przekroczeniu 1,6 V_{RHE}.



Rysunek 40. Krzywe woltamperometryczne dla pierścienia platynowego pokrytego tlenkami zarejestrowane przy 2500 rpm. Elektrolit: roztwór H_2O_2 w 0,1 M KOH lub czysty 0,1 M KOH.

Biorąc wszystko powyższe pod uwagę, można wywnioskować, że wzrost natężenia prądu po przekroczeniu potencjału 1,35 V_{RHE} jest rezultatem zmiany kinetyki reakcji utleniania H_2O_2, która to zmiana jest efektem przemian strukturalnych tlenków na powierzchni platyny. Jak pokazano na Rysunku 41, dla utleniania H_2O_2 na platynie pokrytej tlenkami w środowisku 0,1 M KOH natężenie prądu przekracza wartość obserwowaną w plateau dokładnie przy potencjale +1,275 V_{RHE}. Wartość ta jest zgodna z danymi literaturowymi [119], według których powierzchniowa warstwa tlenków na platynie podlega przemianom strukturalnym w zakresie potencjałów między 1,1 a 1,3 V_{RHE}.



Rysunek 41. Pochodna i_R względem E_R dla utleniania H_2O_2 na pierścieniu platynowym pokrytym tlenkami. Elektrolit: 1 mM H_2O_2 w 0,1 M KOH. Szybkość wirowania elektrody: 2500 rpm.

Mechanizm utleniania H_2O_2 na platynie został zaproponowany przez Halla i współpracowników [120]. Zgodnie z tym mechanizmem, H_2O_2 tworzy związek kompleksowy z Pt(II), co przedstawia reakcja (3.6).

$$H_2O_2 + Pt(OH)_2 \overset{K_1}{\rightleftarrows} Pt(OH)_2 \cdot H_2O_2 \tag{3.6}$$

W utworzonym kompleksie powierzchniowym $Pt(OH)_2 \cdot H_2O_2$ dochodzi do wewnętrznego przeniesienia elektronu, czego konsekwencją jest powstanie metalicznej platyny oraz uwolnienie cząsteczek wody i tlenu, jak opisuje to reakcja (3.7).

$$Pt(OH)_2 \cdot H_2O_2 \overset{k_2}{\rightarrow} Pt + 2H_2O + O_2 \tag{3.7}$$

Następnie metaliczna platyna jest elektrochemicznie utleniana do Pt(II) w reakcji (3.8), która jest źródłem obserwowanego natężenia prądu.

$$Pt + 2H_2O \overset{k_3}{\rightarrow} Pt(OH)_2 + 2H^+ + 2e^- \tag{3.8}$$

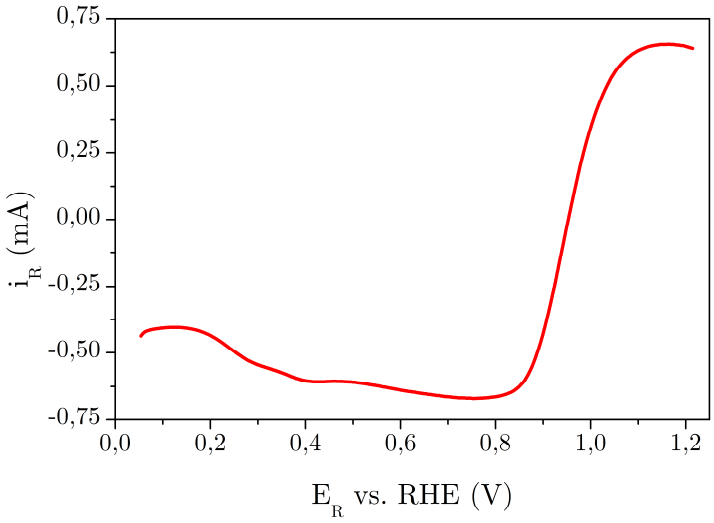
Według innej publikacji Halla i współpracowników [121], stałe szybkości k_2 oraz k_3 zmieniają się wraz z potencjałem w ten sposób, że wartość k_3 jest większa niż wartość k_2 dla potencjałów powyżej +271 mV vs. Ag/AgCl/3 M NaCl (co odpowiada +0,881 V_{RHE}), natomiast poniżej tej wartości stała szybkości k_3 staje się mniejsza niż k_2. Oznacza to, że prąd kinetyczny jest limitowany, zależnie od potencjału, przez reakcję (3.7) lub reakcję (3.8). Przy niższych wartościach potencjału k_2 jest większe niż k_3, stąd prąd kinetyczny jest kontrolowany w przeważającym stopniu przez elektrochemiczne wtórne utlenianie metalicznej platyny. Przy wyższych potencjałach k_3 przekracza wartość k_2 i w efekcie prąd kinetyczny limitowany jest szybkością rozpadu kompleksu powierzchniowego $Pt(OH)_2 \cdot H_2O_2$. Fakt, że stała szybkości k_3 jest większa niż stała szybkości k_2 przy wyższych potencjałach wydaje się być zrozumiały, jeżeli wziąć pod uwagę, że wtórne utlenienie platyny wymaga przeniesienia elektronu z powierzchni elektrody do jej wnętrza, podczas gdy w czasie rozpadu kompleksu $Pt(OH)_2 \cdot H_2O_2$ dochodzi jedynie do transferu elektronu w obrębie samego kompleksu [121]. Opierając się na powyższym mechanizmie, można przypuszczać, że przemiany strukturalne powierzchniowych tlenków platyny prowadzą do wzrostu wartości stałej szybkości k_2, co powoduje obserwowany wzrost natężenia prądu dla reakcji utleniania H_2O_2.

Szczegółowa analiza krzywych woltamperometrycznych na Rysunku 40 pozwala stwierdzić, że rejestrowane natężenie prądu na pierścieniu i_R nie osiąga teoretycznych wartości $i_{R,l,c}$ nawet przy potencjale 1,6 V_{RHE}, czyli przy najwyższej wartości potencjału, przy której nie dochodzi jeszcze do utleniania jonów hydroksylowych. Zatem utlenianie H_2O_2 na platynie pokrytej tlenkami przebiega w środowisku alkalicznym w warunkach mieszanej kontroli dyfuzyjno-kinetycznej niezależnie od stosowanego potencjału. Wyniki te są istotne, ponieważ pierścień platynowy jest podczas badań nad elektroredukcją tlenu czasem także polaryzowany do potencjału 1,5 V_{RHE} [122-131] (zamiast standardowej wartości 1,2 V_{RHE}).

Potencjał elektrody pierścieniowej równy 1,2 V_{RHE} nie zapewnia najwyższego możliwego stosunku i_R do $i_{R,l,c}$. Jednak, co ważniejsze, przy takiej wartości potencjału na krzywej woltamperometrycznej obecne jest dobrze wykształcone plateau i stąd odpowiedź elektrody pierścieniowej na nadtlenek wodoru jest mniej podatna na możliwe fluktuacje potencjału. Poza tym, potencjał 1,2 V_{RHE} pozwala uzyskać natężenie prądu i_R, które nie jest obciążone składową wynikającą z utleniania jonów hydroksylowych.

3.3.2 Utlenianie oraz redukcja H_2O_2 na pierścieniu platynowym pozbawionym tlenków

W przeciwieństwie do platyny pokrytej tlenkami, platyna pozbawiona warstwy tlenkowej zapewnia pełną kontrolę dyfuzyjną utleniania H_2O_2 w środowisku alkalicznym. Dla pierścienia platynowego pokrytego tlenkami uzyskuje się natężenie prądu 0,395 mA (Rysunek 35) przy potencjale 1,2 V_{RHE}, szybkości wirowania 2500 rpm i zastosowaniu 0,1 M KOH z dodatkiem 1 mM H_2O_2. W tych samych warunkach dla pierścienia platynowego pozbawionego tlenków rejestruje się prąd o natężeniu 0,647 mA (Rysunek 42).



Rysunek 42. Krzywa woltamperometryczna (po korekcie uwzględniającej występowanie natężenia prądu tła) dla pierścienia platynowego pozbawionego warstwy tlenkowej w odtlenionym 0,1 M KOH z dodatkiem 1 mM H_2O_2. Szybkość skanowania: 10 mV s^{-1}. Częstotliwość wirowania elektrody: 2500 rpm.

Stosunek tych dwóch wartości wynosi 0,611, co pozostaje w zgodzie z stosunkiem $i_R/i_{R,l,c}$, który dla 2500 rpm wynosi 0,614 (Rysunek 38). O całkowitej kontroli dyfuzyjnej reakcji utleniania H_2O_2 na platynie pozbawionej tlenków świadczy także zgodność wielkości natężenia prądu anodowego (utlenianie H_2O_2) oraz prądu katodowego (redukcja H_2O_2) na Rysunku 42. Ponadto natężenie prądu o wartości 0,647 mA rejestrowane dla pierścienia platynowego pozbawionego warstewki tlenkowej jest spójne z wcześniejszymi badaniami

nad utlenianiem H_2O_2 na powierzchni monokryształów platyny [132] oraz na platynie polikrystalicznej [133].

Tabela 5. Wyniki badań dotyczących utleniania H_2O_2 na platynie.

Natężenie prądu lub gęstość prądu dla 1,2 V_{RHE}	Warunki	Źródło
0,647 mA	wirująca elektroda pierścieniowa, elektrolit: 1 mM H_2O_2 w 0,1 M KOH nasyconym N_2, szybkość wirowania elektrody: 2500 rpm, szybkość skanowania: 10 mV s^{-1}, temperatura: 25,0±0,1°C, elektroda: polikrystaliczna Pt	niniejsza praca
1,8 mA cm^{-2}	wirująca elektroda dyskowa, elektrolit: 1 mM H_2O_2 w 0,1 M KOH nasyconym Ar, szybkość wirowania elektrody: 1600 rpm, szybkość skanowania: 100 mV s^{-1}, temperatura pokojowa, elektroda: polikrystaliczna Pt	Katsounaros et al. [133]
3,4 mA cm^{-2}	HMRDE - wirująca elektroda dyskowa dotykająca jedynie menisku elektrolitu (ang. *Hanging Meniscus Rotating Disk Electrode*), elektrolit: 1,7 mM H_2O_2 w 0,1 M NaOH nasyconym Ar, szybkość wirowania elektrody: 2500 rpm, szybkość skanowania: 50 mV s^{-1}, temperatura pokojowa, elektroda: Pt(111)	Briega-Martos et al. [132]

Natężenie prądu na pierścieniu platynowym (0,647 mA) zarejestrowane przy częstotliwości 2500 rpm w odtlenionym 0,1 M KOH z dodatkiem 1 mM H_2O_2 zostało przeliczone na wartości, które byłyby otrzymane w warunkach, w których badania prowadzili Katsounaros i współpracownicy [133] oraz Briega-Martos i współpracownicy [132]. Aby uwzględnić różnice w stosowanej metodzie (wirująca elektroda dyskowa, wirująca elektroda pierścieniowa), szybkości wirowania elektrody oraz stężeniu H_2O_2 posłużono się równaniami (3.9-3.11).

$$i_{R,l,c} = i_{D,l,c}\left(\frac{r_3^3}{r_1^3} - \frac{r_2^3}{r_1^3}\right)^{2/3} \tag{3.9}$$

$$i_{D,l,c} \propto \omega^{1/2} \tag{3.10}$$

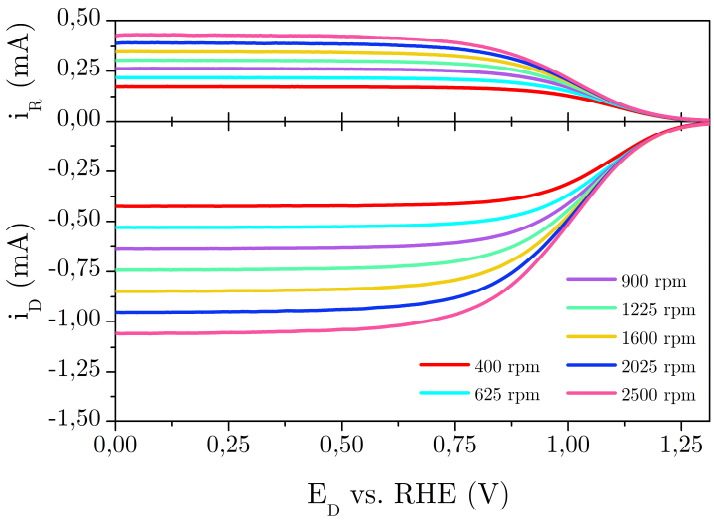
$$i_{D,l,c} \propto c_{H_2O_2} \tag{3.11}$$

Natężenie prądu na elektrodzie pierścieniowej równe 0,647 mA odpowiada gęstościom prądu 1,819 mA cm^{-2} i 3,866 mA cm^{-2} w warunkach, w których badania prowadzili Katsounaros i współpracownicy [133] oraz Briega-Martos i współpracownicy [132]. Wartości te są bliskie wartościom zamieszczonym w Tabeli 5. Błąd względny wynosi odpowiednio

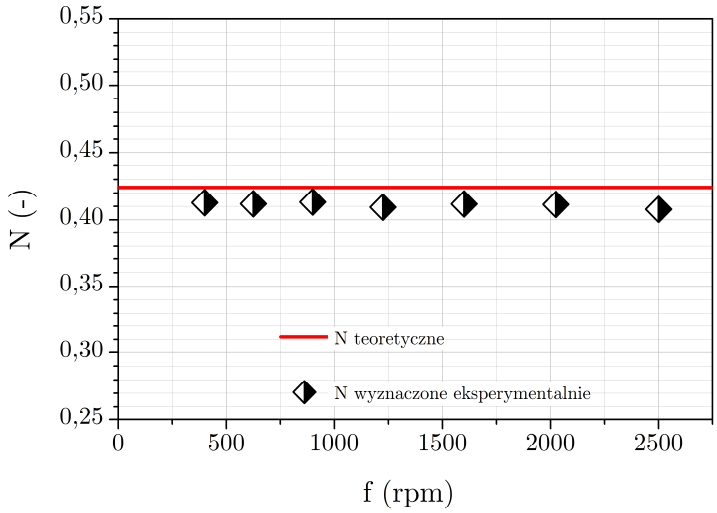
1,6% oraz 14%. Należy jednak mieć na uwadze, że 14-procentowy błąd tłumaczyć można faktem, że prąd limitowany dyfuzyjnie przy zastosowaniu elektrody wirującej dotykającej jedynie menisku elektrolitu (ang. *hanging meniscus rotating disk electrode*) jest niższy niż w przypadku konwencjonalnej wirującej elektrody dyskowej zanurzonej w elektrolicie na pewną głębokość [134]. Zatem wartość natężenia prądu rejestrowana w niniejszej pracy dla utleniania H_2O_2 na platynie pozbawionej tlenków jest spójna z dostępnymi danymi literaturowymi.

3.3.3 Wyznaczanie współczynnika efektywności zbierania dla wirującej elektrody dyskowo-pierścieniowej

Ponieważ powierzchnia rzeczywista węgla szklistego jest bliska jego powierzchni geometrycznej, to można się spodziewać, że współczynnik efektywności zbierania N dla elektrody wirującej z dyskiem z węgla szklistego oraz pierścieniem platynowym będzie niezależny od szybkości wirowania elektrody. Przypuszczenie to zostało potwierdzone eksperymentalnie przy zastosowaniu 10 mM $K_3[Fe(CN)_6]$ w odtlenionym 0,1 M KOH (Rysunek 43).



Rysunek 43. Krzywe natężenie prądu-potencjał (po korekcie uwzględniającej występowanie natężenia prądu tła) dla elektrody wirującej z dyskiem z węgla szklistego oraz pierścieniem platynowym zarejestrowane w odtlenionym 0,1 M KOH z dodatkiem 0,010 M $K_3[Fe(CN)_6]$. Potencjał elektrody pierścieniowej wynosił 1,5 V_{RHE}.



Rysunek 44. Teoretyczne oraz uzyskane eksperymentalnie wartości współczynnika efektywności zbierania N dla elektrody wirującej z dyskiem z węgla szklistego oraz pierścieniem platynowym.

Warto dodać, że otrzymana doświadczalnie wartość N równa 0,41 (Rysunek 44) jest zgodna z teoretyczną wartością (0,42) policzoną na podstawie wymiarów elektrody dyskowo-pierścieniowej w oparciu o równanie Albery'ego i Bruckensteina (3.12) [135].

$$N = 1 - F(\alpha/\beta) + \beta^{2/3}[1 - F(\alpha) - (1 + \alpha + \beta)^{2/3}\{1 - F[(\alpha/\beta)(1 + \alpha + \beta)]\}] \quad (3.12)$$

Występujące w równaniu Albery'ego i Bruckensteina współczynniki α oraz β definiowane są równaniami (3.13) i (3.14), natomiast funkcja F dana jest równaniem (3.15), które po rozwiązaniu występującej w nim całki przyjmuje postać (3.16).

$$\alpha = (r_2/r_1)^3 - 1 \quad (3.13)$$

$$\beta = \frac{r_3^3 - r_2^3}{r_1^3} \quad (3.14)$$

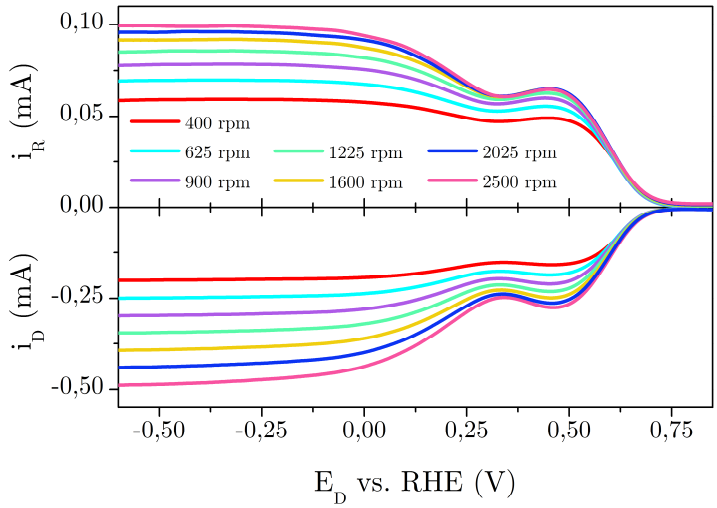
$$F(\theta) = \left(\frac{\sqrt{3}}{2\pi}\right)\int_0^{\theta} \frac{d\lambda}{\lambda^{2/3}(1+\lambda)} \quad (3.15)$$

$$F(\theta) \cong \left(\frac{\sqrt{3}}{4\pi}\right)\ln\left\{\frac{\left(1+\theta^{1/3}\right)^3}{1+\theta}\right\} + \frac{3}{2\pi}\arctan\left(\frac{2\theta^{1/3}-1}{3^{1/2}}\right) + \frac{1}{4} \quad (3.16)$$

3.3.4 Elektroredukcja tlenu na elektrodzie dyskowej z węgla szklistego

Wirująca elektroda dyskowa z pierścieniem platynowym pokrytym tlenkami, którego potencjał wynosił 1,2 V_{RHE} została zastosowana w badaniach nad elektroredukcją tlenu na węglu szklistym w 0,1 M KOH nasyconym tlenem. Jak przedstawiono na Rysunku 45,

na krzywych woltamperometrycznych dla węgla szklistego obecne są dwie fale. Obie te fale przypisywane są elektroredukcji tlenu z wytworzeniem H_2O_2 jako głównego produktu i, jak sugeruje Baez i współpracownicy [136], dotyczą one redukcji przebiegającej na dwóch rodzajach centrów aktywnych obecnych na powierzchni węgla szklistego.



