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Studies of capacitive and faradaic processes in electrochemical capacitors and in redox flow batteries

Badanie pojemnościowych i faradajowskich procesów w kondensatorach elektrochemicznych oraz w ogniwach przepływowych redoks

PhD Thesis

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"A smooth sea never made a skilled sailor"
Franklin D. Roosevelt

This thesis would never be possible without the presence of all the people that crossed my life during the last years…

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Abstract

This dissertation is dedicated to the study of innovative energy storage/generation devices, i.e., electrochemical capacitors (ECs) and redox flow batteries (RFBs).

The first part of this thesis is devoted to a literature review (Chapter I) concerning electrochemical capacitors and redox flow batteries. In overall, from hundreds of papers, books and chapters, the most essential information related to the topic of dissertation have been chosen. The literature review starts from general introduction to electrochemical capacitors field, their operation principles, types of electrode and electrolyte materials focusing mostly on environmental friendly water-based electrolytes and activated carbon electrodes. A special emphasis is put on the capacitor lifespan and the current state-of-art in this context. A brief outlook of possible capacitor failure reasons is included in the theoretical part of this thesis.

Secondly, the thesis includes the general introduction to redox flow batteries world. The review focuses on vanadium redox flow batteries since they are the most known technology further used in the experimental part of this thesis. Herein, the special attention is given to the oxygen functional groups on electrode (carbon felt) surface. The need of carbon felt pre-treatment (oxidation) and its influence on vanadium redox reaction in RFB was widely commented. Next, the concept of “dual-circuit redox flow battery” as an additional unit in whole vanadium redox flow battery (VRFB) system is fully described and explained. This part of thesis focuses also on water electrolysis and advantages of indirect water splitting for hydrogen production from “dual-circuit redox flow battery”. The principles and main limitations of currently used technologies for “dual-circuit RFB” system balance are presented in this part of the thesis.

Each literature part finishes with a short summary of EC and RFB systems, highlighting their properties, limitations and research challenges that formed the basis of the research for this dissertation.

The main research objective in Chapter II is to identify the failure reasons of carbon/carbon ECs operating in aqueous medium (alkali metal salt solution as electrolyte). Three research papers (**P1-P3**) concerning this problem are attached to the thesis. Each manuscript concerns different parameters, i.e., type of lifetime test, influence of applied voltage, type of electrolyte which might have an impact of EC lifespan. Studies of ageing process in ECs are performed using so-called *post-mortem* approach showing the relation between electrochemical performance and physico-chemical characteristics. The properties of aged electrodes were studied and compared to the pristine ones (before the ageing). It has been proven that mostly oxidation of positive electrode stands for the main reason of ECs failure, whereas the negative electrode in most cases remains

unchanged. Moreover, solid-state deposit of carbonate has been found on the electrodes surface after the capacitor ageing tests.

Chapter II covers the proof that each system behaves individually and there is not one “know-how” which directly helps to improve the capacitor lifespan. Nevertheless, understanding the ageing mechanisms of individual cell will allow the proper improvement actions to be involved taking into account the rule of counteracting the cause.

The research in frame of Chapter III is focused on lifetime extension. Firstly, the electrochemical protocol (alternate polarization) which prolongs capacitor operation time has been proposed (**P4**). The second part of the research in Chapter III concerns the recycling of carbon electrodes. In this context, re-use of negative electrode after ECs operation with 1 mol L^{-1} $LiNO_3$ electrolyte has been widely analyzed.

Chapter IV includes the summary of publication entitled “*Vanadium-oxygen cell for positive electrolyte discharge in dual-circuit vanadium redox flow battery*” (**P5**). In so-called “dual-circuit redox flow battery” hydrogen evolution reaction (HER) can be driven on user demand (e.g., to produce H_2 for fuel cell-based car) on the negative side of VRFB. However, during HER reaction, protons are consumed, thus, charge and proton imbalance is observed in the system. The paper aims to the development of electrochemical cell (vanadium-oxygen) able to balance the whole “dual-circuit redox flow battery” using a water oxidation reaction as the proton supplier. It was proven that this approach is a very suitable one since it ensures a sustainable way with an excellent stability comparing to the previous research ideas in this area.