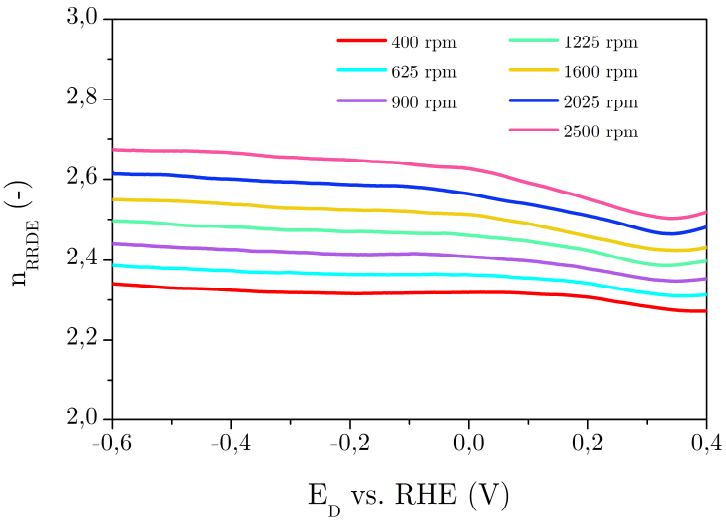
Rysunek 45. Krzywe natężenie prądu-potencjał (po korekcie uwzględniającej występowanie natężenia prądu tła) dla redukcji tlenu na węglu szklistym w 0,1 M KOH nasyconym tlenem. Potencjał pierścienia platynowego pokrytego tlenkami wynosił 1,2 V_{RHE}.

Maksymalne natężenie prądu na elektrodzie pierścieniowej i_R rejestrowane podczas redukcji O_2 na węglu szklistym zmieniało się w zakresie od 0,059 mA do 0,099 mA, odpowiednio dla 400 rpm i 2500 rpm. Porównywalne wartości byłyby uzyskiwane przy potencjale 1,2 V_{RHE} dla pierścienia platynowego pokrytego tlenkami w 0,1 M KOH zawierającym ~0,28 mM H_2O_2.

Co istotne, natężenie prądu na elektrodzie pierścieniowej i_R rejestrowane podczas redukcji O_2 na dysku z węgla szklistego wynika z utleniania H_2O_2 w warunkach mieszanej kontroli dyfuzyjno-kinetycznej. Tymczasem teoria metody wirującej elektrody dyskowo-pierścieniowej oparta jest na założeniu, że reakcja przebiegająca na elektrodzie pierścieniowej jest limitowana wyłącznie przez dyfuzję. Aby spełnić to założenie, teoretyczne natężenie prądu na elektrodzie pierścieniowej w warunkach całkowitej kontroli dyfuzyjnej może zostać wyznaczone na podstawie wartości i_R oraz znanego stosunku i_R do $i_{R,l,c}$.

Aby zademonstrować jak mieszana kontrola dyfuzyjno-kinetyczna reakcji utleniania H_2O_2 na pierścieniu platynowym pokrytym tlenkami wpływa na badania nad elektroredukcją tlenu, liczba wymienianych elektronów n_{RRDE} została wyznaczona dla procesu elektroredukcji tlenu na węglu szklistym w 0,1 M KOH w oparciu o wartości i_R oraz na podstawie wartości $i_{R,l,c}$. Jak zaprezentowano na Rysunku 46, wartości n_{RRDE} wyznaczone w oparciu o i_R uzyskane w warunkach mieszanej kontroli dyfuzyjno-kinetycznej wzrastają wraz ze wzrostem szybkości wirowania elektrody.

Zależność n_{RRDE} od szybkości wirowania elektrody może być obserwowana w sytuacji, gdy H_2O_2 generowany na elektrodzie dyskowej ulega rozkładowi podczas przeniesienia z dysku na elektrodę pierścieniową [137] lub kiedy powstały H_2O_2 ulega dalszym reakcjom na elektrodzie dyskowej. Jednak w obu tych przypadkach n_{RRDE} maleje wraz ze wzrostem szybkości wirowania. Czas przeniesienia substancji elektroaktywnej między dyskiem a pierścieniem zmienia się razem z częstotliwością wirowania elektrody. Z tego względu rozkład H_2O_2 zachodzi w mniejszym stopniu przy wyższych szybkościach wirowania [138]. W rezultacie większa ilość nadtlenku wodoru jest utleniana na elektrodzie pierścieniowej w przypadku stosowania wyższych częstotliwości wirowania elektrody, co skutkuje niższymi wartościami n_{RRDE}. Analogiczna sytuacja występuje wówczas, gdy nadtlenek wodoru ulega dalszej redukcji na elektrodzie dyskowej.

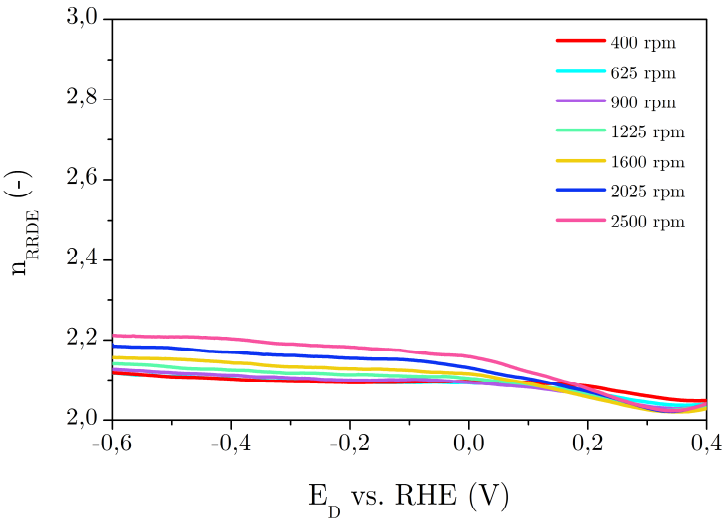


Rysunek 46. Liczba wymienianych elektronów n_{RRDE} dla procesu elektroredukcji tlenu na węglu szklistym w 0,1 M KOH wyznaczona na podstawie natężenia prądu na elektrodzie pierścieniowej i_R zarejestrowanego w warunkach mieszanej kontroli dyfuzyjno-kinetycznej.

Liczba wymienianych elektronów n_{RRDE} zależna od szybkości wirowania elektrody może być także uzyskiwana w przypadku, gdy na dysku osadzona jest warstwa katalizatora, a używana jest stała wartość współczynnika efektywności zbierania N do wyznaczania wartości n_{RRDE}, lekceważąc fakt, że warstwa katalizatora zaburza geometrię układu [67] i w rezultacie N staje się zależne od szybkości wirowania elektrody. W takiej sytuacji n_{RRDE} pozornie wzrasta wraz ze wzrostem szybkości wirowania elektrody. Jednak w niniejszej pracy elektroredukcja tlenu badana była na niemodyfikowanym węglu szklistym (bez naniesionej warstwy katalizatora) i jak dowiedziono eksperymentalnie wartość N była stała i równa 0,41 (Rysunek 44).

Biorąc wszystko powyższe pod uwagę można stwierdzić, że żadne ze zjawisk opisanych wyżej nie wyjaśnia zależności n_{RRDE} od szybkości wirowania elektrody (Rysunek 46). Co ciekawe, jak można zobaczyć na Rysunku 47, zależność ta jest niemal całkowicie wyeliminowana, gdy n_{RRDE} wyznaczane jest w oparciu o $i_{R,l,c}$, jak wymaga tego

teoria metody wirującej elektrody dyskowo-pierścieniowej. Dodatkowo porównanie Rysunku 46 i Rysunku 47 pozwala zauważyć, że wartości n_{RRDE} są zawyżone w przypadku, kiedy do ich wyznaczenia wykorzystywane są wartości i_R uzyskane w warunkach mieszanej kontroli dyfuzyjno-kinetycznej. Zatem dzięki prowadzeniu obliczeń w oparciu o wartości $i_{R,l,c}$, które byłyby obserwowane w przypadku całkowitej kontroli dyfuzyjnej, wartości n_{RRDE} wyznaczane są z większą dokładnością i precyzją niż w sytuacji, gdy do obliczeń wykorzystuje się wartości i_R.



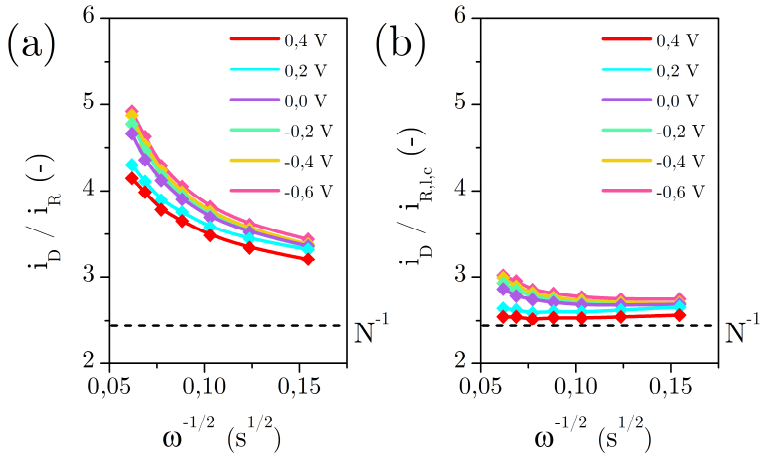
Rysunek 47. Liczba wymienianych elektronów n_{RRDE} dla procesu elektroredukcji tlenu na węglu szklistym w 0,1 M KOH wyznaczona na podstawie natężenia prądu na elektrodzie pierścieniowej $i_{R,l,c}$, które byłoby rejestrowane w warunkach całkowitej kontroli dyfuzyjnej.

Wartości n_{RRDE} policzone na podstawie $i_{R,l,c}$ (Rysunek 47) są zgodne z wynikami uzyskanymi za pomocą wirującej elektrody dyskowej przez Tammeveskiego i współpracowników [51] (n=2,25 dla potencjału -0,189 V_{RHE}). Ponadto wartości te są także zgodne z danymi [139,140] pozyskanymi przy zastosowaniu wirującej elektrody dyskowej ze złotym pierścieniem (n_{RRDE}=2,1 dla potencjału -0,189 V_{RHE}). Według Zhou i współpracowników [67], złoty pierścień zapewnia pełną kontrolę dyfuzyjną reakcji utleniania H_2O_2 w elektrolitach alkalicznych, chociaż dostępne są również wyniki badań przeczące tej tezie [92].

Rysunek 30 (zamieszczony w Rozdziale nr 2) prezentuje teoretyczne zależności i_D/i_R vs. $\omega^{-1/2}$ wyprowadzone dla czterech możliwych mechanizmów elektroredukcji tlenu (obejmujących powstawanie H_2O_2), przy założeniu, że reakcja na pierścieniu podlega pełnej kontroli dyfuzyjnej. Ponieważ zależności i_D/i_R vs. $\omega^{-1/2}$ są specyficzne dla danego mechanizmu elektroredukcji tlenu, umożliwiają one jego identyfikację. Jak można zauważyć na Rysunku 48a, dla redukcji O_2 na węglu szklistym w 0,1 M KOH zależność i_D/i_R vs. $\omega^{-1/2}$ wykreślona na podstawie i_R uzyskanego w warunkach mieszanej kontroli dyfuzyjno-kinetycznej nie przypomina żadnej z zależności zamieszczonych na Rysunku 30. Natomiast

ta sama zależność wykreślona na podstawie $i_{R,l,c}$, zamieszczona na Rysunku 48b wykazuje podobieństwo do Rysunku 30c oraz Rysunku 30d.

Niestety rozróżnienie pomiędzy mechanizmem odpowiadającym Rysunkowi 30c oraz Rysunkowi 30d nie jest możliwe z uwagi na ujemny współczynnik nachylenia wykresów $i_D/i_{R,l,c}$ vs. $\omega^{-1/2}$ dla potencjałów równych bądź mniejszych niż 0,0 V_{RHE}. Takie ujemne współczynniki nachylenia, jak również niezadowalająca liniowość, są często opisywane w literaturze [141], m.in. także dla redukcji O_2 na utlenionym węglu szklistym [142]. Różnica między mechanizmami odpowiadającymi Rysunkowi 30c oraz Rysunkowi 30d polega na tym, czy utworzony nadtlenek wodoru ulega dalszej redukcji. Baez i współpracownicy [136] wykluczyli redukcję H_2O_2 na węglu szklistym w elektrolitach alkalicznych. Z kolei według Tammeveskiego i współpracowników [51] proces ten w rzeczywistości zachodzi, ale jego szybkość jest pomijalnie mała.



Rysunek 48. Wykresy zależności (a) i_D/i_R vs. $\omega^{-1/2}$ oraz (b) $i_D/i_{R,l,c}$ vs. $\omega^{-1/2}$ dla redukcji O_2 na węglu szklistym w 0,1 M KOH nasyconym tlenem dla różnych wartości potencjałów elektrody dyskowej E_D (wyrażonych względem odwracalnej elektrody wodorowej).

Wartości $i_{R,l,c}$ zostały policzone na podstawie uzyskanych eksperymentalnie wartości i_R oraz znanego stosunku $i_R/i_{R,l,c}$, którego zależność od częstotliwości wirowania elektrody została przedstawiona na Rysunku 38. Stosunek $i_R/i_{R,l,c}$ został wyznaczony na podstawie wyników badań nad utlenianiem H_2O_2 na platynie pokrytej tlenkami w elektrolitach zawierających 0,05-1 mM H_2O_2. Stąd wyznaczone wartości $i_R/i_{R,l,c}$ dotyczą jedynie określonego zakresu $i_R(r_3^3 - r_2^3)^{-2/3}$, zależnego od szybkości wirowania elektrody, jak to zostało przedstawione w Tabeli 6.

Należy podkreślić, że stosunek $i_R/i_{R,l,c}$ wykreślony jako funkcja częstotliwości wirowania elektrody na Rysunku 38 dotyczy wirującej elektrody dyskowo-pierścieniowej o dowolnych wymiarach promieni r_2 oraz r_3. Z tego względu natężenie prądu na elektrodzie pierścieniowej znormalizowane względem jej wymiarów $i_R(r_3^3 - r_2^3)^{-2/3}$ jest stosowane do określenia zakresu, w którym ważne są wartości $i_R/i_{R,l,c}$ przedstawione na Rysunku 38, zamiast samej wartości i_R.

Tabela 6. Zakresy $i_R(r_3^3 - r_2^3)^{-2/3}$, dla których obowiązują wartości $i_R/i_{R,l,c}$ podane na Rysunku 38.

Częstotliwość wirowania elektrody (rpm)	$i_R(r_3^3 - r_2^3)^{-\frac{2}{3}}$ $(\mathrm{A\,m^{-2}})$
400	1,070 – 21,99
625	1,264 – 26,37
900	1,432 – 30,26
1225	1,604 – 34,22
1600	1,736 – 37,55
2025	1,862 – 40,41
2500	1,972 – 43,60

W przypadku stężeń nadtlenku wodoru przekraczających 1 mM, adsorpcja H_2O_2 prowadzi do wysycenia powierzchni elektrody platynowej i w konsekwencji powierzchniowe stężenie H_2O_2 staje się niezależne od stężenia w głębi elektrolitu [118]. Dlatego należy się spodziewać, że stosunek $i_R/i_{R,l,c}$ na Rysunku 38, który został wyznaczony dla utleniania H_2O_2 w zakresie stężeń 0,05-1 mM nie będzie obowiązywał, gdy stężenie H_2O_2 przekroczy 1 mM. Z tych samych powodów można oczekiwać, że stosunek $i_R/i_{R,l,c}$ nie będzie obowiązywał, jeżeli wartość $i_R(r_3^3 - r_2^3)^{-2/3}$ przekroczy dopuszczalny zakres przedstawiony w Tabeli 6, który został wyznaczony w oparciu o odpowiedź pierścienia platynowego pokrytego tlenkami na 1 mM H_2O_2.

Dotychczas zidentyfikowano co najmniej pięć różnych tlenków platyny (PtO, Pt_3O_4, α-PtO_2, β-PtO_2 oraz β'-PtO_2), a istnienie dwóch innych struktur (Pt_2O and Pt_3O_8) jest przedmiotem dyskusji [143]. Dodatkowo platyna może występować w formie związków $M_xPt_3O_4$, w których M jest litowcem, metalem ziem alkalicznych lub metalem przejściowym [143,144]. PtO, Pt_3O_4 oraz $M_xPt_3O_4$ mają charakter metaliczny, natomiast PtO_2 wykazuje właściwości półprzewodnikowe [143].

Kiedy elektroda platynowa polaryzowana jest do potencjału wyższego niż 1,1 V_{RHE}, jest ona pokrywana tlenkiem PtO, który występuje w formie co najwyżej dwóch monowarstw [119]. Jeżeli jednak potencjał jest zwiększany powyżej 1,6 V_{RHE}, to dochodzi do wytworzenia tlenku PtO_2 [119]. Warstwa PtO_2 może być znacznie grubsza niż warstwa PtO i składać się nawet z 60 monowarstw [145].

Według pomiarów przeprowadzonych przez Shibatę [145] utworzenie tlenku PtO nie wiąże się ze znacznym spadkiem przewodnictwa, co nie powinno dziwić, jeżeli wziąć pod uwagę, że grubość pojedynczej warstwy PtO została oszacowana na 0,8-1,6 Å [146]. Natomiast w przypadku PtO_2 oporność wzrasta liniowo wraz z ilością tlenku obecnego na powierzchni [145].

Podsumowując, kiedy podczas badań nad elektroredukcją tlenu potencjał platynowej elektrody pierścieniowej wynosi 1,2 V_{RHE}, powierzchnia elektrody pokrywana jest tlenkiem PtO (nie PtO_2), co nie zmienia znacząco przewodnictwa elektrycznego elektrody, ale wpływa na kinetykę reakcji utleniania H_2O_2.

3.4 Wnioski

Przedstawione wyniki badań dowodzą, że utlenianie nadtlenku wodoru przy potencjale 1,2 V_{RHE} na platynie pokrytej tlenkami przebiega w warunkach mieszanej kontroli dyfuzyjno-kinetycznej. W rezultacie, gdy wirująca elektroda dyskowa z pierścieniem platynowym jest wykorzystywana w badaniach nad elektroredukcją tlenu w środowisku alkalicznym, rejestrowane natężenie prądu na elektrodzie pierścieniowej jest dużo niższe niż natężenie prądu, które byłoby obserwowane w przypadku pełnej kontroli dyfuzyjnej, która jest wymagana przez teorię metody wirującej elektrody dyskowo-pierścieniowej. Stosunek mierzonego natężenia prądu na pierścieniu do natężenia prądu w warunkach całkowitej kontroli dyfuzyjnej zmienia się monotonicznie wraz z szybkością wirowania elektrody i przy potencjale 1,2 V_{RHE} wynosi odpowiednio 79,9% oraz 61,4% dla 400 rpm i 2500 rpm.

Na przykładzie redukcji tlenu na węglu szklistym w 0,1 M KOH, udało się wykazać, że mieszana kontrola dyfuzyjno-kinetyczna utleniania H_2O_2 na pierścieniu platynowym pokrytym tlenkami uniemożliwia poprawne określenie mechanizmu elektroredukcji tlenu za pomocą zależności i_D/i_R vs. $\omega^{-1/2}$ oraz prowadzi do zawyżonych wartości liczby elektronów wymienianych w tym procesie.

Aby uzyskać wiarygodne wyniki badań nad elektroredukcją tlenu w środowisku alkalicznym przy użyciu wirującej elektrody dyskowej z pierścieniem platynowym pokrytym tlenkami zaproponowano nową procedurę opartą o metodę Koutecký'ego-Levicha, która to procedura nie była nigdy dotąd stosowana ani opisywana w literaturze

Chociaż procedura ta została w niniejszej pracy szczegółowo zaprezentowana jedynie w kontekście badań nad elektroredukcją tlenu, to ma ona charakter ogólny i może być wykorzystywana także podczas badania każdego innego procesu elektrochemicznego, dla którego reakcja przebiegająca na elektrodzie pierścieniowej nie jest limitowana wyłącznie przez dyfuzję. Tym samym zaproponowana procedura znacznie rozszerza potencjalny zakres zastosowań metody wirującej elektrody dyskowo-pierścieniowej, bowiem pełna kontrola dyfuzyjna reakcji na pierścieniu nie jest już koniecznie wymagana.

4. Kontrola przebiegu elektroredukcji tlenu przy zastosowaniu elektrolitów alkalicznych na bazie mieszanin dimetylosulfotlenek-woda

4.1 Aparatura, odczynniki oraz układ pomiarowy

Sporządzono siedem różnych elektrolitów alkalicznych na bazie mieszanin DMSO-woda, które zawierały od 0,0 do 93,3 obj.% DMSO. Elektrolity zostały przygotowane na bazie wody dejonizowanej oraz odczynników o klasie czystości cz.d.a.: wodorotlenek potasu (POCH, Polska), dimetylosulfotlenek (>99%, Sigma Aldrich, Chiny). Stężenie KOH wynosiło 0,1 M, za wyjątkiem elektrolitów nr 6 i 7, które stanowiły nasycone roztwory KOH o stężeniu niższym niż 0,1 M.

Tabela 7 podaje skład mieszanin DMSO-woda (wyrażony jako udział objętościowy, masowy i molowy DMSO) użytych do przygotowania elektrolitów alkalicznych. Mieszaninom przypisane są numery od 1 do 7 i takie oznaczenia są konsekwentnie stosowane w niniejszej pracy.

Tabela 7. Mieszaniny DMSO-woda, na bazie których przygotowano elektrolity alkaliczne.

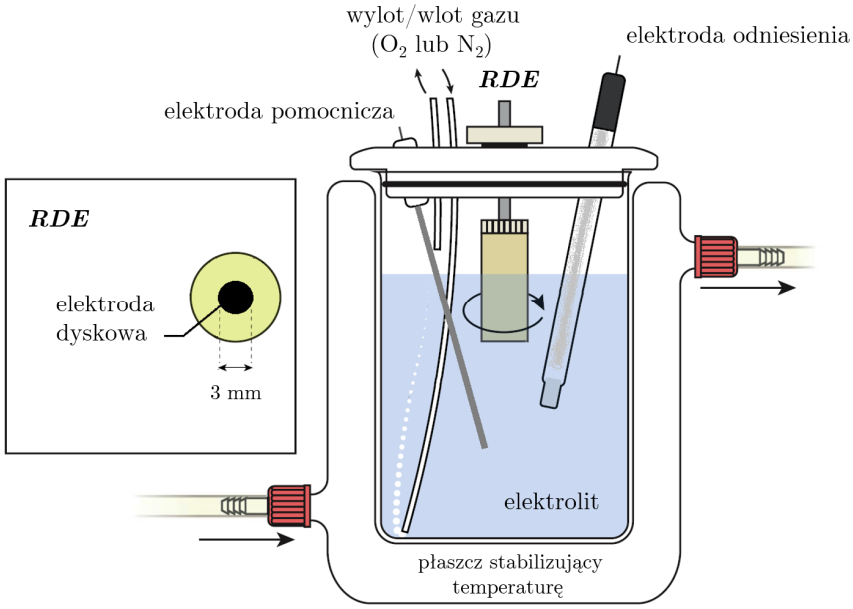
Nr	Skład mieszaniny DMSO-woda	obj. % DMSO	mas. % DMSO	mol. % DMSO
1	H_2O	0,0	0,0	0,0
2	9 H_2O : 1 DMSO (v/v)	10,0	10,9	2,7
3	2 H_2O : 1 DMSO (v/v)	33,3	35,5	11,2
4	1 H_2O : 1 DMSO (v/v)	50,0	52,4	20,2
5	1 H_2O : 2 DMSO (v/v)	66,7	68,7	33,6
6	1 H_2O : 9 DMSO (v/v)	90,0	90,8	69,5
7	1 H_2O : 14 DMSO(v/v)	93,3	93,9	78,0

Lepkość dynamiczną sporządzonych elektrolitów mierzono za pomocą reometru rotacyjnego (Anton Paar MCR 302, Austria).

Gęstość elektrolitów wyznaczano za pomocą piknometru (IsoLab Laborgeräte, Niemcy).

Badania elektrochemiczne przeprowadzono przy użyciu potencjostatu/galwanostatu VMP3 (BioLogic, Francja) oraz aparatu RRDE-3A (ALS, Japonia), do którego podłączono wirującą elektrodę dyskową (r_1=1,5 mm) z węgla szklistego (ALS). Pręt grafitowy i elektroda tlenkowo-rtęciowa Hg/HgO/6 M KOH (RE-61AP, ALS) pełniły rolę odpowiednio elektrody pomocniczej oraz elektrody odniesienia. Wszystkie pomiary wykonywane były w stałej temperaturze (25,0±0,1°C), którą zapewniał termostat

cyrkulacyjny (CC-K6 with Pilot ONE, Huber, Niemcy) podłączony do naczynia z płaszczem stabilizującym temperaturę (T-GL 250, Schott Duran, Niemcy), w którym to naczyniu znajdowało się ok. 225 mL elektrolitu. Schemat układu elektrochemicznego przedstawiono na Rysunku 49.



Rysunek 49. Schemat układu elektrochemicznego [96].

4.2 Metodyka badań

4.2.1 Wyznaczenie lepkości kinematycznej elektrolitów alkalicznych na bazie mieszanin DMSO-woda

Lepkość kinematyczna ν elektrolitów alkalicznych na bazie mieszanin DMSO-woda była wyznaczana pośrednio, na podstawie gęstości ρ oraz lepkości dynamicznej η (4.1).

$$\nu = \frac{\eta}{\rho} \tag{4.1}$$

Zarówno pomiary gęstości, jak i pomiary lepkości dynamicznej przeprowadzane były w temperaturze 25°C.

4.2.2 Oszacowanie rozpuszczalności O_2 w elektrolitach alkalicznych na bazie mieszanin DMSO-woda

Rozpuszczalność O_2 w elektrolitach alkalicznych na bazie mieszanin DMSO-woda została oszacowana na podstawie danych literaturowych, które prezentują zależność rozpuszczalności O_2 [mM] vs. obj.% H_2O dla mieszanin DMSO-woda z dodatkiem 0,1 M Et_4NClO_4 [147].

Objętościowa zawartość wody (obj.% H_2O) w mieszaninach DMSO-woda została przeliczona na objętościową zawartość dimetylosulfotlenku (obj.% DMSO) według równania (4.2).

$$obj.\%\ DMSO\ [\%] = 100\ [\%] - obj.\%\ H_2O\ [\%] \tag{4.2}$$

Zgodnie z prawem Henry'ego stężenie rozpuszczonego tlenu jest wprost proporcjonalne do ciśnienia parcjalnego tlenu [1]. Dane literaturowe [147] dotyczą sytuacji, gdy ciśnienie parcjalne tlenu wynosi 0,21 atm. Dane dla p_{O_2} równego 1 atm zostały uzyskane zgodnie z równaniem (4.3).

$$c_{O_2}(p_{O_2} = 1\ atm) = \frac{c_{O_2}(p_{O_2} = 0{,}21\ atm)}{0{,}21} \tag{4.3}$$

W celu uzyskania wartości rozpuszczalności O_2 dla mieszanin DMSO-woda o składzie odpowiadającym siedmiu elektrolitom testowanym w niniejszej pracy zastosowano interpolację wielomianową. Współczynniki regresji wielomianowej oraz ich błędy standardowe wyznaczono za pomocą *Excel Data Analysis Toolpak*.

4.2.3 Oszacowanie współczynnika dyfuzji O_2 w elektrolitach alkalicznych na bazie mieszanin DMSO-woda

Współczynniki dyfuzji O_2 w elektrolitach alkalicznych na bazie mieszanin DMSO-woda zostały oszacowane na podstawie danych literaturowych, które prezentują zależność współczynnik dyfuzji O_2 [$10^{-9} \cdot m^2\ s^{-1}$] vs. obj.% H_2O dla mieszanin DMSO-woda z dodatkiem 0,1 M Et_4NClO_4 [147].

Objętościowa zawartość wody (obj.% H_2O) w mieszaninach DMSO-woda została przeliczona na objętościową zawartość dimetylosulfotlenku (obj.% DMSO) zgodnie z równaniem (4.2).

W celu uzyskania wartości współczynników dyfuzji O_2 dla mieszanin DMSO-woda o składzie odpowiadającym siedmiu elektrolitom testowanym w niniejszej pracy zastosowano interpolację wielomianową. Współczynniki regresji wielomianowej oraz ich błędy standardowe wyznaczono za pomocą *Excel Data Analysis Toolpak*.

4.2.4 Wyznaczenie stężenia nasyconych roztworów KOH w mieszaninach DMSO-woda

Dokładne stężenie KOH w roztworach nasyconych zostało wyznaczone eksperymentalnie z uwagi na znaczne rozbieżności dostępnych w literaturze danych na temat rozpuszczalności KOH w DMSO oraz jego wodnych roztworach. Vasilescu i współpracownicy [148] uzyskali roztwór nasycony w bezwodnym DMSO o stężeniu 3 mM KOH. Vitkovskaya i współpracownicy [149] twierdzą, że rozpuszczalność KOH w bezwodnym DMSO wynosi ~$2{,}8 \cdot 10^{-2}$ M. Natomiast znacznie wyższe stężenie (0,11 M KOH w bezwodnym DMSO)

występuje w publikacji Crama i współpracowników [150]. Według Trofimova i współpracowników [151] rozpuszczalność KOH w czystym DMSO jest równa $3{,}7 \cdot 10^{-2}$ M i pozostaje stała, kiedy stężenie wody rośnie do 9%. Z kolei biuletyn techniczny [152] dotyczący dimetylosulfotlenku sporządzony przez *Gaylord Chemical Corporation* podaje, że dodatek wody do DMSO powoduje wzrost rozpuszczalności wodorotlenków metali alkalicznych.

Biorąc pod uwagę wysoką temperaturę wrzenia dimetylosulfotlenku (189°C [153]) oraz fakt, że relatywnie długi czas (od kilku godzin do jednego dnia [151]) może być wymagany do ustalenia stężeń równowagowych w mieszaninie KOH-DMSO-H_2O, rozpuszczalność KOH (w temperaturze 25°C) została wyznaczona na podstawie maksymalnej liczby moli KOH, która ulega całkowitemu rozpuszczeniu w ciągu dwóch dni w mieszaninie DMSO-woda o znanej objętości.

4.2.5 Elektroredukcja tlenu na elektrodzie dyskowej z węgla szklistego

4.2.5.1 Przebieg pomiarów

Do badania elektroredukcji tlenu na elektrodzie z węgla szklistego została wykorzystana woltamperometria z liniowo zmieniającym się potencjałem (LSV – ang. *linear sweep voltammetry*) o szybkości skanowania 10 mV s^{-1}. Pomiary dotyczące elektroredukcji tlenu były wykonywane w elektrolitach nasyconych tlenem pod ciśnieniem 1 atm, dla szybkości wirowania elektrody równych 400, 625, 900, 1225, 1600, 2025 oraz 2500 rpm (wartości te zostały wybrane w taki sposób, aby zapewnić równe odstępy względem $\omega^{1/2}$). W celu wyznaczenia natężenia prądu tła dla elektrody dyskowej, wykonywano pomiary także w elektrolitach odtlenionych. Elektrolity nasycone tlenem oraz elektrolity pozbawione tlenu uzyskiwano poprzez przepuszczanie odpowiednio tlenu (99,5%, Air Products, Polska) lub azotu (99,9992%, Air Products, Polska) przez okres 15 min bezpośrednio przed pomiarami. W trakcie pomiarów elektrochemicznych strumień odpowiedniego gazu kierowany był powyżej lustra elektrolitu.

Przed każdą serią pomiarów elektrochemicznych, elektroda dyskowa z węgla szklistego była polerowana za pomocą proszku diamentowego (1 μm) i aluminy (0,05 μm) (PK-3 polishing kit, ALS, Japonia). Następnie elektroda była opłukiwana etanolem oraz wodą dejonizowaną. Dodatkowo, aby uniknąć możliwego zanieczyszczenia powierzchni elektrody pozostałościami zawiesin polerskich, elektroda była także umieszczana w łaźni ultradźwiękowej na okres 5 minut.

4.2.5.2 Wyznaczanie liczby elektronów wymienianych podczas elektroredukcji tlenu

Liczba elektronów wymienianych podczas elektroredukcji tlenu w alkalicznych elektrolitach na bazie mieszanin DMSO-woda została wyznaczona poprzez porównanie mierzonej gęstości natężenia prądu na elektrodzie dyskowej z teoretyczną gęstością natężenia prądu dla n=2,20 w warunkach pełnej kontroli dyfuzyjnej.

Teoretyczna gęstość natężenia prądu limitowanego dyfuzją $j_{D,l,c}$ dla n=2,20 została wyznaczona na podstawie równania Levicha (4.4) [43], do którego podstawiano wartości szybkości kątowej wirowania elektrody oraz parametrów fizykochemicznych (lepkości kinematycznej, rozpuszczalności tlenu, współczynnika dyfuzji tlenu) odpowiedniego elektrolitu.

$$j_{D,l,c} = 0{,}62nFD^{2/3}\omega^{1/2}\nu^{-1/6}c \tag{4.4}$$

Znając wartość $j_{D,l,c}$ dla n=2,20, można wyznaczyć liczbę wymienianych elektronów n na podstawie mierzonej gęstości natężenia prądu j_D, stosując równanie (4.5).

$$n = \frac{j_D}{j_{D,l,c}\,(n = 2{,}20)} \cdot 2{,}20 \tag{4.5}$$

Oczywiście obie wartości natężenia gęstości prądu j_D oraz $j_{D,l,c}$ muszą dotyczyć tych samych warunków eksperymentalnych (taka sama szybkość kątowa wirowania elektrody, ten sam elektrolit).

4.2.5.3 Wyznaczanie gęstości natężenia prądu kinetycznego dla elektroredukcji tlenu

Gęstości natężenia prądu kinetycznego dla redukcji O_2 w elektrolitach alkalicznych na bazie mieszanin DMSO-woda zostały wyznaczone przy zastosowaniu procedury opisanej w książce Pleskova i Filinovskiego [54]. Procedura ta opiera się na równaniu Koutecký'ego-Levicha (4.6).

$$\frac{1}{j} = \frac{1}{nFkc} + \frac{1}{0{,}62nFD^{2/3}\nu^{-1/6}c} \cdot \omega^{-1/2} \tag{4.6}$$

Gęstość natężenia prądu kinetycznego ($j_k = nFkc$) jest wyznaczana poprzez ekstrapolację zależności j^{-1} vs. $\omega^{-1/2}$ dla $\omega^{-1/2} \rightarrow 0$. Metoda Koutecký'ego-Levicha zakłada, że liczba wymienianych elektronów n jest niezależna od szybkości wirowania elektrody. Jeżeli założenie takie nie jest spełnione, to wartości j_k uzyskane za pomocą tej procedury powinny być traktowane jako wartości orientacyjne.

4.3 Wyniki badań i dyskusja

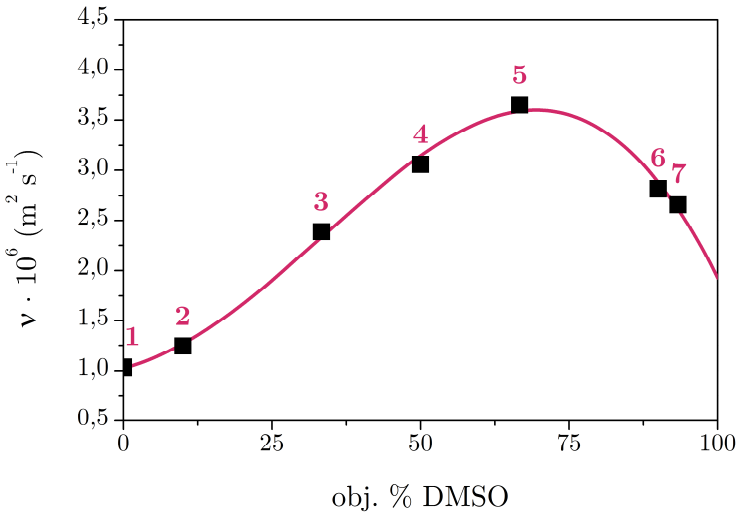
4.3.1 Wyznaczenie lepkości kinematycznej elektrolitów alkalicznych na bazie mieszanin DMSO-woda

Wartości gęstości oraz lepkości dynamicznej wyznaczone eksperymentalnie dla elektrolitów alkalicznych na bazie mieszanin DMSO-woda zostały zamieszczone w Tabeli 8 razem z wyznaczonymi na ich podstawie wartościami lepkości kinematycznej.

Tabela 8. Gęstość, lepkość dynamiczna oraz lepkość kinematyczna elektrolitów alkalicznych na bazie mieszanin DMSO-woda w temperaturze 25°C.

Nr	Skład mieszaniny woda-DMSO	obj. % DMSO	mas. % DMSO	mol. % DMSO	ϱ (g mL^{-1})	η (mPa·s)	$\nu \cdot 10^6$ (m^2 s^{-1})
1	H_2O	0,0	0,0	0,0	1,003	1,04	1,03
2	9 H_2O : 1 DMSO (v/v)	10,0	10,9	2,7	1,016	1,26	1,24
3	2 H_2O : 1 DMSO (v/v)	33,3	35,5	11,2	1,053	2,51	2,39
4	1 H_2O : 1 DMSO (v/v)	50,0	52,4	20,2	1,076	3,29	3,06
5	1 H_2O : 2 DMSO (v/v)	66,7	68,7	33,6	1,092	3,99	3,65
6	1 H_2O : 9 DMSO (v/v)	90,0	90,8	69,5	1,100	3,10	2,82
7	1 H_2O : 14 DMSO(v/v)	93,3	93,9	78,0	1,098	2,92	2,66

Zależność lepkości kinematycznej od zawartości DMSO w mieszaninie wykorzystanej do przygotowania elektrolitów alkalicznych została także przedstawiona na Rysunku 50.