The content of Chapter V is devoted to the oxidation of the surface of carbon felt (CF) electrodes used for VRFB. A novel molten salt CF oxidation method was studied taking into account various reaction conditions (temperature and time of treatment). The correlation between electrode conductivity, hydrophilicity and VRFB performance was investigated.

The thesis finishes with general conclusions and further research perspectives. The link between oxygen presence and its influence on the performance of each electrochemical system is widely summarized.

Streszczenie

Niniejsza rozprawa doktorska poświęcona jest badaniom innowacyjnych urządzeń do magazynowania i konwersji energii, tj. kondensatorów elektrochemicznych (EC) oraz ogniw przepływowych redoks (RFB).

Pierwsza część pracy poświęcona została przeglądowi literaturowemu dotyczącemu kondensatorów elektrochemicznych oraz ogniw przepływowych redoks. Spośród setek artykułów, książek i rozdziałów, wybrano najważniejsze informacje związane bezpośrednio z tematem dysertacji. Przegląd literaturowy rozpoczyna się od ogólnego wprowadzenia do zagadnienia kondensatorów elektrochemicznych, zasady ich działania, rodzajów materiałów elektrodowych oraz elektrolitów w głównej mierze skupiając uwagę na przyjaznych dla środowiska elektrolitach wodnych i elektrodach wykonanych z węgla aktywnego. Szczególny nacisk położono na trwałość cykliczną kondensatorów i aktualny stan wiedzy w tym kontekście. Krótki przegląd możliwych przyczyn utraty właściwości kondensatorów został zawarty w części teoretycznej niniejszej pracy.

W kolejnej części, praca zawiera ogólne wprowadzenie do ogniw przepływowych redoks. Przegląd koncentruje się na ogniwach wanadowych, ponieważ są one najbardziej znaną technologią stosowaną w części eksperymentalnej niniejszej pracy. Szczegółową uwagę zwraca się na tlenowe grupy funkcyjne na powierzchni elektrody (filcu węglowego). Potrzeba wstępnej obróbki filcu węglowego (utleniania) i jej wpływ na reakcję redoks wanadu w ogniwie przepływowym redoks została głęboko przeanalizowana. Następnie szczegółowo przedstawiono działanie binarnego układu przepływowego redoks *z ang.* „dual-circuit redox flow battery”, jako dodatkowej jednostki całego systemu wanadowego ogniwa. W tej części pracy skupiono się również na elektrolizie wody i zaletach pośredniego rozkładu wody w celu produkcji wodoru z systemu „dual-circuit redox flow battery”. Przedstawiono zasady i główne ograniczenia obecnie stosowanych technologii do bilansowania binarnego systemu wanadowego ogniwa redoks.

Każda z części przeglądu literaturowego kończy się krótkim podsumowaniem obu urządzeń magazynujących energię (kondensatorów elektrochemicznych i ogniw przepływowych redoks) podkreślając ich właściwości, ograniczenia i wyzwania badawcze, które stanowiły podstawę badań w niniejszej rozprawie.

Głównym celem badań w Rozdziale II jest zidentyfikowanie przyczyn uszkodzenia symetrycznego kondensatora z elektrodami na bazie materiału węglowego operującego w środowisku wodnym (roztwór soli metali alkalicznych jako elektrolit). Do rozprawy dołączono trzy prace badawcze dotyczące tego problemu badawczego (**P1-P3**). Każdy artykuł dotyczy innych parametrów, tj., rodzaju testu trwałości, zastosowanego napięcia, rodzaju elektrolitu, które mogą mieć wpływ na żywotność układów. Badania procesu starzenia kondensatora elektrochemicznego prowadzone były w trybie *post-mortem*, który przedstawia

związek pomiędzy parametrami elektrochemicznymi i właściwościami fizykochemicznymi. Zbadano właściwości elektrod po starzeniu i porównano je z właściwościami pierwotnymi (przed procesem starzenia). Udowodniono, że główną przyczyną uszkodzenia kondensatora elektrochemicznego jest utlenianie elektrody dodatniej, przy czym właściwości elektrody ujemnej w większości przypadków pozostają niezmienne. Co więcej, po testach starzenia kondensatorów zauważone zostały ślady osadu soli (węglanu) na powierzchni elektrod.