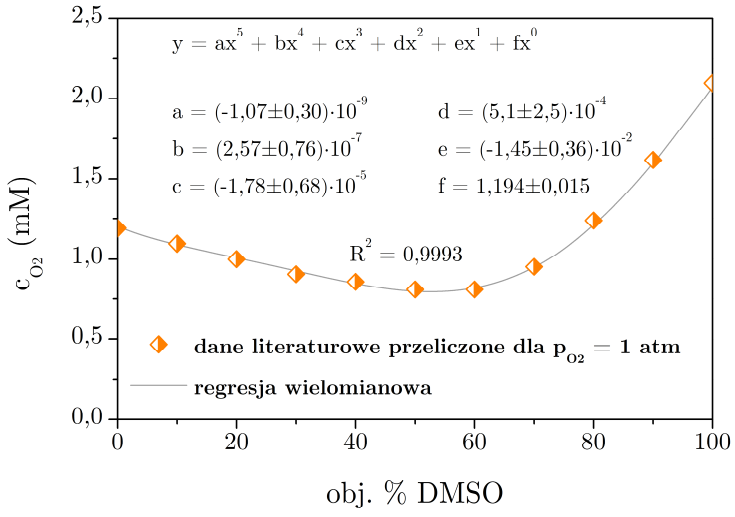
Rysunek 50. Lepkość kinematyczna elektrolitów alkalicznych na bazie mieszanin dwuskładnikowych woda-DMSO w temperaturze 25°C. Numery na wykresie odpowiadają mieszaninom wyszczególnionym w Tabeli 8.

4.3.2 Oszacowanie rozpuszczalności O_2 w elektrolitach alkalicznych na bazie mieszanin DMSO-woda

Dane literaturowe po odpowiednim przeliczeniu (rozpuszczalność tlenu [mM] dla p_{O_2} = 1 atm vs. obj.% DMSO) zamieszczono w Tabeli 9, a także przedstawiono w formie wykresu punktowego na Rysunku 51.

Tabela 9. Rozpuszczalność tlenu w mieszaninach DMSO-woda w temperaturze 25°C. Dane literaturowe [147] przedstawiono na szarym tle.

obj.% H_2O	c_{O_2} (mM) (p_{O_2}= 0,21 atm)	c_{O_2} (mM) (p_{O_2}= 1 atm)	obj.% DMSO
0	0,44	2,1	100
10	0,34	1,6	90
20	0,26	1,2	80
30	0,20	0,95	70
40	0,17	0,81	60
50	0,17	0,81	50
60	0,18	0,86	40
70	0,19	0,90	30
80	0,21	1,0	20
90	0,23	1,1	10
100	0,25	1,2	0



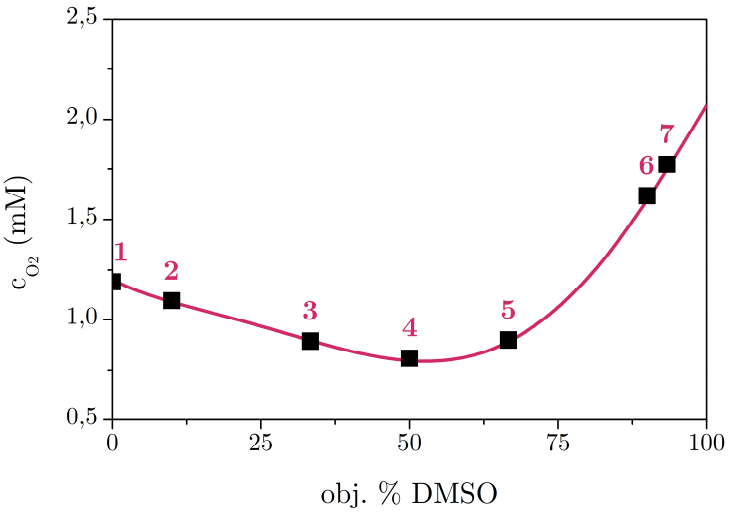
Rysunek 51. Rozpuszczalność tlenu w mieszaninach DMSO-woda w temperaturze 25°C.

Na Rysunku 51 zaznaczono także linią ciągłą model regresji wielomianowej dla prezentowanych danych oraz podano wartości współczynników regresji i współczynnika determinacji.

Rozpuszczalność O_2 dla mieszanin DMSO-woda stosowanych w niniejszej pracy została wyznaczona poprzez interpolację wielomianową. Standardowy błąd dla wartości rozpuszczalności O_2 uzyskanych tym sposobem wynosi 0,015 mM. Wyznaczone wartości rozpuszczalności zamieszczono w Tabeli 10 oraz przedstawiono na Rysunku 52.

Tabela 10. Rozpuszczalność O_2 mieszanin dwuskładnikowych woda-DMSO w temperaturze 25°C.

Nr	Skład mieszaniny woda-DMSO	obj. % DMSO	mas. % DMSO	mol. % DMSO	c_{O_2} (mM)
1	H_2O	0,0	0,0	0,0	1,2
2	9 H_2O : 1 DMSO (v/v)	10,0	10,9	2,7	1,1
3	2 H_2O : 1 DMSO (v/v)	33,3	35,5	11,2	0,89
4	1 H_2O : 1 DMSO (v/v)	50,0	52,4	20,2	0,81
5	1 H_2O : 2 DMSO (v/v)	66,7	68,7	33,6	0,90
6	1 H_2O : 9 DMSO (v/v)	90,0	90,8	69,5	1,6
7	1 H_2O : 14 DMSO(v/v)	93,3	93,9	78,0	1,8



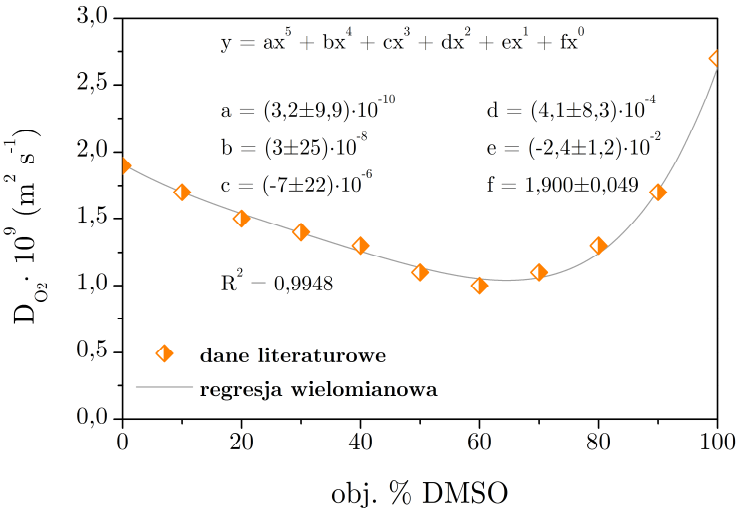
Rysunek 52. Rozpuszczalność O_2 w mieszaninach dwuskładnikowych woda-DMSO w temperaturze 25°C. temperaturze 25°C. Numery na wykresie odpowiadają mieszaninom wyszczególnionym w Tabeli 10.

4.3.3 Oszacowanie współczynnika dyfuzji O_2 w elektrolitach alkalicznych na bazie mieszanin DMSO-woda

Dane literaturowe po odpowiednim przeliczeniu (współczynnik dyfuzji O_2 [$10^{-9} \cdot m^2\ s^{-1}$] vs. obj.% DMSO) zamieszczono w Tabeli 11, a także przedstawiono w formie wykresu punktowego na Rysunku 53.

Tabela 11. Współczynnik dyfuzji tlenu w mieszaninach DMSO-woda w temperaturze 25˚C. Dane literaturowe [147] przedstawiono na szarym tle.

obj.% H_2O	$D_{O_2} \cdot 10^9$ (m^2 s^{-1})	obj.% DMSO	obj.% H_2O	$D_{O_2} \cdot 10^9$ (m^2 s^{-1})	obj.% DMSO
0	2,7	100	60	1,3	40
10	1,7	90	70	1,4	30
20	1,3	80	80	1,5	20
30	1,1	70	90	1,7	10
40	1,0	60	100	1,9	0
50	1,1	50			



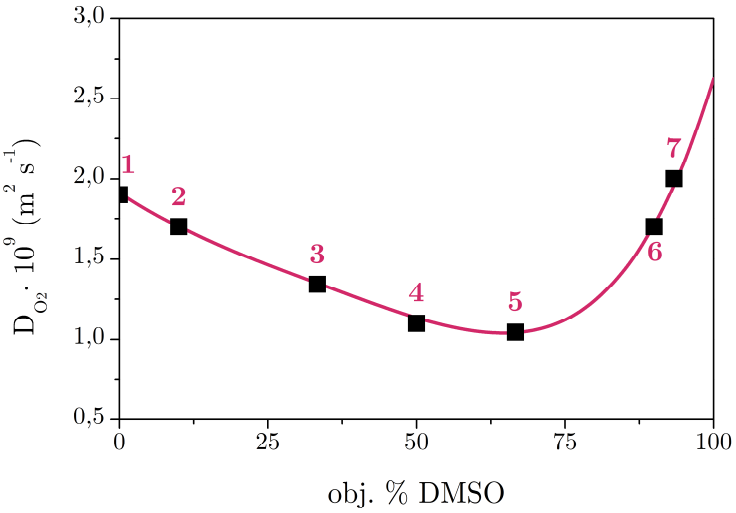
Rysunek 53. Współczynnik dyfuzji tlenu w mieszaninach DMSO-woda w temperaturze 25˚C.

Na Rysunku 53 zaznaczono także linią ciągłą model regresji wielomianowej dla prezentowanych danych oraz podano wartości współczynników regresji i współczynnika determinacji.

Współczynniki dyfuzji O_2 dla mieszanin DMSO-woda stosowanych w niniejszej pracy zostały wyznaczone poprzez interpolację wielomianową. Standardowy błąd dla wartości współczynników dyfuzji O_2 uzyskanych tym sposobem wynosi $4{,}9 \cdot 10^{-11}$ m^2 s^{-1}. Wyznaczone wartości współczynników dyfuzji zamieszczono w Tabeli 12 oraz przedstawiono na Rysunku 54.

Tabela 12. Współczynniki dyfuzji O_2 dla mieszanin dwuskładnikowych DMSO-woda w temperaturze 25°C.

Nr	Skład mieszaniny woda-DMSO	obj. % DMSO	mas. % DMSO	mol. % DMSO	$D_{O_2} \cdot 10^9$ ($m^2\ s^{-1}$)
1	H_2O	0,0	0,0	0,0	1,9 [147]
2	9 H_2O : 1 DMSO (v/v)	10,0	10,9	2,7	1,7 [147]
3	2 H_2O : 1 DMSO (v/v)	33,3	35,5	11,2	1,3
4	1 H_2O : 1 DMSO (v/v)	50,0	52,4	20,2	1,1 [147]
5	1 H_2O : 2 DMSO (v/v)	66,7	68,7	33,6	1,0
6	1 H_2O : 9 DMSO (v/v)	90,0	90,8	69,5	1,7 [147]
7	1 H_2O : 14 DMSO(v/v)	93,3	93,9	78,0	2,0



Rysunek 54. Współczynniki dyfuzji O_2 dla mieszanin dwuskładnikowych woda-DMSO w temperaturze 25°C. Numery na wykresie odpowiadają mieszaninom wyszczególnionym w Tabeli 12.

4.3.4 Wyznaczenie stężenia nasyconych roztworów KOH w mieszaninach DMSO-woda

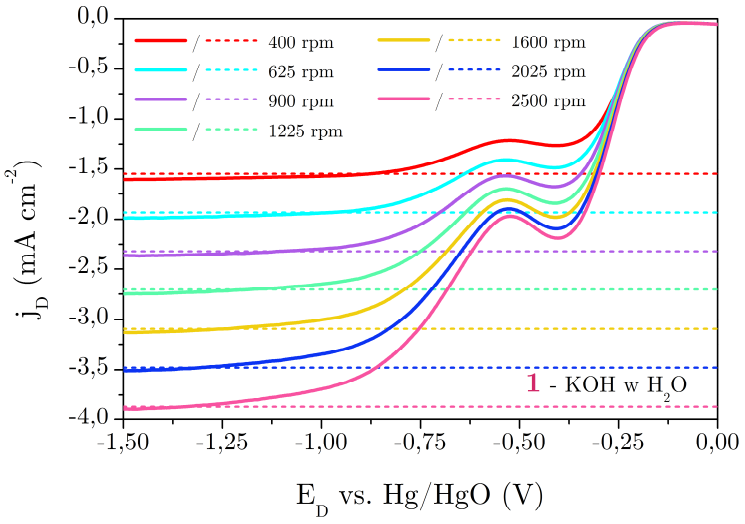
Elektrolity nr 6 i 7 stanowiły roztwory nasycone o stężeniach KOH równych odpowiednio (97,5±2,5) mM oraz (90,0±2,5) mM.

4.3.5 Elektroredukcja tlenu na elektrodzie dyskowej z węgla szklistego

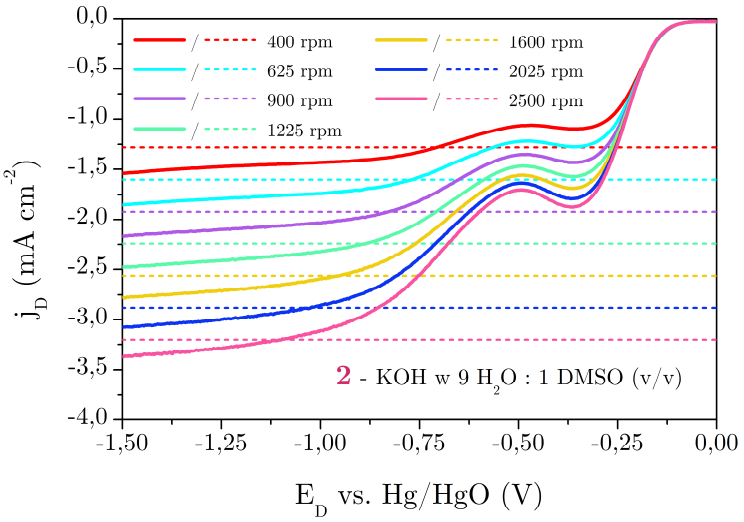
Krzywe woltamperometryczne dla redukcji tlenu w wodnym roztworze 0,1 M KOH (bez dodatku DMSO) widoczne są na Rysunku 55, natomiast krzywe zarejestrowane w elektrolitach zawierających DMSO zaprezentowano na Rysunkach 56-61. Aby móc

z łatwością porównywać wyniki uzyskane dla różnych elektrolitów, wszystkie wykresy przedstawiono w tej samej skali.

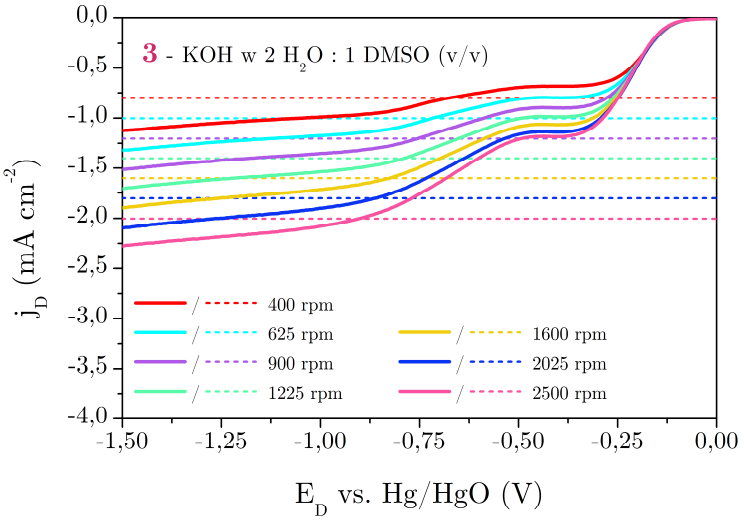
W elektrolicie wodnym (bez dodatku DMSO) (Rysunek 55), redukcja tlenu pojawia się w formie charakterystycznych dwóch fal. Obie te fale są wynikiem zachodzenia tego samego procesu elektrodowego (redukcji tlenu prowadzącej do wytworzenia nadtlenku wodoru jako produktu głównego [142]), a występowanie dwóch fal powiązane jest z obecnością dwóch typów centrów aktywnych na powierzchni węgla szklistego [118]. Gdy zawartość DMSO w elektrolicie rośnie, granice pomiędzy tymi dwiema falami zacierają się, ale ogólny kształt krzywych woltamperometrycznych pozostaje zachowany. Taka tendencja utrzymuje się jeszcze dla elektrolitu zawierającego 66,7 obj.% DMSO (Rysunek 59). Gdy DMSO stanowi 90 obj.% dwie fale stają się nierozróżnialne i zlewają się w jedną słabo wykształconą falę (Rysunek 60). Dalszy wzrost zawartości DMSO (do 93 obj.%) sprawia, że wysokości uzyskiwanych fal stają się praktycznie niezależne od szybkości wirowania elektrody (Rysunek 61).



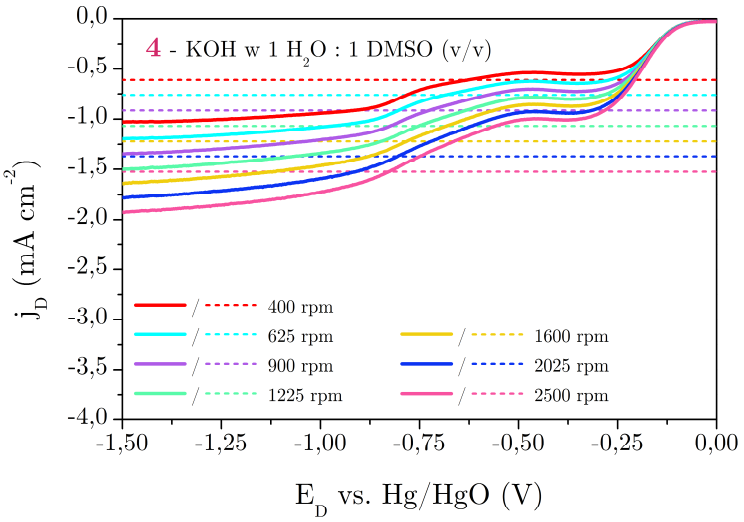
Rysunek 55. Elektroredukcja tlenu na węglu szklistym w wodnym elektrolicie alkalicznym nasyconym tlenem. Linie ciągłe przedstawiają krzywe woltamperometryczne uzyskane eksperymentalnie (po korekcie uwzględniającej występowanie prądu tła), natomiast liniami przerywanymi oznaczono teoretyczne gęstości natężenia prądu w warunkach całkowitej kontroli dyfuzyjnej wyznaczone na podstawie równania Levicha dla n=2,20.