Rozdział II przedstawia dowody na to, że każdy system zachowuje się indywidualnie i nie ma jednego rozwiązania, które bezpośrednio wpłynie na wydłużenie trwałości kondensatorów. Niemniej jednak, poznanie mechanizmów starzenia się poszczególnych ogniw pozwoli na podjęcie odpowiednich działań z uwzględnieniem zasady przeciwdziałania przyczyn.

Badania przedstawione w Rozdziale III koncentrują się na przedłużeniu trwałości cyklicznej kondensatora. Po pierwsze, opracowany został protokół elektrochemiczny (przemienna polaryzacja), który wydłuża czas działania kondensatora (**P4**). Druga część badań w Rozdziale III dotyczy recyklingu elektrod węglowych. W tym kontekście, podjęto próby ponownego użycia elektrody ujemnej po pracy w kondensatorze z 1 mol L^{-1} roztworem wodnym $LiNO_3$ jako elektrolitem.

Rozdział IV zawiera podsumowanie publikacji zatytułowanej “*Vanadium-oxygen cell for positive electrolyte discharge in dual-circuit vanadium redox flow battery*” (**P5**). W tak zwanym układzie binarnym ogniwa przepływowego redoks, *z ang*. “dual-circuit redox flow battery”, który stanowi ogniwo przepływowe redoks połączone z reaktorem katalitycznym, reakcja wydzielania wodoru może być przeprowadzona na żądanie użytkowania. Proces zachodzi po ujemnej stronie ogniwa przepływowego redoks. Niemniej jednak, podczas reakcji wydzielania wodoru, potrzebne są protony i tym samym dochodzi do zachwiania równowagi ładunkowej całego systemu. Celem pracy jest opracowanie współdziałającego ogniwa elektrochemicznego (wanad-tlen) zdolnego do utrzymania równowagi ładunkowej całego systemu *„dual-circuit vanadium redox flow battery”.* W tym celu wykorzystano reakcję utleniania wody jako źródło protonów. W porównaniu z poprzednio zaproponowanymi rozwiązaniami udowodniono, że ogniwo wanad-tlen jest odpowiednim, przyjaznym dla środowiska rozwiązaniem i cechuje się dobrą stabilnością.

Treść Rozdziału V poświęcona została utlenianiu powierzchni elektrod filcowych stosowanych w wanadowych ogniwach przepływowych redoks. Podjęto próbę utleniania filcu węglowego za pomocą stopionej soli z uwzględnieniem różnych warunków reakcji (temperatura i czas obróbki). Zbadano korelację między przewodnictwem elektrod, ich hydrofilowością a wydajnością pracy wanadowego ogniwa przepływowego redoks.

Praca kończy się ogólnymi wnioskami i dalszymi perspektywami badawczymi. Zależność pomiędzy obecnością tlenu a jego wpływem na działanie każdego układu elektrochemicznego została szeroko podsumowana.

Table of contents

Acknowledgements 3

Abstract 5

Streszczenie 7

Chapter I – Literature review 11

1. Motivation and context of the research 12

2. Electrochemical capacitors – state of art 15

   2.1. The operation principle of electrochemical capacitor 15

   2.2. Carbon electrodes for electrochemical capacitors 17

   2.3. Activated carbon 18

   2.4. Electrolytes for electrochemical capacitors 19

   2.5. Neutral salt aqueous electrolytes 20

   2.6. Redox-active aqueous electrolytes 21

   2.7. Lifespan of the electrochemical capacitors 22

   2.8. Summary 26

3. Redox flow batteries – state of art 27

   3.1. Working mechanism and basic principles 27

   3.2. Basic parameters of RFB 31

   3.3. Redox flow battery chemistry and a brief history behind 32

   3.4. Criterion of redox pair selection for RFB 34

   3.5. Vanadium redox flow batteries 36

   3.6. Concept of “dual-circuit redox flow battery” 47

   3.7. Summary 51

The aim of the work 52

Chapter II Ageing process of water-based electrochemical capacitors elucidated *via post-mortem* analysis 54

Chapter III Possible methods for capacitor lifetime extension 60

Chapter IV Vanadium-oxygen cell studies 69

Chapter V Alkali metal salt carbon felt oxidation on VRFB performance 74

General conclusions 89

Symbols and abbreviations 92

References 95

Scientific achievements 105

Co-authorship statements 114

Publications 140

Chapter I

Literature review

1. Motivation and context of the research

The annual world energy consumption is increasing constantly, especially in the last few decades. It is estimated that energy demand will be doubled in every 20 years, especially considering that world population is continuously growing and our modern lifestyle requires more and more energy/power units. Therefore, unpredictability of the consumer demand toward energy reserves and global warming caused by harmful substances remaining after the process of burning oil, gas or coal, alternative sources of energy are still being sought. They should not only be obtained in the less harmful way to the environment, but also afford any unexpected rise in energy demand [1].

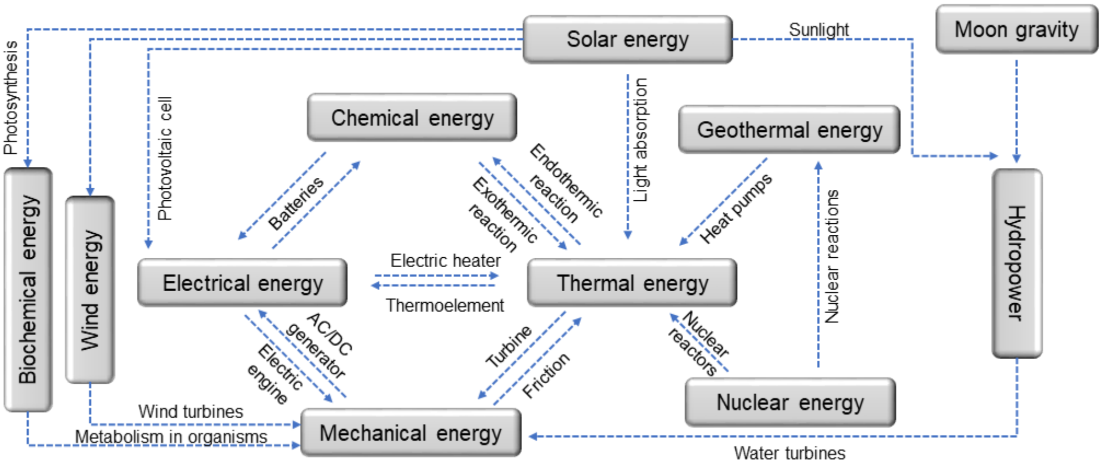

Fig. 1 Available energy sources and the methods of their transmission [2].

As seen in Fig. 1, energy storage technologies can be divided into a few groups, i.e., electrical, chemical, thermal and mechanical. There are specific interrelations between each group, allowing the energy to be converted. Traditional and one of the first ways to gain energy is to obtain it from coal, oil or natural gas burning. The major advantage is their high calorific value and relatively low cost of extraction. However, as it is well-known, fossil fuels are a non-renewable energy source, which in practice means that their reserves are limited [2]. Keeping in mind the constant consumption rate as currently, it is estimated that fossil fuel deposits will deplete in 40, 160 or 60 years for petroleum, coal or natural gas, respectively [1-3]. It is also assessed that in the last 200 years CO_2 emission has increased by 31%. Moreover, due to the global warming, the average temperature has increased by about 0.4 - 0.8^{o}C [4]. Therefore, there is a particular importance toward renewable energy sources that use the energy of solar radiation, wind, geothermal or hydrothermal and then converts them into electricity. Currently, renewable energy sources ensure about 20% of the total energy demand in the world [5]. However, despite the fact, that they have found the application in many areas, significantly reducing usage of fossil fuels, they are not able to replace fossil fuels completely in the near future. The main problem is the capricious nature of the weather that cannot be easily foreseen and - to some extent - renewable energy resources do not ensure proper quantities all the time. Moreover, the integration of intermittent energy sources into the electrical grid faces with many challenges of grid stability and supply security. Therefore, it is essential to support renewable energy sources by conventional power plants or other electrical energy storage systems (EES) that offer a perfect fit for power/energy imbalance between its generation and demand [6-7]. Among them, electrochemical capacitors and redox flow batteries are well-suited for such application, however, they both demonstrate completely different properties, advantages and challenges.