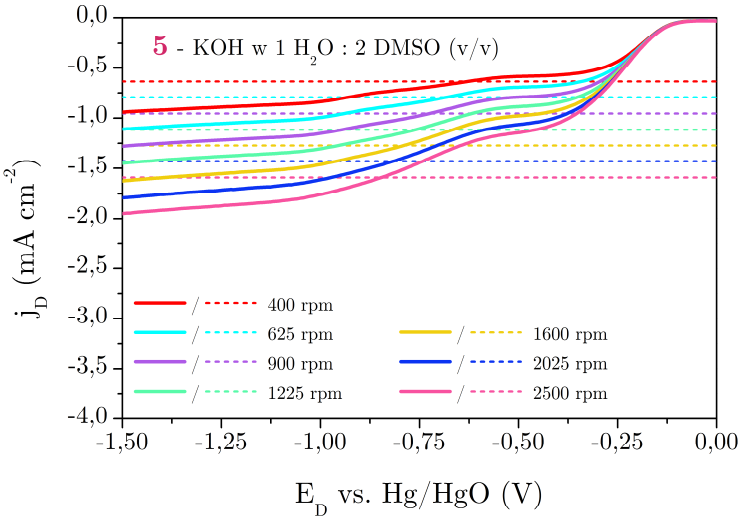
Rysunek 56. Elektroredukcja tlenu na węglu szklistym w elektrolicie alkalicznym na bazie mieszaniny woda-DMSO (9 H_2O : 1 DMSO) nasyconym tlenem. Linie ciągłe przedstawiają krzywe woltamperometryczne uzyskane eksperymentalnie (po korekcie uwzględniającej występowanie prądu tła), natomiast liniami przerywanymi oznaczono teoretyczne gęstości natężenia prądu w warunkach całkowitej kontroli dyfuzyjnej wyznaczone na podstawie równania Levicha dla n=2,20.



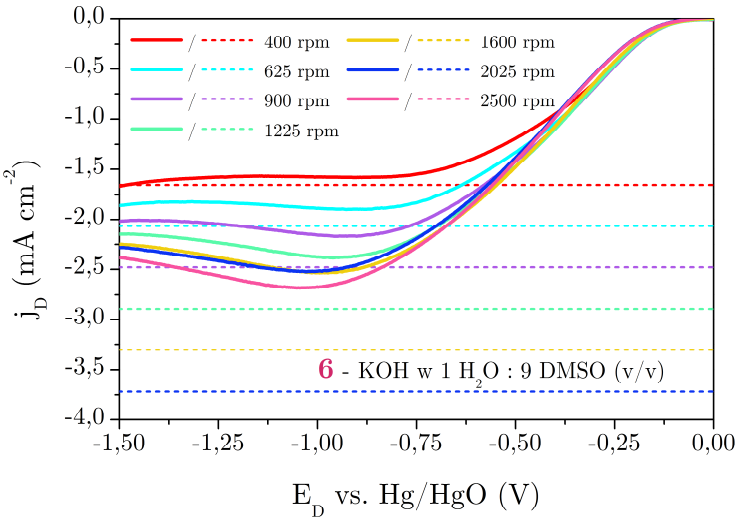
Rysunek 57. Elektroredukcja tlenu na węglu szklistym w elektrolicie alkalicznym na bazie mieszaniny woda-DMSO (2 H_2O : 1 DMSO) nasyconym tlenem. Linie ciągłe przedstawiają krzywe woltamperometryczne uzyskane eksperymentalnie (po korekcie uwzględniającej występowanie prądu tła), natomiast liniami przerywanymi oznaczono teoretyczne gęstości natężenia prądu w warunkach całkowitej kontroli dyfuzyjnej wyznaczone na podstawie równania Levicha dla n=2,20.



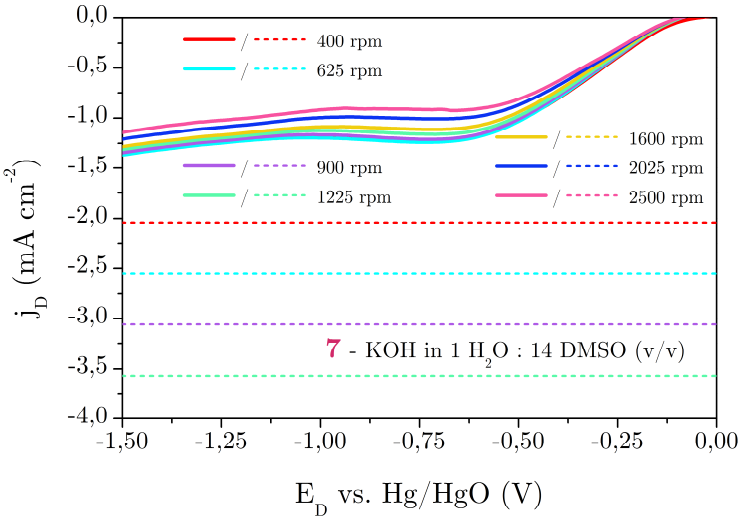
Rysunek 58. Elektroredukcja tlenu na węglu szklistym w elektrolicie alkalicznym na bazie mieszaniny woda-DMSO (1 H_2O : 1 DMSO) nasyconym tlenem. Linie ciągłe przedstawiają krzywe woltamperometryczne uzyskane eksperymentalnie (po korekcie uwzględniającej występowanie prądu tła), natomiast liniami przerywanymi oznaczono teoretyczne gęstości natężenia prądu w warunkach całkowitej kontroli dyfuzyjnej wyznaczone na podstawie równania Levicha dla n=2,20.



Rysunek 59. Elektroredukcja tlenu na węglu szklistym w elektrolicie alkalicznym na bazie mieszaniny woda-DMSO (1 H_2O : 2 DMSO) nasyconym tlenem. Linie ciągłe przedstawiają krzywe woltamperometryczne uzyskane eksperymentalnie (po korekcie uwzględniającej występowanie prądu tła), natomiast liniami przerywanymi oznaczono teoretyczne gęstości natężenia prądu w warunkach całkowitej kontroli dyfuzyjnej wyznaczone na podstawie równania Levicha dla n=2,20.



Rysunek 60. Elektroredukcja tlenu na węglu szklistym w elektrolicie alkalicznym na bazie mieszaniny woda-DMSO (1 H_2O : 9 DMSO) nasyconym tlenem. Linie ciągłe przedstawiają krzywe woltamperometryczne uzyskane eksperymentalnie (po korekcie uwzględniającej występowanie prądu tła), natomiast liniami przerywanymi oznaczono teoretyczne gęstości natężenia prądu w warunkach całkowitej kontroli dyfuzyjnej wyznaczone na podstawie równania Levicha dla n=2,20.



Rysunek 61. Elektroredukcja tlenu na węglu szklistym w elektrolicie alkalicznym na bazie mieszaniny woda-DMSO (1 H_2O : 14 DMSO) nasyconym tlenem. Linie ciągłe przedstawiają krzywe woltamperometryczne uzyskane eksperymentalnie (po korekcie uwzględniającej występowanie prądu tła), natomiast liniami przerywanymi oznaczono teoretyczne gęstości natężenia prądu w warunkach całkowitej kontroli dyfuzyjnej wyznaczone na podstawie równania Levicha dla n=2,20.

Wyniki badań przedstawione na Rysunkach 55-61 dowodzą, że obecność DMSO w elektrolicie wpływa na przebieg elektroredukcji tlenu na węglu szklistym. Aby określić możliwe przyczyny takiego zjawiska na początku omówione zostały właściwości fizykochemiczne DMSO oraz mieszanin dwuskładnikowych DMSO-woda.

Dimetylosulfotlenek jest popularnym rozpuszczalnikiem aprotycznym stosowanym wobec wielu związków nieorganicznych i organicznych, co wynika z jego wysokiej stałej dielektrycznej (ε_r = 47,09 w 293,15 K [154]). DMSO jest silnie higroskopijny [155], chociaż szybkość z jaką pochłania on parę wodną z otoczenia jest względnie niska [156]. Unikalną cechą dimetylosulfotlenku jest jego całkowita mieszalność z wodą, co oznacza, że właściwości fizykochemiczne układu DMSO-woda mogą być regulowane poprzez zmianę składu mieszaniny.

Dodatek DMSO powoduje monotoniczny wzrost gęstości, podczas gdy jego wpływ na lepkość, rozpuszczalność tlenu oraz współczynnik dyfuzji tlenu jest bardziej złożony. Jak widać na Rysunkach 50, 52 oraz 54, wraz ze wzrostem zawartości DMSO wszystkie te trzy wielkości przechodzą przez ekstrema (maksimum w przypadku lepkości oraz minima dla rozpuszczalności tlenu i współczynnika dyfuzji tlenu). Ekstrema te świadczą o powstawaniu mieszaniny nieidealnej, co spowodowane jest silnymi oddziaływaniami pomiędzy DMSO a cząsteczkami wody. Dimetylosulfotlenek jako polarny rozpuszczalnik aprotyczny tworzy z cząsteczkami wody kompleksy międzycząsteczkowe DMSO·2H_2O, które charakteryzują się dużym momentem dipolowym równym 4,6 D [154]. Dla porównania wartości momentów dipolowych dla wody oraz dimetylosulfotlenku wynoszą odpowiednio 1,85 D [157] oraz 3,9 D [158].

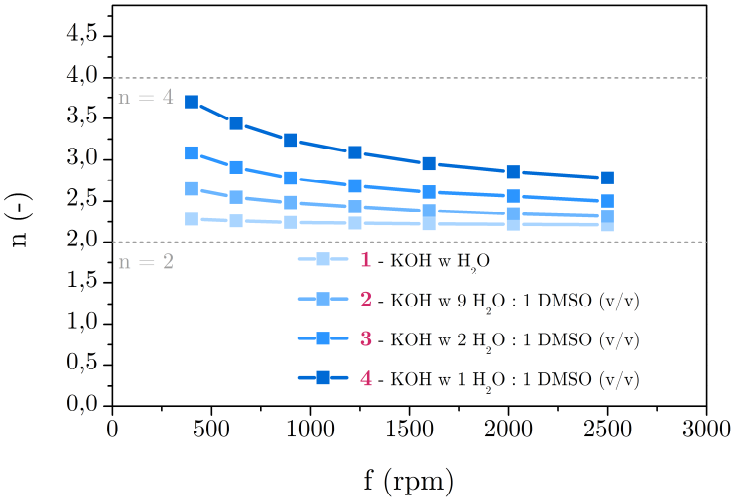
Maksimum lepkości występuje, gdy na jedną cząsteczkę dimetylosulfotlenku przypadają dwie cząsteczki wody [155], co w przybliżeniu odpowiada mieszaninie woda-DMSO oznaczonej numerem 5. Struktura mieszaniny o takim składzie jest wyjątkowa, bowiem w tym przypadku wszystkie cząsteczki wody są poprzez wiązanie wodorowe związane z cząsteczkami dimetylosulfotlenku [154]. Innymi słowy, mieszanina nr 5 jest złożona praktycznie tylko z kompleksów DMSO·2H_2O [154].

Aby zweryfikować hipotezę, że obecność w elektrolicie kompleksów DMSO·2H_2O wpływa na przebieg elektroredukcji tlenu na węglu szklistym, gęstości natężenia prądu j_D zarejestrowane podczas redukcji O_2 (linie ciągłe na Rysunkach 55-61) zostały porównane z teoretycznymi gęstościami natężenia prądu w warunkach pełnej kontroli dyfuzyjnej (linie przerywane na Rysunkach 55-61) dla liczby wymienianych elektronów równej 2,20 (tj. wartości n uzyskiwanej w elektrolicie wodnym bez dodatku DMSO).

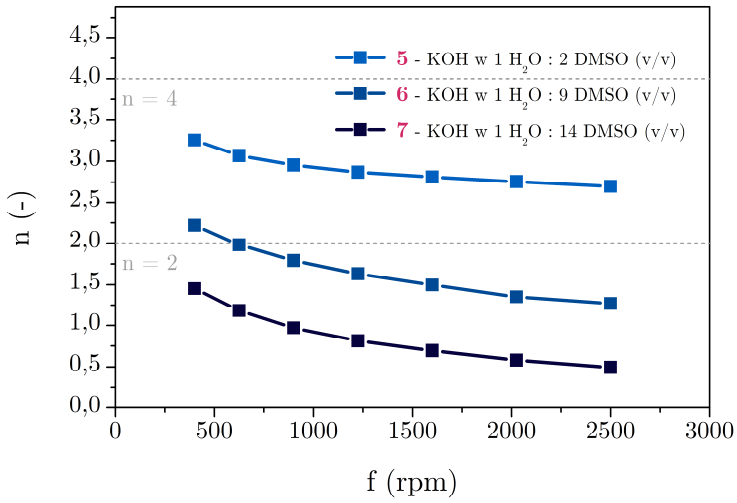
Jak można zauważyć na Rysunkach 56-59, gdy DMSO stanowi nie więcej niż 66,7 obj.% mieszaniny dwuskładnikowej, uzyskiwane gęstości natężenia prądu przekraczają gęstości natężenia prądu limitowanego dyfuzją wyznaczone dla n=2,20. Odwrotna sytuacja występuje w przypadku elektrolitów, w których dimetylosulfotlenek obecny jest w dużej przewadze (Rysunki 60-61) – uzyskiwane gęstości natężenia prądu nie osiągają wówczas wartości przewidzianych dla n=2,20 w warunkach całkowitej kontroli dyfuzyjnej.

W obu tych przypadkach (rejestrowana gęstość prądu wyższa lub niższa niż gęstość prądu limitowanego dyfuzją) liczba elektronów wymienianych podczas elektroredukcji tlenu nie jest równa 2,20 ($n \neq 2{,}20$), jak dla alkalicznego elektrolitu wodnego (Rysunek 55). Oznacza to, że obecność DMSO ma wpływ na średnią liczbę elektronów przyłączanych do cząsteczki O_2 podczas jej redukcji na węglu szklistym, a stąd także na produkty wytwarzane w wyniku tego procesu.

Jak zaprezentowano na Rysunku 62, liczba elektronów wymienianych podczas elektroredukcji tlenu sukcesywnie wzrasta, gdy udział DMSO rośnie od 0,0 do 50,0 obj.%. Bez dodatku dimetylosulfotlenku redukcja O_2 przy potencjale -1,5 V vs. Hg/HgO przebiega głównie jako proces dwuelektronowy ($n = 2{,}28$ dla 400 rpm, $n = 2{,}21$ dla 2500 rpm), podczas gdy obecność DMSO powoduje stopniową zmianę charakteru procesu w kierunku pełnej czteroelektronowej redukcji. Tendencja taka utrzymuje się aż do osiągnięcia maksymalnej liczby wymienianych elektronów ($n = 3{,}70$ dla 400 rpm, $n = 2{,}78$ dla 2500 rpm) w elektrolicie alkalicznym na bazie mieszaniny nr 4. Elektrolit powstały na bazie mieszaniny nr 5 zapewnia już nieco niższe wartości n ($n = 3{,}26$ dla 400 rpm, $n = 2{,}70$ dla 2500 rpm), a dalszy wzrost zawartości DMSO skutkuje gwałtownym spadkiem wartości liczby wymienianych elektronów (Rysunek 63). Podsumowując, elektrolitami zapewniającymi najwyższe wartości n podczas procesu elektroredukcji tlenu na węglu szklistym są elektrolity bogate w kompleksy międzycząsteczkowe DMSO-woda.



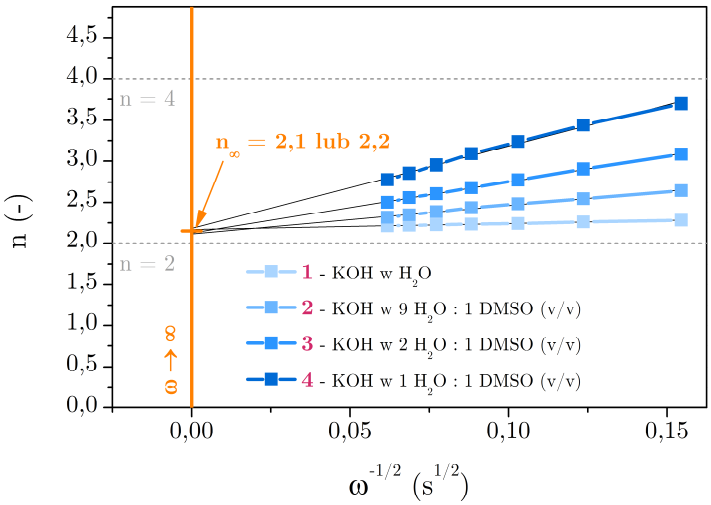
Rysunek 62. Liczba elektronów wymienianych podczas redukcji O_2 na węglu szklistym w elektrolitach alkalicznych nasyconych tlenem powstałych na bazie mieszanin DMSO-woda. Potencjał elektrody dyskowej: E_D = -1,5 V vs. Hg/HgO.



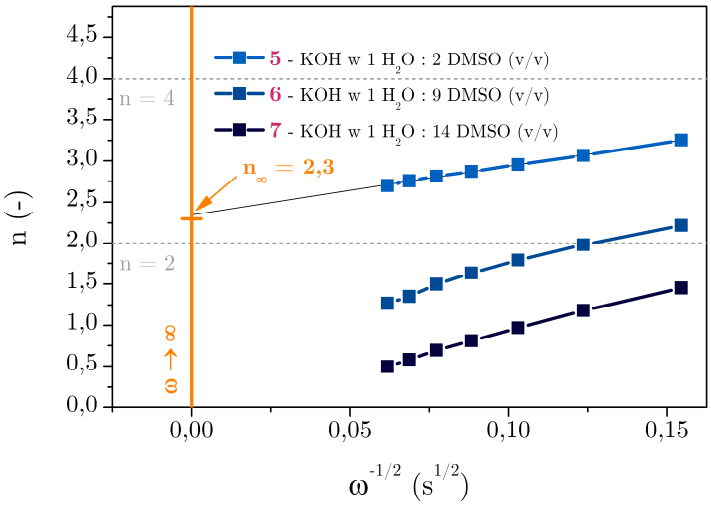
Rysunek 63. Liczba elektronów wymienianych podczas redukcji O_2 na węglu szklistym w elektrolitach alkalicznych nasyconych tlenem powstałych na bazie mieszanin DMSO-woda. Potencjał elektrody dyskowej: E_D = -1,5 V vs. Hg/HgO.

Dane zamieszczone na Rysunkach 62 i 63 zostały przedstawione także w formie wykresów n vs. $\omega^{-1/2}$ (Rysunki 64 i 65). Dzięki takiej transformacji możliwe jest uzyskanie dodatkowych informacji na temat mechanizmu procesu elektroredukcji tlenu. Zlinearyzowana postać umożliwia oszacowanie za pomocą ekstrapolacji wartości n dla $\omega^{-1/2} \rightarrow 0$ (czyli dla $\omega \rightarrow \infty$). Liczba wymienianych elektronów dla $\omega \rightarrow \infty$ (oznaczona dla uproszczenia jako n_∞) dotyczy sytuacji, gdy H_2O_2 (lub HO_2^-) powstały na skutek redukcji O_2 nie może ulegać dalszej redukcji na elektrodzie dyskowej, bowiem jest natychmiast usuwany z jej powierzchni. Stąd n_∞ obejmuje jedynie dwie reakcje równoległe: dwuelektronową oraz bezpośrednią czteroelektronową redukcję O_2. W konsekwencji możliwe staje się rozróżnienie pomiędzy nadtlenkiem wodoru (lub jonem HO_2^-) powstającym jako produkt przejściowy a nadtlenkiem wodoru będącym produktem końcowym. Ilustrację powyższej koncepcji stanowi Rysunek 66.

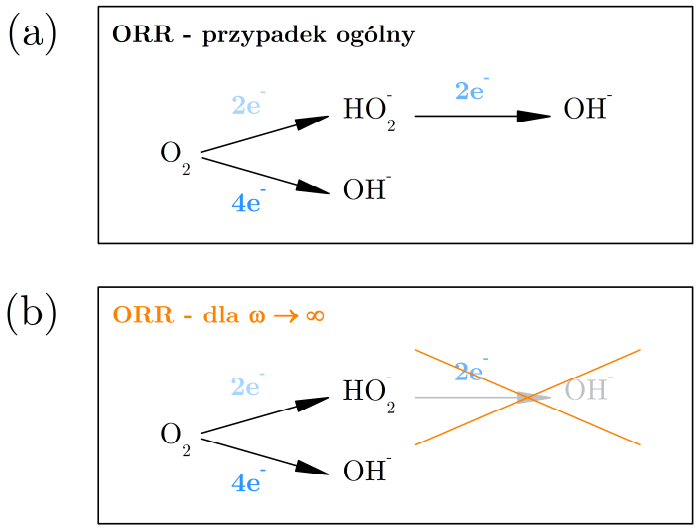
Rysunek 64 pokazuje, że dla wszystkich elektrolitów alkalicznych zawierających od 0,0 do 50,0 obj.% DMSO, n_∞ pozostaje niemal stałe i wynosi 2,1 lub 2,2. Nieco wyższa, ale wciąż zbliżona wartość (n_∞ równe 2,3) jest uzyskiwana dla elektrolitu na bazie mieszaniny nr 5. Dodatek dimetylosulfotlenku (aż do 66,7 obj.%) nie zmienia znacząco wartości n_∞, czyli nie ma wpływu na stosunek szybkości dwuelektronowej redukcji tlenu do szybkości bezpośredniej czteroelektronowej redukcji O_2. Obecność DMSO (w opisanym wyżej zakresie) wywiera natomiast wpływ na wartość n, która jest wypadkową wszystkich trzech reakcji przedstawionych na Rysunku 66a. Zatem można wywnioskować, że obecność kompleksów międzycząsteczkowych $DMSO{\cdot}2H_2O$ ułatwia redukcję HO_2^-.



Rysunek 64. Liczba elektronów wymienianych podczas redukcji O_2 na węglu szklistym w elektrolitach alkalicznych nasyconych tlenem powstałych na bazie mieszanin DMSO-woda. Potencjał elektrody dyskowej: E_D = -1,5 V vs. Hg/HgO. Dokładne wartości n_∞ podane są w Tabeli 13 razem z błędem standardowym oraz innymi parametrami regresji liniowej.



Rysunek 65. Liczba elektronów wymienianych podczas redukcji O_2 na węglu szklistym w elektrolitach alkalicznych nasyconych tlenem powstałych na bazie mieszanin DMSO-woda. Potencjał elektrody dyskowej: E_D = -1,5 V vs. Hg/HgO. Dokładne wartości n_∞ podane są w Tabeli 13 razem z błędem standardowym oraz innymi parametrami regresji liniowej.



Rysunek 66. Elektroredukcja tlenu w środowisku alkalicznym: (a) ogólny schemat procesu oraz (b) schemat uproszczony dla szybkości wirowania elektrody dążącej do nieskończoności.

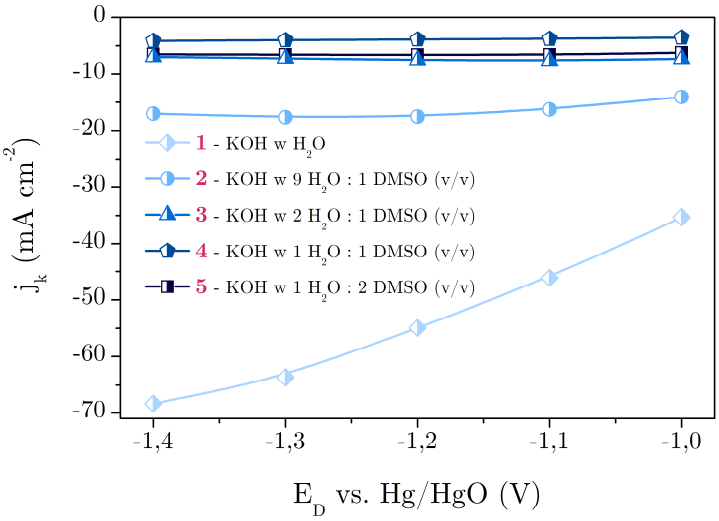
Tabela 13. Regresja liniowa ($n = A{\cdot}\omega^{-1/2} + n_\infty$) dla zestawów danych zaprezentowanych na Rysunkach 64 i 65. Współczynniki regresji liniowej, ich błędy standardowe oraz współczynniki determinacji R^2 wyznaczono za pomocą *Excel Data Analysis Toolpak*.

nr elektrolitu	A ($s^{-1/2}$)	ΔA ($s^{-1/2}$)	n_∞ (-)	Δn_∞ (-)	R^2 (-)
1	0,739	0,018	2,168	0,002	0,9970
2	3,50	0,12	2,113	0,013	0,9938
3	6,25	0,10	2,126	0,010	0,9987
4	10,01	0,32	2,182	0,032	0,9950
5	5,87	0,10	2,348	0,010	0,9986

Co wydaje się być sprzeczne z intuicją, elektrolit na bazie mieszaniny nr 5 zapewnia trochę niższe wartości liczby wymienianych elektronów (n = 3,26 dla 400 rpm, n = 2,70 dla 2500 rpm) niż elektrolit powstały z mieszaniny nr 4 (n = 3,70 dla 400 rpm, n = 2,78 dla 2500 rpm). Można to wyjaśnić, jeżeli weźmie się pod uwagę nie tylko tworzenie kompleksów DMSO-woda, ale także solwatację jonów przez cząsteczki rozpuszczalnika w mieszaninach dimetylosulfotlenek-woda. Mieszanina nr 5 jest praktycznie złożona wyłącznie z kompleksów $DMSO{\cdot}2H_2O$ [154]. Jednakże, kiedy do tej mieszaniny dodawany jest KOH, część cząsteczek wody nie może związać się z cząsteczkami DMSO za pośrednictwem wiązań wodorowych, bowiem solwatują one jony obecne w elektrolicie. Zostało już udowodnione (na przykładzie KCl [159]), że w mieszaninie woda-dimetylosulfotlenek solwatacja jonów przez cząsteczki wody jest uprzywilejowana niezależnie od składu tej mieszaniny. Zatem, elektrolit alkaliczny (0,1 M KOH) zawierający najwyższe

możliwe stężenie kompleksów $DMSO{\cdot}2H_2O$ musi charakteryzować się nieco wyższą zawartością wody niż mieszanina nr 5.

Liczba wymienianych elektronów *n* świadczy jedynie o wydajności konwersji energii podczas procesu elektrochemicznej redukcji tlenu. Aby uzyskać informacje dotyczące kinetyki tego procesu, oszacowano gęstość natężenia prądu kinetycznego uzyskiwanego dla elektrolitów z dodatkiem dimetylosulfotlenku. Jak widać na Rysunku 67, gęstości natężenia prądów kinetycznych dla elektrolitów na bazie mieszanin DMSO-woda są o rząd wielkości niższe niż w przypadku elektrolitu wodnego (bez dodatku DMSO). Zatem dimetylosulfotlenek poprawia wydajność elektrochemicznej konwersji tlenu, ale jednocześnie wywiera negatywny wpływ na kinetykę tego procesu.



Rysunek 67. Gęstość natężenia prądu kinetycznego dla redukcji O_2 na węglu szklistym w elektrolitach alkalicznych nasyconych tlenem powstałych na bazie mieszanin DMSO-woda.

Spadek gęstości natężenia prądu kinetycznego w elektrolitach z dodatkiem dimetylosulfotlenku można próbować wiązać z adsorpcją DMSO na powierzchni elektrody. Powszechnie wiadomym jest, że hamowanie procesu elektrodowego na skutek adsorpcji może być spowodowane zmniejszeniem dostępnej powierzchni elektrody (efekt blokowania) [40]. Inną możliwą przyczyną jest zwiększenie na skutek adsorpcji energii aktywacji procesu niezbędnej, aby substancja elektroaktywna znalazła się w zaadsorbowanej warstwie i doszło do wymiany ładunku między tą substancją elektroaktywną a powierzchnią elektrody [40]. Wpływ adsorpcji na kinetykę procesu elektrodowego może także wynikać z efektu elektrostatycznego – w obecności zaadsorbowanych cząsteczek dochodzi do zmiany efektywnej różnicy potencjałów między elektrodą a płaszczyzną największego zbliżenia [40].

Wydaje się jednak, że w przypadku elektroredukcji tlenu na węglu szklistym spadek gęstości natężenia prądu kinetycznego w obecności dimetylosulfotlenku nie jest powiązany z adsorpcją. Dotychczas nie ukazała się żadna publikacja potwierdzająca adsorpcję cząsteczek DMSO na powierzchni węgla szklistego. Dla porównania,

adsorpcja dimetylosulfotlenku na powierzchniach metalicznych jest dość szczegółowo opisana [160-172].

Dodatkowo, adsorpcja DMSO na węglu szklistym wydaje się być mało prawdopodobna, jeżeli wziąć pod uwagę fakt, że DMSO stosowane jest do wytwarzania roztworów i zawiesin, które używane są do modyfikowania powierzchni węgla szklistego. Na przykład enzymy katalaza [173,174] oraz peroksydaza chrzanowa [175] mogą być zaadsorbowane na węglu szklistym z roztworów, w których rolę rozpuszczalnika pełni DMSO. Analogiczna sytuacja występuje w przypadku heminy [176], NAD^+ [177] oraz różnego rodzaju kompleksów (na przykład kompleksów chitozanu z jonami żelaza [178] i kompleksów ftalocyjanin i porfiryn z jonami kobaltu [179]. Oprócz tego DMSO używany jest jako środek dyspergujący do wytwarzania na powierzchni węgla szklistego cienkich warstw nanorurek węglowych [180], a także do nanoszenia nanopłatków grafenu [181].

W kontekście potencjalnej adsorpcji DMSO na powierzchni węgla szklistego warto zacytować fragment publikacji Moirouxa i Elvinga [177]:

„Wydaje się, że stosowanie rozpuszczalnika organicznego takiego jak DMSO (...) nie zmienia znacząco przebiegu adsorpcji NAD^+ na węglu szklistym; jedyne zauważalne zmiany są związane z obecnością jonów Bu_4N^+, które stanowią elektrolit podstawowy w DMSO i mogą przynajmniej częściowo hamować adsorpcję NAD^+ w orientacji planarnej."

"It appears that the use of an organic solvent such as DMSO (...) does not change appreciably the adsorption behavior of NAD^+ at the GCE [glassy carbon electrode]; the only noticeable changes are related to the presence of Bu_4N^+ ions as supporting electrolyte in DMSO since they may at least partially hinder the adsorption of NAD^+ in the planar conformation."

Z powodów opisanych powyżej adsorpcja DMSO na węglu szklistym nie jest rozważana jako przyczyna zmian obserwowanych w przebiegu procesu elektroredukcji tlenu. Aby określić w jaki dokładnie sposób dimetylosulfotlenek wpływa na mechanizm i kinetykę tego procesu wymagane byłyby dalsze badania.

Ponadto możliwe jest inne wyjaśnienie spadku gęstości natężenia prądu kinetycznego w obecności DMSO. Mianowicie, zgodnie z obserwacjami poczynionymi przez Galusa [182], reakcje elektrodowe zawsze przebiegają wolniej, kiedy substancja elektroaktywna jest redukowana z elektrolitu, w którym rozpuszczalnik jest silną zasadą Lewisa.

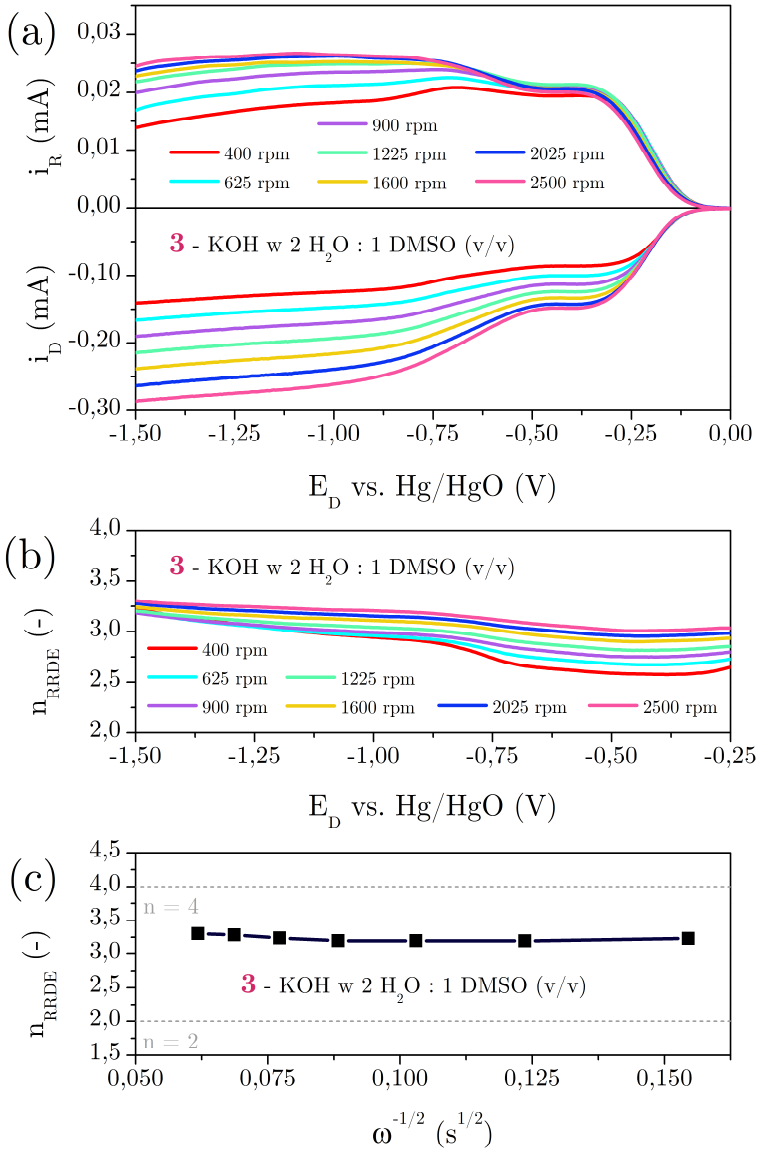
Należy podkreślić, że wartości liczby wymienianych elektronów n dla potencjału E_D = -1,5 V vs. Hg/HgO przedstawione na Rysunkach 62 i 63 oraz na Rysunkach 64 i 65 zostały wyznaczone na podstawie równania Levicha, przyjmując założenie, że gęstość natężenia prądu na elektrodzie dyskowej dla potencjału -1,5 V jest limitowana dyfuzją. Innymi słowy, aby wyznaczyć wartości n, gęstość natężenia prądu przy E_D = -1,5 V została porównana z gęstością natężenia prądu kontrolowanego dyfuzyjnie, który byłaby obserwowana w takich samych warunkach dla n = 2,20. Z tego względu, wartości n

prezentowane na Rysunkach 62 i 63 oraz na Rysunkach 64 i 65 nie powinny być traktowane jako wartości rzeczywiste, ale raczej należy je uważać za minimalną liczbę elektronów wymienianych podczas redukcji O_2 przebiegającej w danym elektrolicie przy określonych wartościach potencjału i częstotliwości wirowania elektrody. W niniejszej pracy zdecydowano się wyznaczyć liczbę wymienianych elektronów w oparciu o równanie Levicha, mając na uwadze, że standardowe podejścia, tj. metoda Koutecký'ego-Levicha oraz pomiary za pomocą wirującej elektrody dyskowo-pierścieniowej, nie mogą zapewnić w tym przypadku wiarygodnych wyników. Szczegółowe wyjaśnienie, dlaczego oba te podejścia są w tym przypadku nieprawidłowe można znaleźć w literaturze [67] oraz w Rozdziale 3 niniejszej pracy. Dla przejrzystości krótki opis wyjaśniający tę kwestię zamieszczono także poniżej razem z przykładowymi wynikami uzyskanymi przy zastosowaniu wirującej elektrody dyskowo-pierścieniowej.

Metoda Koutecký'ego-Levicha nie jest odpowiednia do wyznaczania liczby elektronów wymienianych podczas elektroredukcji tlenu zarówno z teoretycznego, jak i praktycznego punktu widzenia, co zostało szczegółowo opisane przez Zhou i współpracowników [67]. Pomiary za pomocą wirującej elektrody dyskowo-pierścieniowej także nie mogą gwarantować dokładnych wartości liczby elektronów wymienianych podczas redukcji O_2 w elektrolitach na bazie mieszanin dwuskładnikowych DMSO-woda, jako że natężenie prądu rejestrowane w tych warunkach na pierścieniu platynowym jest dużo niższe niż można by się tego spodziewać. Przykładowe krzywe natężenie prądu-potencjał dla alkalicznego elektrolitu z dodatkiem DMSO przedstawiono na Rysunku 68a.

Fakt, że natężenie prądu na elektrodzie pierścieniowej jest dużo niższe niż oczekiwane można wyjaśnić silną adsorpcją cząsteczek DMSO na powierzchni pierścienia platynowego [160]. Dla Pt(100) energia adsorpcji wyznaczona w oparciu o teorię funkcjonałów gęstości (DFT - ang. *density functional theory*) wynosi bowiem -108 kJ mol^{-1} [161]. Należy mieć również na uwadze, że utlenianie HO_2^- na platynie pokrytej tlenkami przebiega w warunkach mieszanej kontroli dyfuzyjno-kinetycznej, co zostało opisane w Rozdziale 3.

Dowodem na to, że natężenie prądu na pierścieniu platynowym zarejestrowane w elektrolitach z dodatkiem DMSO nie powinno stanowić podstawy do dalszych obliczeń oraz interpretacji przebiegu procesu elektroredukcji tlenu w tychże elektrolitach są wyniki przedstawione na Rysunku 68b oraz Rysunku 68c, gdzie liczba wymienianych elektronów n_{RRDE} wyznaczona na podstawie danych z Rysunku 68a została wykreślona odpowiednio jako funkcja potencjału elektrody dyskowej oraz jako funkcja $\omega^{-1/2}$. Na Rysunku 68b oraz Rysunku 68c można zauważyć, że dla danej wartości E_D liczba wymienianych elektronów rośnie wraz ze wzrostem szybkości wirowania elektrody, podczas gdy taka zależność jest z teoretycznego punktu widzenia niemożliwa, jak zostało to dowiedzione w Podrozdziale 3.3.4 niniejszej pracy. Z tego powodu w badaniach nad elektroredukcją tlenu w elektrolitach na bazie mieszanin DMSO-woda posłużono się wirującą elektrodą dyskową zamiast wirującą elektrodą dyskowo-pierścieniową.