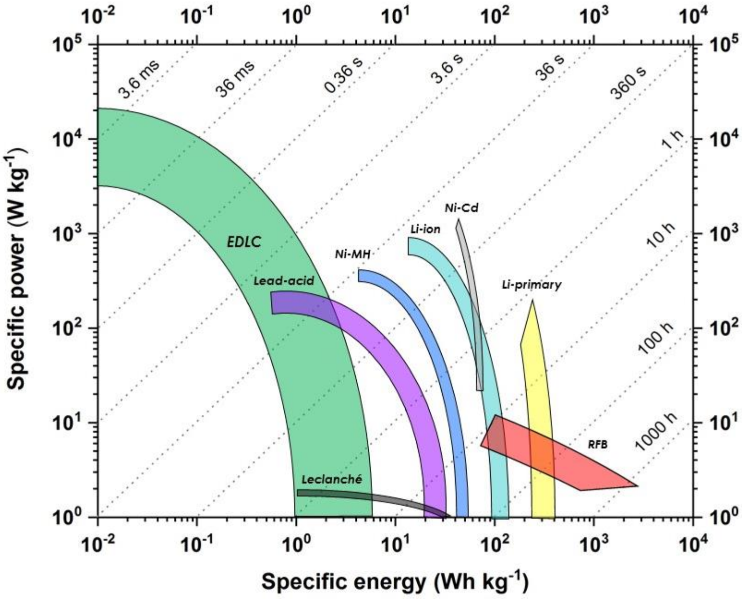

Fig. 2 Ragone plot for different energy storage systems.

According to Fig. 2 which presents the correlation of specific power and specific energy for different energy storage systems, electrochemical capacitors (ECs) lie in a high-power (up to 10 kW kg^{-1}) and low-energy region (from 5 to 15 Wh kg^{-1}) owing to the operation time between 1 and 10 s. These key features make the

ECs perfect in high peak current applications, e.g., memory back-ups, alternating current filtering, consumer electronics, batteries incorporation, etc.

In the case of batteries, an inverse dependency between power and energy can be seen. They harvest a higher energy (120- 240 Wh kg^{-1}) than ECs in expense of lower power density (250-340 W kg^{-1}). This results in an operation time of even few hours that makes the batteries a perfect choice for electromobility storage [3]. In this context, redox flow batteries (RFB) are a particular type of energy storage/generation system as their power and energy are independent on each other - contrary to other battery technologies. In other words, power of RFB is bound to the size and number of electrochemical cells in the stack, whereas energy is governed by electrolyte (active species concentration and electrolyte volume). Therefore, RFBs are a perfect approach for large scale application since they are able to deliver relatively high energy [4].

Proper energy storage system must be chosen depending on consumer demand, i.e., for specific application, considering advantages and disadvantages of individual technology. Each system relies on different charge storage mechanisms; in case of batteries chemical energy can be transferred into an electrical one *via* reduction-oxidation reaction, while charge storage mechanism of ECs relies mainly on electrical surface-confined electrostatic or faradaic processes. Even if characteristic of energy storage devices is now well-known and number of papers concerning this subject increases, there is still a room for improvement in order to shift our energy infrastructure towards low-cost, longer service life and CO_2 emission-free technologies.

This thesis is particularly devoted to two kinds of energy storage systems, i.e., electrochemical capacitors and redox flow batteries. As both systems possess different limitations, the work performed is generally based on the successful performance improvement of these energy storage devices.