Rysunek 68. (a) Krzywe natężenie prądu-potencjał (po korekcie uwzględniającej występowanie natężenia prądu tła) dla redukcji tlenu na węglu szklistym w elektrolicie alkalicznym na bazie mieszaniny woda-DMSO (2 H_2O : 1 DMSO) nasyconym tlenem. Liczba wymienianych elektronów wyznaczona z pomiarów metodą RRDE (b) jako funkcja potencjału elektrody dyskowej oraz (c) dla E_D = -1,5 V vs. Hg/HgO. Współczynnik efektywności zbierania N wynosił 0,41. Potencjał pierścieniowej elektrody platynowej był równy +0,335 V vs. Hg/HgO. Przed pomiarami dotyczącymi elektroredukcji tlenu pierścień platynowy był kondycjonowany w elektrolicie z dodatkiem DMSO przy zastosowaniu woltamperometrii cyklicznej, jak opisano to w Podrozdziale 3.1.

4.4 Wnioski

Zaprezentowane wyniki badań stanowią pierwszy raport na temat elektrochemicznej redukcji tlenu na elektrodzie węglowej w alkalicznych elektrolitach na bazie mieszanin DMSO-woda. Jak wykazano, obecność dimetylosulfotlenku w elektrolicie alkalicznym silnie

wpływa na przebieg elektroredukcji O_2 na węglu szklistym. Bez dodatku DMSO proces ORR przy potencjale -1,5 V vs. Hg/HgO zachodzi głównie jako redukcja dwuelektronowa, natomiast wraz ze wzrostem zawartości dimetylosulfotlenku (aż do 50 obj.%) obserwuje się stopniową zmianę charakteru procesu w kierunku pełnej czteroelektronowej redukcji. W elektrolicie alkalicznym na bazie mieszaniny 1 H_2O : 1 DMSO (v/v) uzyskano liczbę wymienianych elektronów równą 3,70 przy częstotliwości wirowania elektrody 400 rpm.

Zaproponowano dotychczas wiele różnych technik poprawiających wydajność elektrochemicznej konwersji energii podczas procesu redukcji tlenu na elektrodach węglowych. Należą do nich choćby domieszkowanie materiałów węglowych heteroatomami oraz zwiększanie liczby defektów obecnych w materiałach węglowych, przy czym obie te techniki polegają na modyfikacji właściwości elektrycznych materiału węglowego. Przedstawione wyniki badań dowodzą, że do kontrolowania przebiegu procesu elektrochemicznej redukcji tlenu na elektrodzie węglowej użyte mogą być także elektrolity alkaliczne zawierające kompleksy międzycząsteczkowe DMSO-woda o wysokim momencie dipolowym. Niemniej jednak, w przypadku elektrolitów alkalicznych z dodatkiem dimetylosulfotlenku poprawie wydajności elektrochemicznej konwersji O_2 towarzyszy spadek natężenia gęstości prądu kinetycznego.

IV

Podsumowanie

Pierwszym osiągnięciem badawczym przedstawionym w niniejszej pracy jest zaproponowanie modyfikacji istniejącej metody elektroanalitycznej - metody wirującej elektrody dyskowo-pierścieniowej (RRDE), która to modyfikacja poszerza potencjalny zakres zastosowań tejże metody oraz jej dokładność.

W metodzie wirującej elektrody dyskowo-pierścieniowej obie elektrody, dysk i pierścień, osadzone są koncentrycznie na jednym wale (Rysunek 27), który obraca się wokół własnej osi z zadaną częstotliwością zapewniającą laminarny przepływ elektrolitu do powierzchni elektrody. Istotą metody RRDE jest możliwość badania procesu elektrodowego przebiegające na dysku przy zastosowaniu elektrody pierścieniowej pełniącej rolę selektywnego detektora. Metoda RRDE najczęściej stosowana jest do badania procesu elektroredukcji tlenu (ORR) i wówczas na elektrodzie pierścieniowej utleniany jest nadtlenek wodoru, będący produktem ubocznym albo pośrednim reakcji przebiegającej na dysku.

Teoria metody RRDE opiera się na założeniu, że reakcja zachodząca na pierścieniu jest kontrolowana wyłącznie przez proces dyfuzji. Innymi słowy, substancja elektroaktywna generowana na dysku musi ulegać reakcji elektrodowej na pierścieniu natychmiast po tym, gdy zostanie dostarczona na powierzchnię elektrody pierścieniowej.

Najczęstszym podejściem spotykanym w literaturze jest stosowanie metody RRDE do badań nad procesem ORR bez żadnej weryfikacji, czy powyższe założenie jest prawdziwe. Niniejsza praca natomiast jasno pokazuje, że w środowisku alkalicznym utlenianie nadtlenku wodoru na pierścieniu platynowym pokrytym tlenkami podlega mieszanej kontroli dyfuzyjno-kinetycznej. Zatem podstawowe założenie metody RRDE nie jest spełnione, a jej stosowanie w tych warunkach nie może prowadzić do wiarygodnych wyników.

W niniejszej pracy poza wykazaniem istnienia problemu z metodą RRDE w kontekście badań nad procesem ORR, zaproponowano także rozwiązanie tego problemu. Otóż przedstawiono i zweryfikowano eksperymentalnie procedurę, dzięki której eliminowany jest błąd pomiarowy powstający, gdy reakcja na elektrodzie pierścieniowej nie jest limitowana dyfuzyjnie.

Wprowadzona modyfikacja pozwala na dokładniejsze niż dotychczas wyznaczanie liczby wymienianych elektronów podczas procesu ORR, a także określanie mechanizmu tego procesu. Obie te kwestie są niezwykle istotne do prawidłowej oceny katalizatorów procesu ORR stosowanych w ogniwach paliwowych.

Jednak najistotniejszy, z punktu widzenia dokonania badawczego, jest fakt, że zaproponowana modyfikacja metody RRDE ma charakter ogólny, tj. nie dotyczy jedynie procesu elektroredukcji tlenu, ale z powodzeniem może być stosowana także podczas badania każdego innego procesu elektrochemicznego, dla którego reakcja przebiegająca na elektrodzie pierścieniowej nie jest limitowana wyłącznie przez dyfuzję.

W rezultacie, zaproponowana modyfikacja poszerza potencjalny zakres zastosowań metody RRDE, ponieważ warunek odnośnie reakcji na pierścieniu kontrolowanej czysto

dyfuzyjnie nie musi być już koniecznie spełniony, aby za pomocą metody RRDE uzyskiwać wiarygodne wyniki.

Warto zaznaczyć również, że zaproponowana modyfikacja metody RRDE jest pierwszym i, jak na razie, jedynym rozwiązaniem pozwalającym wyeliminować błąd powstający w sytuacji, kiedy reakcja na pierścieniu nie przebiega przy całkowitej kontroli dyfuzyjnej.

Drugim osiągnięciem badawczym przedstawionym w niniejszej pracy jest opisanie nietypowego przebiegu procesu elektroredukcji tlenu na węglu szklistym w elektrolitach, w których obecne są kompleksy międzycząsteczkowe woda-dimetylosulfotlenek charakteryzujące się dużym momentem dipolowym.

Proces elektroredukcji tlenu (ORR) jest podstawą funkcjonowania ogniw paliwowych, w których dochodzi do bezpośredniej konwersji energii chemicznej paliwa (np. wodoru) i utleniacza (tlenu) w energię elektryczną. Chociaż ogniwa paliwowe są powszechnie kojarzone z nowoczesnymi technologiami i innowacyjnością, to tak naprawdę zostały wynalezione już ponad 150 lat temu. Największą przeszkodą dla ich szerokiego wykorzystania jest konieczność stosowania drogich katalizatorów (bazujących przede wszystkim na platynie), które wymagane są do zwiększenia szybkości, z natury powolnego, procesu ORR przebiegającego na katodzie.

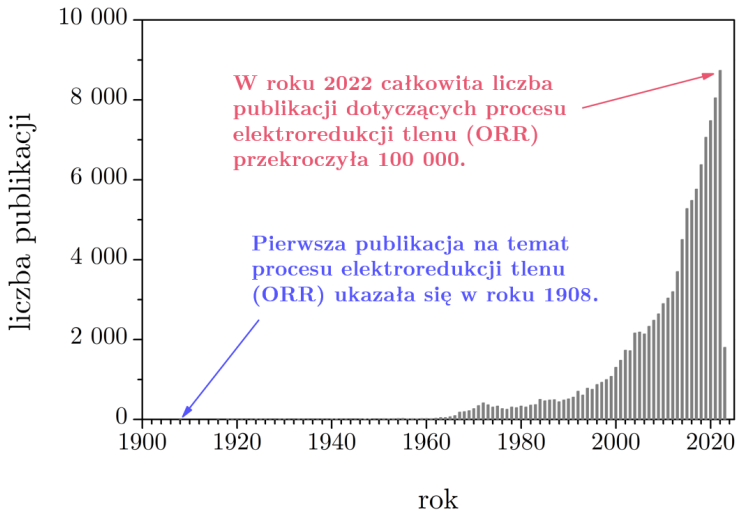
Ostatnie doniesienia sugerują, że w środowisku alkalicznym jako zamienniki katalizatorów opartych na platynie stosowane mogą być znacznie tańsze materiały węglowe. Jednakże materiały te przeważnie nie zapewniają całkowitej redukcji tlenu, co negatywnie wpływa na wydajność elektrochemicznej konwersji energii. Aby rozwiązać ten problem, zaproponowano wiele metod modyfikacji materiałów węglowych, m.in. domieszkowanie heteroatomami (N, B, O itp.) oraz zwiększanie liczby defektów geometrycznych (krawędzi, zniekształceń sieci krystalicznej itp.) występujących w materiałach węglowych.

W niniejszej pracy przedstawiono inne rozwiązanie, tj. w celu poprawy wydajności procesu ORR na elektrodzie węglowej nie dokonano modyfikacji materiału węglowego, lecz wykorzystano elektrolit alkaliczny na bazie mieszaniny dwuskładnikowej woda-DMSO. Elektrolit taki oferuje nowe możliwości w porównaniu do konwencjonalnych elektrolitów wodnych. Charakterystyczną cechą mieszanin dwuskładnikowych woda-DMSO jest fakt, że właściwości takiej mieszaniny nie są średnią właściwości jej składników. Wynika to z silnych oddziaływań między cząsteczkami DMSO a cząsteczkami wody. Woda jest donorem wiązania wodorowego, natomiast DMSO – jego akceptorem. W rezultacie tworzą się międzycząsteczkowe kompleksy woda-dimetylosulfotlenek ($DMSO{\cdot}2H_2O$), cechujące się dużym momentem dipolowym (4,6 D).

Spośród wyników przedstawionych w niniejszej pracy najistotniejszy, z punktu widzenia dokonania badawczego, jest fakt, że podczas gdy dla konwencjonalnego elektrolitu wodnego liczba elektronów wymienianych podczas procesu ORR na węglu szklistym osiąga wartość jedynie $n = 2{,}28$, to przy zastosowaniu elektrolitu na bazie mieszaniny woda-DMSO

uzyskuje się wartości równe nawet $n = 3{,}70$. Oznacza to, że niemal całkowita (czteroelektronowa) redukcja tlenu jest możliwa na niemodyfikowanym węglu szklistym, co nigdy wcześniej nie zostało jeszcze dowiedzione i opisane.

Pomimo ogromnej liczby artykułów dotyczących procesu ORR publikowanych każdego roku (Rysunek 69), badania przedstawione w niniejszej pracy są pierwszymi, i jak na razie jedynymi, które łączą tematykę elektroredukcji tlenu na materiałach węglowych z tematyką elektrolitów na bazie mieszanin dwuskładnikowych woda-aprotyczny rozpuszczalnik polarny.



Rysunek 69. Liczba artykułów na temat elektroredukcji tlenu publikowanych w poszczególnych latach według bazy danych *Scopus*. Fraza '*oxygen reduction reaction*' była wyszukiwana w tytule artykułu, abstrakcie oraz słowach kluczowych. Stan na dzień 02.03.2023 r.

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Aktywność naukowa

Publikacje naukowe

1. Katarzyna Szwabińska, Grzegorz Lota
   Tuning the course of the oxygen reduction reaction at a carbon electrode using alkaline electrolytes based on binary DMSO-water solvent mixtures
   Electrochemistry Communications 141 (2022) 107359-1-107359-6 | IF = 5,443

2. Szymon Znaniecki, Katarzyna Szwabińska, Jarosław Wojciechowski, Andrzej Skrzypczak, Marek Baraniak, Grzegorz Lota
   Capacitor lifetime prolonged by addition of organic ammonium salt with cyclohexyl substituent and 2,5-dihydroxybenzenesulfonic anion
   Electrochemistry Communications 140 (2022), 107326-1-107326-6 | IF = 5,443

3. Szymon Znaniecki, Katarzyna Szwabińska, Jarosław Wojciechowski, Andrzej Skrzypczak, Grzegorz Lota
   Ionic liquid modified electrochemical capacitor with long-term performance
   ChemElectroChem 8 (2021) 3685-3694 | IF = 4,782

4. Katarzyna Szwabińska, Grzegorz Lota
   Mixed diffusion-kinetic control of H_2O_2 oxidation at an oxide-covered platinum electrode in alkaline electrolyte: Implications for oxygen electroreduction studies with a rotating ring disk electrode
   ChemElectroChem 8 (2021) 839-849 | IF = 4,782

5. Maciej Cieplak, Katarzyna Szwabinska, Marta Sosnowska, Chandra Bikram K.C., Pawel Borowicz, Krzysztof Noworyta, Francis D'Souza, Wlodzimierz Kutner
   Selective electrochemical sensing of human serum albumin by semi-covalent molecular imprinting
   Biosensors and Bioelectronics 74 (2015) 960-966 | IF = 7,476

Patenty

1. Maciej Cieplak, Katarzyna Szwabińska, Chandra Bikram K.C., Paweł Borowicz, Krzysztof Noworyta, Francis D'Souza, Włodzimierz Kutner
   Nowy przewodzący polimer bisbitiofenowy molekularnie wdrukowany za pomocą białka, w tym ludzkiej albuminy, sposób jego przygotowania i jego zastosowanie
   PL-227055(B1) | 31.10.2017

Zgłoszenia patentowe

1. Jarosław Wojciechowski, Szymon Znaniecki, Katarzyna Szwabińska, Andrzej Skrzypczak, Grzegorz Lota, Marek Baraniak
   Nowe ciecze jonowe z anionem 2,5-dihydroksybenzenosulfonowym oraz kationem amoniowym zawierającym podstawnik cykloalkilowy, sposób otrzymywania i zastosowanie jako środki ochrony elementów stalowych przed korozją
   P.439974 | 23.12.2021

Udział w projektach naukowych

1. Wykonawca w projekcie NCN – OPUS 16 (2018/31/B/ST8/01619)
   Badanie wpływu modyfikacji elektrolitu oraz materiału elektrodowego cieczami jonowymi z anionem 2,5-dihydroksybenzenosulfonowym na parametry pracy układów elektrochemicznych
   21.10.2019 – 21.07.2023
2. Wykonawca w projekcie NCBiR – PBSIII (PBS3/A5/43/2015)
   Ciecze jonowe jako dodatek poprawiający właściwości eksploatacyjne mas aktywnych rozruchowych akumulatorów kwasowo-ołowiowych
   08.01.2015 – 30.06.2015

Staże naukowe

1. Instytut Chemii Fizycznej Polskiej Akademii Nauk | 01.09.2021 – 30.11.2021
2. Sieć Badawcza Łukasiewicz – Instytut Metali Nieżelaznych Oddział w Poznaniu, Centralne Laboratorium Akumulatorów i Ogniw | 03.04.2018 – 23.07.2018
3. Sieć Badawcza Łukasiewicz – Instytut Metali Nieżelaznych Oddział w Poznaniu, Centralne Laboratorium Akumulatorów i Ogniw | 01.09.2017 – 30.09.2017
4. University of Tehran | 01.07.2017 – 31.08.2017
5. Instytut Chemii Fizycznej Polskiej Akademii Nauk | 01.08.2014 – 30.09.2014

Inna aktywność naukowa

1. Udział w szkole letniej *'PhD Summer School: Micro and Nano Sensors 2019'* Technical University of Denmark | 19.08.2019 – 30.08.2019
2. Dwukrotny udział w międzynarodowej olimpiadzie *'International Scientific Olympiad (Chemistry)'* organizowanej przez irańskie Ministerstwo Nauki, Badań i Technologii | 2016, 2017
3. Finalistka LVIII Olimpiady Chemicznej | 2012

Komunikaty ustne wygłoszone na konferencjach międzynarodowych

1. Bren Mark B. Felisilda, Katarzyna Szwabińska, Karolina Majewska, Alonso Gamero-Quijano, Micheál D. Scanlon, Martin Jönsson-Niedziółka
   Electropolymerization of interfacial conducting polymer thin films using Fenton's reagent at a polarized liquid-liquid interface
   73rd Annual Meeting of the International Society of Electrochemistry | 12.09.2022 - 16.09.2022

2. Szymon Znaniecki, Katarzyna Szwabińska, Jarosław Wojciechowski, Andrzej Skrzypczak, Marek Baraniak, Grzegorz Lota
   Long-term performance of aqueous electrolyte capacitor modified by organic ammonium salt
   73rd Annual Meeting of the International Society of Electrochemistry | 12.09.2022 - 16.09.2022

3. Jarosław Wojciechowski, Katarzyna Szwabińska, Krzysztof Fic, Grzegorz Lota
Electrochemical capacitor with variable polarization
The 23rd International Conference on Advanced Batteries, Accumulators, Fuel Cells and Special Electrochemical Technologies (ABAF 23) | 21.08.2022 – 24.08.2022

4. Grzegorz Lota, Szymon Znaniecki, Katarzyna Szwabińska, Jarosław Wojciechowski, Marek Baraniak, Andrzej Skrzypczak
Capacitor lifetime prolonged by addition of organic ammonium salt
The 23rd International Conference on Advanced Batteries, Accumulators, Fuel Cells and Special Electrochemical Technologies (ABAF 23) | 21.08.2022 – 24.08.2022

5. Jarosław Wojciechowski, Andrzej Skrzypczak, Katarzyna Szwabińska, Szymon Znaniecki, Marek Baraniak, Grzegorz Lota
Effect of ionic liquid additives on electrochemical capacitor performance
5th International Scientific Conference 'Alternative Energy Sources, Materials & Technologies' (AESMT'22) | 27.06.2022 - 28.06.2022

6. Katarzyna Szwabińska, Grzegorz Lota
Oxygen reduction at glassy carbon electrode in alkaline electrolytes based on binary DMSO-water solvent mixtures
4th Cross-Border Seminar on Electroanalytical Chemistry (CBSEC) | 11.04.2022 - 13.04.2022

7. Grzegorz Lota, Szymon Znaniecki, Katarzyna Szwabińska, Jarosław Wojciechowski, Andrzej Skrzypczak, Katarzyna Lota
Long-term performance of electrochemical capacitors
The 22nd International Conference on Advanced Batteries, Accumulators, Fuel Cells and Special Electrochemical Technologies (ABAF 22) | 22.08.2021 – 25.08.2021