Since electrochemical capacitors and redox flow batteries operation is based on completely different mechanism (from its nature), possibly that what is usually destructive for one device, it is of a vital importance in the second one. In this context, the role of oxygen in both systems was extensively studied taking into account various parameters such as: cycle life, electrode oxygen content, charging-discharging efficiency, energy density limitation and many others.

2. Electrochemical capacitors – state of art

This chapter aims to provide an overview on electrochemical capacitors taking into account their operation principles, construction and research solutions over the last few decades. The fundamental role of porous carbon texture on capacitor properties will be highlighted. Moreover, a significance of surface carbon groups will be extensively introduced. An emphasis will be put on aqueous salt electrolytes since they ensure an environmental benign and relatively high conductivity values reflected on capacitor power rating. The particular attention will be devoted to the ageing phenomenon of electric double-layer capacitors (EDLC). Various research methods of EDLC lifespan testing will be herein presented. In addition, the literature review summarizes the main operation issues faced by electrochemical capacitors and the current research strategies adapted for overall performance and lifetime enhancement. The literature part of this thesis finishes with general conclusions and introduces to the consecutive parts of this PhD dissertation.

2.1. The operation principle of electrochemical capacitor

Electrical double layer capacitor is composed of two high surface area electrodes (mostly activated carbon with well-developed surface area) coated on current collector, separated by insulator and immersed in the electrolyte [5]. Its operation principle is based on electric double-layer formation at the electrode/electrolyte interface [6]. During charging, the oppositely charged ions are adsorbed on electrode surface (Fig. 3A). The inverse process takes place during discharge process; the ions are desorbed from electrode to the electrolyte bulk (Fig. 3B) [7, 8].

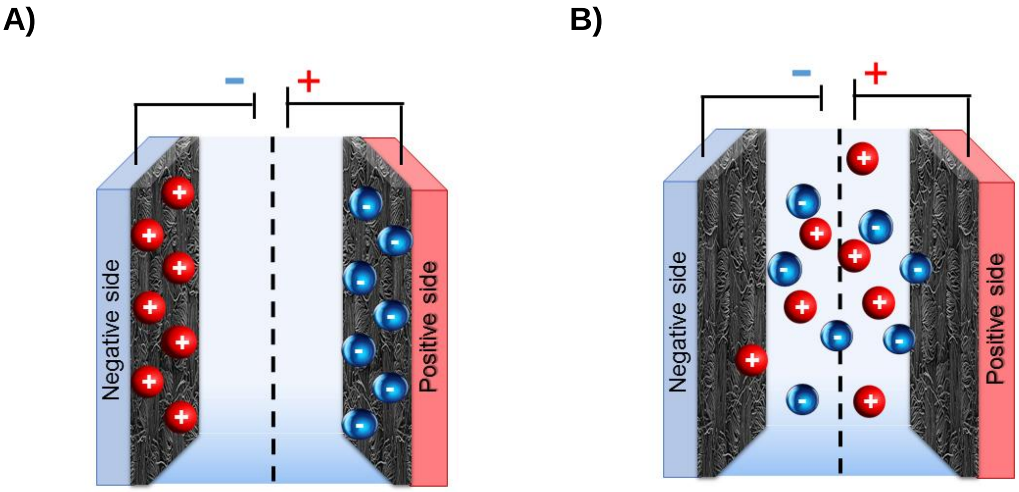

Fig. 3 Electrochemical capacitor scheme in the: A) charged; B) discharged mode.

The electric double-layer (EDL) capacitance represents the charge at electrode/electrolyte interface. Therefore, the more developed specific surface area (S_{BET}) of electrode, the more charge can be accumulated (higher capacitance). One may also consider that S_{BET} should be characterized by appropriately sized pores (able to adsorb electrolyte ions) [9, 10]. EDL capacitance can be calculated according to formula:

$$C_{EDL} = \frac{S\varepsilon_r\varepsilon_0}{d} \tag{1}$$

where: ε_r – relative electrolyte permittivity [-]; ε_0 – vacuum permittivity [F m^{-1}]; d – EDL thickness [m]; S – surface area of electrodes [m^2].

Since the capacitor system composes of two electrodes connected in series, its total capacitance (C) can be calculated according to the formula:

$$\frac{1}{C} = \frac{1}{C_+} + \frac{1}{C_-} \tag{2}$$

where: C_+, C_- - capacitance of the positive and negative electrode, respectively [F].

When the symmetric system is considered (composed of the same materials on the positive and negative side), it can be assumed that $C_+ = C_-$ Thus, the system capacitance is the half of the electrode capacitance:

$$C = \frac{C_e}{2} \tag{3}$$

where: C - total system capacitance [F], $C_e = C_+ = C_-$ - electrode capacitance [F].

The energy of electrochemical capacitor is proportional to the capacitance and the square of the operating voltage:

$$E_C = \frac{1}{2} C U^2 \tag{4}$$

where: E_c – energy [Wh]; C – system capacitance [F]; U – voltage [V].

Therefore, two various strategies of energy increase can be distinguished. One may enhance the capacitance (e.g., by introducing the redox active species in electrode or electrolyte) while another one increases the operating voltage (e.g., with organic electrolytes).

Nevertheless, selected electrolyte should be characterized by relatively high conductivity to obtain high power of the ECs device:

$$P_C = \frac{U^2}{4R} \tag{5}$$

where, P_C – power [W]; U – voltage [V]; R – system resistance [Ω].

2.2. Carbon electrodes for electrochemical capacitors

Different forms of carbons can be implemented in ECs devices including: activated carbons (AC) [11], carbon nanotubes (CNTs) [12, 13], onion-like carbons (OLC) [14], carbon black (CB) [15], carbide-derived carbons (CDCs) [16], template carbons [17]. Usually composites from various materials are created with addition of binder (PTFE or PVDF, with weight percentage of 3-10%) [15, 18]. Activated carbon stands for the basis (80-95%) of the total electrode mass, while CB, CNTs or OLC are added in a small amount (ca. 5%) to enhance electrode conductivity [15, 19]. Electrode material with electrolyte plays a dominant role by determining the maximum operating voltage of ECs [6]. Moreover, according to Eq. 1 to achieve high capacitance values, the materials with high specific surface area are required [9, 20]. Specific surface area (S_{BET}) of carbon materials can be determined by adsorption of different gases; mostly N_2 at 77 K and CO_2 at 273 K are used [21, 22].

Essentially micropores (pore size up to 2 nm) contribute to energy storage phenomenon in ECs. However, mesopores (2-50 nm) provide the tunnels for facilitated ions transport, especially when the relatively big cations (e.g., ionic liquids) are used [23]. The ions must occupy the carbon surface and to provide an effective ions adsorption during capacitor operation, the pore size should match the ion size [24-26].

2.3. Activated carbon

Due to relatively high specific surface area (S_{BET}>1000 m^2 g^{-1}), versatility and low cost, activated carbons are mostly used for ECs. They are usually obtained from synthetic or natural precursors which are well-abundant and rich in carbon [27-29]. Various bio-derived precursors can be selected for activated carbon production (coconut shell, seaweeds, plant stem, fruit stones, bamboo and many others) [28, 30]. One must remember that origin of chosen biomass cannot stand as edible product since the world population still suffer in many places from hunger [30, 31]. Given that, only some leftovers should be considered. Moreover, one should consider the availability of the precursor (e.g., olive stones are not widely present in Poland but in Spain), price, carbonization yield (min. 30-50%) and elemental content (heteroatom presence). The activated carbon preparation involves carbonization process, i.e., precursor heat-treatment in the inert gas atmosphere. Afterwards, the obtained material is activated either chemically (with KOH, H_3PO_4, $ZnCl_2$) or physically (by CO_2 or steam) [32, 33]. This process is inevitable to ensure microporous character of material. Commercially available carbons (e.g., Cabot, Kuraray) are rather physically activated; chemical activation is too expensive for industrial application [28]. Only few of the precursors does not require the activation process. As the example, Burley tobacco stem at the same time undergoes carbonization and self-activation process thanks to natural occurrence of calcium, potassium, magnesium, and sodium element. Obviously for each carbonization process the suitable temperature has to be estimated and in the case of Burley tobacco, the most developed specific surface area was obtained at 800^{o}C [34]. One should also mention fibrous activated carbons - Kynol®. This material does not require the use of binder and is prepared in one-step synthesis from phenol-aldehyde fibers made by acid-catalyzed cross-linking of novolac resin [35].