8. Katarzyna Szwabińska, Grzegorz Lota
Mixed diffusion-kinetic control of H_2O_2 oxidation at Pt in an alkaline electrolyte: Implications for oxygen electroreduction studies with RRDE
Graduate Student Symposium on Advantageous Electrochemistry | 10.09.2020 – 11.09.2020

9. Katarzyna Szwabińska, Łukasz Kolanowski, Małgorzata Graś, Piotr Krawczyk, Grzegorz Lota
Carbon cathode materials for electro-Fenton process
Polish Scientific Networks 2019 - Science&Technology | 19.09.2019 - 21.09.2019

10. Łukasz Kolanowski, Jarosław Wojciechowski, Małgorzata Graś, Katarzyna Szwabińska, Piotr Krawczyk, Katarzyna Lota, Grzegorz Lota
Electroactive materials doped by heteroatoms for energy storage and conversion
The 20th International Conference on Advanced Batteries, Accumulators, Fuel Cells and Special Electrochemical Technologies (ABAF 20) | 25.08.2019 - 28.08.2019

11. Wlodzimierz Kutner, Maciej Cieplak, Katarzyna Szwabinska, Marta Sosnowska, Chandra Bikram K.C., Pawel Borowicz, Krzysztof Noworyta, Francis D'Souza
Conducting molecularly imprinted polymers for determination of selected small proteins
The 67th Annual Meeting of the International Society of Electrochemistry | 21.08.2016 - 26.08.2016

12. Maciej Cieplak, Katarzyna Szwabinska, Chandra Bikram K.C., Pawel Borowicz, Krzysztof Noworyta, Francis D'Souza, Wlodzimierz Kutner
Selective electrochemical sensing of human albumin by semi-covalent imprinting
227th ECS Meeting | 24.05.2015 - 28.05.2015

Postery zaprezentowane na konferencjach międzynarodowych

1. Katarzyna Szwabińska, Grzegorz Lota
Oxygen reduction at glassy carbon electrode in alkaline electrolytes based on binary DMSO-water solvent mixtures
18th International Conference on Electroanalysis | 05.06.2022 - 09.06.2022

2. Maciej Cieplak, Katarzyna Szwabinska, Marta Sosnowska, Chandra Bikram K.C., Pawel Borowicz, Krzysztof Noworyta, Francis D'Souza, Wlodzimierz Kutner
Electrochemical sensing of human serum albumin by thiophene-based molecularly imprinted polymer
PhD Summer School: Micro and Nano Sensors 2019 | 19.08.2019 - 30.08.2019

3. Maciej Cieplak, Katarzyna Szwabinska, Chandra Bikram K.C., Pawel Borowicz, Krzysztof Noworyta, Francis D'Souza, Wlodzimierz Kutner
Selective electrochemical sensing of human serum albumin by semi-covalent imprinting
The 7th International Workshop on Surface Modification for Chemical and Biochemical Sensing | 06.11.2015 - 10.11.2015

Komunikaty ustne wygłoszone na konferencjach krajowych

1. Szymon Znaniecki, Katarzyna Szwabińska, Jarosław Wojciechowski, Andrzej Skrzypczak, Marek Baraniak, Grzegorz Lota
   Poprawa żywotności kondensatora elektrochemicznego poprzez zastosowanie dodatku organicznych soli amoniowych z podstawnikiem cykloheksylowym i anionem 2,5-dihydroksybenzenosulfonowym
   X Kongres Technologii Chemicznej | 11.05.2022 – 14.05.2022

2. Jarosław Wojciechowski, Szymon Znaniecki, Katarzyna Szwabińska, Andrzej Skrzypczak, Grzegorz Lota
   Wpływ dodatku cieczy jonowych na parametry pracy kondensatora elektrochemicznego
   X Kongres Technologii Chemicznej | 11.05.2022 – 14.05.2022

3. Szymon Znaniecki, Jarosław Wojciechowski, Katarzyna Szwabińska, Andrzej Skrzypczak, Grzegorz Lota
   Modyfikacja kondensatorów z 1 M Na_2SO_4 dodatkiem cieczy jonowych z anionem 2,5-dihydroksybenzenosulfonowym
   63. Zjazd Naukowy Polskiego Towarzystwa Chemicznego | 13.09.2021 – 17.09.2021

4. Katarzyna Szwabińska, Grzegorz Lota
   Mieszana kontrola dyfuzyjno-kinetyczna reakcji utleniania H_2O_2 na Pt w elektrolicie alkalicznym: Konsekwencje dla badań elektroredukcji tlenu metodą RRDE
   Kopernikańskie E-Seminarium Doktoranckie | 07.09.2020

5. Katarzyna Szwabińska, Grzegorz Lota
   Mixed diffusion-kinetic control of H_2O_2 oxidation at Pt in an alkaline electrolyte: Implications for oxygen electroreduction studies with RRDE
   National Scientific Conference '1st Summer Scientific On-line School' | 08.08.2020

6. Katarzyna Szwabińska, Łukasz Kolanowski, Małgorzata Graś, Piotr Krawczyk, Grzegorz Lota
   Materiały węglowe jako katody w procesie elektro-Fentonowskim
   V Kuźnia Młodych Talentów Akademii Młodych Uczonych PAN | 02.07.2019 - 05.07.2019

7. Łukasz Kolanowski, Grzegorz Lota, Piotr Krawczyk, Katarzyna Szwabińska, Małgorzata Graś, Jarosław Wojciechowski
   Elektroaktywne materiały węglowe domieszkowane heteroatomami
   V Kuźnia Młodych Talentów Akademii Młodych Uczonych PAN | 02.07.2019 - 05.07.2019

8. Katarzyna Szwabińska, Łukasz Kolanowski, Małgorzata Graś, Florence Fourcade, Abdeltif Amrane, Grzegorz Lota
   Materiały węglowe jako katody w procesie elektro-Fentonowskim
   XIII Kopernikańskie Seminarium Doktoranckie | 16.06.2019 - 18.06.2019

Postery zaprezentowane na konferencjach krajowych

1. Katarzyna Szwabińska, Łukasz Kolanowski, Małgorzata Graś, Florence Fourcade, Abdeltif Amrane, Grzegorz Lota
   Aktywność elektrokatalityczna materiałów węglowych w procesie elektro-Fentonowskim
   62. Zjazd Naukowy Polskiego Towarzystwa Chemicznego | 02.09.2019 - 06.09.2019

2. Marek Baraniak, Katarzyna Szwabińska, Grzegorz Lota, Mateusz Jankowski
   Wpływ dodatku cieczy jonowych na oporność separatora akumulatora kwasowo-ołowiowego
   XIII Kopernikańskie Seminarium Doktoranckie | 16.06.2019 - 18.06.2019

3. Katarzyna Szwabińska, Łukasz Kolanowski, Małgorzata Graś, Katarzyna Lota, Grzegorz Lota
   Elektrochemiczna redukcja tlenu na wybranych materiałach węglowych w środowisku alkalicznym
   X Poznańska Konferencja Naukowa „Chemia – Nauka i Przemysł" | 30.11.2018

4. Kacper Kopczyński, Katarzyna Szwabińska, Grzegorz Lota
   Elektrochemiczne wydzielanie wodoru na powłokach niklowych osadzonych z głębokich eutektyków
   X Poznańska Konferencja Naukowa „Chemia – Nauka i Przemysł" | 30.11.2018

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Last updated October 2022

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Order Date	02-Mar-2023	**Type of Use**	Republish in a thesis/dissertation
Order License ID	1329799-1	**Publisher**	Royal Society of Chemistry
ISSN	2044-4761	**Portion**	Chart/graph/table/figure

LICENSED CONTENT

Publication Title	Catalysis Science & Technology	**Rightsholder**	Royal Society of Chemistry
Article Title	Nitrogen-Doped Porous Carbon Materials: Promising Catalysts or Catalyst Supports for Heterogeneous Hydrogenation and Oxidation	**Publication Type**	e-Journal
		Start Page	3670
		End Page	3693
		Issue	11
		Volume	6
Author/Editor	Royal Society of Chemistry (Great Britain)		
Date	01/01/2011		
Language	English		
Country	United Kingdom of Great Britain and Northern Ireland		

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	Worldwide
Number of Charts / Graphs / Tables / Figures Requested	1	**Translation**	Original language plus one translation
		Copies for the Disabled?	No
Format (select all that apply)	Print, Electronic	**Minor Editing Privileges?**	Yes
Who Will Republish the Content?	Academic institution	**Incidental Promotional Use?**	No
Duration of Use	Life of current edition	**Currency**	EUR
Lifetime Unit Quantity	Up to 499		
Rights Requested	Main product, any product related to main product, and other compilations/derivative products		

NEW WORK DETAILS

Title	Elektrochemiczna redukcja tlenu w elektrolitach: wodnym i na bazie mieszanin DMSO-woda	**Institution Name**	Poznan University of Technology
		Expected Presentation Date	2023-06-20
Instructor Name	Katarzyna Szwabińska		

ADDITIONAL DETAILS

Order Reference Number	ramanujan 5	**The Requesting Person/Organization to Appear on the License**	Katarzyna Szwabińska

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 1	**Title of the Article/Chapter the Portion Is From**	Nitrogen-Doped Porous Carbon Materials: Promising Catalysts or Catalyst Supports for Heterogeneous Hydrogenation and Oxidation
Editor of Portion(s)	li, mingming; Xu, Fan; Li, Haoran; Wang, Yong	**Author of Portion(s)**	li, mingming; Xu, Fan; Li, Haoran; Wang, Yong
Volume of Serial or Monograph	6		
Page or Page Range of Portion	3670-3693	**Issue, if Republishing an Article From a Serial**	11
		Publication Date of Portion	2016-01-01

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Last updated October 2022

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Order Date	03-Mar-2023	**Type of Use**	Republish in a thesis/dissertation
Order License ID	1329810-1	**Publisher**	ROYAL SOCIETY OF CHEMISTRY
ISSN	1364-548X	**Portion**	Chart/graph/table/figure

LICENSED CONTENT

Publication Title	Chemical communications	**Rightsholder**	Royal Society of Chemistry
Article Title	Activated carbon becomes active for oxygen reduction and hydrogen evolution reactions.	**Publication Type**	e-Journal
		Start Page	8156
		End Page	8159
Author/Editor	Royal Society of Chemistry (Great Britain)	**Issue**	52
		Volume	52
Date	01/01/1996		
Language	English		
Country	United Kingdom of Great Britain and Northern Ireland		

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	Worldwide
Number of Charts / Graphs / Tables / Figures Requested	1	**Translation**	Original language plus one translation
		Copies for the Disabled?	No
Format (select all that apply)	Print, Electronic	**Minor Editing Privileges?**	Yes
		Incidental Promotional Use?	No
Who Will Republish the Content?	Academic institution		
Duration of Use	Life of current edition	**Currency**	EUR
Lifetime Unit Quantity	Up to 499		
Rights Requested	Main product, any product related to main product, and other compilations/derivative products		

NEW WORK DETAILS

Title	Elektrochemiczna redukcja tlenu w elektrolitach: wodnym i na bazie mieszanin DMSO-woda	**Institution Name**	Poznan University of Technology
		Expected Presentation Date	2023-06-20
Instructor Name	Katarzyna Szwabińska		

ADDITIONAL DETAILS

Order Reference Number	ramanujan 13	**The Requesting Person/Organization to Appear on the License**	Katarzyna Szwabińska

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 2	**Title of the Article/Chapter the Portion Is From**	Activated carbon becomes active for oxygen reduction and hydrogen evolution reactions.
Editor of Portion(s)	Yan, Xuecheng; Jia, Yi; Odedairo, Taiwo; Zhao, Xiaojun; Jin, Zhao; Zhu, Zhonghua; Yao, Xiangdong	**Author of Portion(s)**	Yan, Xuecheng; Jia, Yi; Odedairo, Taiwo; Zhao, Xiaojun; Jin, Zhao; Zhu, Zhonghua; Yao, Xiangdong
Volume of Serial or Monograph	52	**Issue, if Republishing an Article From a Serial**	52
Page or Page Range of Portion	8156-8159	**Publication Date of Portion**	2016-07-04

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14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

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A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

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B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

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Last updated October 2022

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ISSN	2050-7496	**Portion**	Chart/graph/table/figure

LICENSED CONTENT

Publication Title	Journal of materials chemistry. A, Materials for energy and sustainability	**Publication Type**	e-Journal
		Start Page	11736
Article Title	Carbon for the oxygen reduction reaction: a defect mechanism	**End Page**	11739
		Issue	22
Author/Editor	Royal Society of Chemistry (Great Britain)	**Volume**	3
		URL	http://pubs.rsc.org/en/journals/journalissues/ta
Date	01/01/2013		
Language	English		
Country	United Kingdom of Great Britain and Northern Ireland		
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NEW WORK DETAILS

Title	Elektrochemiczna redukcja tlenu w elektrolitach: wodnym i na bazie mieszanin DMSO-woda	**Institution Name**	Poznan University of Technology
		Expected Presentation Date	2023-06-20
Instructor Name	Katarzyna Szwabińska		

ADDITIONAL DETAILS

Order Reference Number	ramanujan 14	**The Requesting Person/Organization to Appear on the License**	Katarzyna Szwabińska

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 1	**Title of the Article/Chapter the Portion Is From**	Carbon for the oxygen reduction reaction: a defect mechanism
Editor of Portion(s)	Zhao, Huanyu; Sun, Chenghua; Jin, Zhao; Wang, Da-Wei; Yan, Xuecheng; Chen, Zhigang; Zhu, Guangshan; Yao, Xiangdong	**Author of Portion(s)**	Zhao, Huanyu; Sun, Chenghua; Jin, Zhao; Wang, Da-Wei; Yan, Xuecheng; Chen, Zhigang; Zhu, Guangshan; Yao, Xiangdong
Volume of Serial or Monograph	3	**Issue, if Republishing an Article From a Serial**	22
Page or Page Range of Portion	11736-11739	**Publication Date of Portion**	2015-01-01

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14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) *Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).* For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) *Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).* For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants

authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and
- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) *Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).* The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) *Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).* For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Last updated October 2022

Marketplace

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Order Date	03-Mar-2023	**Type of Use**	Republish in a thesis/dissertation
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ISSN	1573-4803	**Portion**	Chart/graph/table/figure

LICENSED CONTENT

Publication Title	Journal of materials science	**Publication Type**	e-Journal
Article Title	Insights into the electrocatalytic behavior of nitrogen and sulfur co-doped carbon nanotubes toward oxygen reduction reaction in alkaline media	**Start Page**	16739
		End Page	16754
		Issue	35
		Volume	57
		URL	http://www.springerlink.com/content/100181/
Date	01/01/1966		
Language	English		
Country	United States of America		
Rightsholder	Springer Nature BV		

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	Worldwide
Number of Charts / Graphs / Tables / Figures Requested	1	**Translation**	Original language plus one translation
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NEW WORK DETAILS

Title	Elektrochemiczna redukcja tlenu w elektrolitach: wodnym i na bazie mieszanin DMSO-woda	**Institution Name**	Poznan University of Technology
		Expected Presentation Date	2023-06-20
Instructor Name	Katarzyna Szwabińska		

ADDITIONAL DETAILS

The Requesting Person/Organization to Appear on the License	Katarzyna Szwabińska

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 8	**Title of the Article/Chapter the Portion Is From**	Insights into the electrocatalytic behavior of nitrogen and sulfur co-doped carbon nanotubes toward oxygen reduction reaction in alkaline media
Editor of Portion(s)	Rambabu, Gutru; Turtayeva, Zarina; Xu, Feina; Maranzana, Gael; Emo, Mélanie; Hupont, Sébastien; Mamlouk, Mohamed; Desforges, Alexandre; Vigolo, Brigitte	**Author of Portion(s)**	Rambabu, Gutru; Turtayeva, Zarina; Xu, Feina; Maranzana, Gael; Emo, Mélanie; Hupont, Sébastien; Mamlouk, Mohamed; Desforges, Alexandre; Vigolo, Brigitte
Volume of Serial or Monograph	57		
Page or Page Range of Portion	16739-16754	**Publication Date of Portion**	2022-09-04

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The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is unlawful, including without limitation if such use would violate applicable sanctions laws or regulations, would be defamatory, violate the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. Any unlawful use will render any licenses hereunder null and void. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) **Effect of Breach.** Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be

paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) *Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).* For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and
- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) *Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).* The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) *Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).* For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Last updated October 2022

Marketplace

This is a License Agreement between Katarzyna Szwabińska ("User") and Copyright Clearance Center, Inc. ("CCC") on behalf of the Rightsholder identified in the order details below. The license consists of the order details, the Marketplace Permissions General Terms and Conditions below, and any Rightsholder Terms and Conditions which are included below.

All payments must be made in full to CCC in accordance with the Marketplace Permissions General Terms and Conditions below.

Order Date	03-Mar-2023	**Type of Use**	Republish in a thesis/dissertation
Order License ID	1329823-1	**Publisher**	ROYAL SOCIETY OF CHEMISTRY
ISSN	1351-4180	**Portion**	Chart/graph/table/figure

LICENSED CONTENT

Publication Title	Focus on catalysts	**Rightsholder**	Elsevier Science & Technology Journals
Article Title	Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry	**Publication Type**	Journal
Author/Editor	Royal Society of Chemistry (Great Britain)	**Start Page**	7
Date	01/01/1994	**Issue**	3
Language	English	**Volume**	2018
Country	United Kingdom of Great Britain and Northern Ireland		

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	Worldwide
Number of Charts / Graphs / Tables / Figures Requested	1	**Translation**	Original language plus one translation
Format (select all that apply)	Print, Electronic	**Copies for the Disabled?**	No
Who Will Republish the Content?	Academic institution	**Minor Editing Privileges?**	Yes
Duration of Use	Life of current edition	**Incidental Promotional Use?**	No
Lifetime Unit Quantity	Up to 499	**Currency**	EUR
Rights Requested	Main product, any product related to main product, and other compilations/derivative products		

NEW WORK DETAILS

Title	Elektrochemiczna redukcja tlenu w elektrolitach: wodnym i na bazie mieszanin DMSO-woda	**Institution Name**	Poznan University of Technology
Instructor Name	Katarzyna Szwabińska	**Expected Presentation Date**	2023-06-20

ADDITIONAL DETAILS

Order Reference Number	ramanujan 20	**The Requesting Person/Organization to Appear on the License**	Katarzyna Szwabińska

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 5, Page 425	**Title of the Article/Chapter the Portion Is From**	Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry
Editor of Portion(s)	N/A	**Author of Portion(s)**	Royal Society of Chemistry (Great Britain)
Volume of Serial or Monograph	2018	**Issue, if Republishing an Article From a Serial**	3
Page or Page Range of Portion	425	**Publication Date of Portion**	2018-03-01

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Marketplace Permissions General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is unlawful, including without limitation if such use would violate applicable sanctions laws or regulations, would be defamatory, violate the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. Any unlawful use will render any licenses hereunder null and void. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) **Effect of Breach.** Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) *Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning*

management systems, academic institution intranets). For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and
- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) *Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).* The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

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