Activated carbons are sometimes modified with nitrogen and oxygen surface-functional groups [36, 37]. To prepare functionalized carbon, the source of desired element is required. O-rich carbons are obtained by their oxidation in air [38], HNO_3 [39] or electrochemical oxidation [40], while N-rich carbons can be realized *via* ammonia [41], urea, melamine or polyaniline chemical treatment [28, 36]. Oxygen surface functionalities (e.g., quinone/hydroquinone [42]) may enhance carbon wettability and the capacitance values of EC system due to its pseudocapacitive character (especially in acidic medium [43]), however, usually at the expense of power density and cycle life. Moreover, higher self-discharge rates are recorded for oxygen-rich carbons due to redox shuttle effects [44]. N-rich carbons have also a beneficial role, however, nitrogen content should not exceed 8 wt.% [45]. It was proven that type of functionality also plays an important role [37, 46, 47]. In case of nitrogen containing groups, pyridinic and pyrrolic nitrogen is a source of pseudocapacitance, while quaternary and pyridinic-N-oxides improves ECs operation at high current loads [37]. Currently, there are various physico-chemical methods enabling surface functional groups analysis. It includes X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), or Fourier Transform Infrared Spectroscopy (FTIR). It was shown that XPS can be also realized in the *in-situ* mode, i.e., during electrode polarization [48].

2.4. Electrolytes for electrochemical capacitors

Three main types of electrolyte used in ECs can be distinguished, i.e., organic or aqueous electrolytes and ionic liquids [49, 50]. Mostly, commercial ECs are based on organic electrolytes due to their wide electrochemical window. For this purpose, 1 mol L^{-1} tetraethylammonium tetrafluoroborate ($TEABF_4$) salt dissolved in acetonitrile (AN) or propylene carbonate (PC) solvent is usually selected owing to high voltage (2.5 - 2.7 V) [51, 52]. Organic medium is characterized by low conductivity (ca. 0.02 S cm^{-1} for $TEABF_4$ [7]), therefore one of the main disadvantage of such electrolytes is low power density of ECs system. Additionally, they are quite expensive (especially ILs), highly toxic and ECs components require additional drying for cell construction in oxygen-free environment [53]. Contrary, water medium electrolytes seem to solve the problem of relatively low power density values, nevertheless, at the expense of operational voltage. Aqueous medium is characterized by high ionic conductivity values (from ca. 50 mS cm^{-1} for neutral salts to ca. 1 S cm^{-1} for 30% H_2SO_4), but they can attain ca. 1.23 V only, due to the thermodynamic stability of water [26, 54-56].

2.5. Neutral salt aqueous electrolytes

In practice, KOH- and H_2SO_4-based capacitors operates only up to 1 V. They are rather used when newly prepared electrode materials are tested [6]. Additionally, they are quite corrosive, and one should use current collectors made of precious metal. Therefore, neutral medium electrolytes seem to be best candidates for further ECs development. It was proven that the capacitor may operate up to 2.2 V with 1 mol^{-1} Li_2SO_4 electrolytic solution [55]. This phenomenon is related with hydrogen sorption on the negative side, as the source of pseudocapacitance. During hydrogen sorption, OH^- anions are present in carbon porosity causing that pH locally increases [57, 58]. The region between dashed lines shows stability of water (Pourbaix diagram in Fig. 4); above A line water oxidizes to O_2 gas and below B line hydrogen is evolved. Therefore, when OH^- anions are produced during hydrogen sorption and pH increases, one may notice that water oxidation potential decreases. The difference in the gas evolution potentials in respect to electrolyte pH was used for operational voltage extension in ECs; two various pH (alkaline for the negative side and neutral for the positive one) were used on the separate compartment of ECs system making a pH gradient. It was shown that utilization of two various electrolytes is beneficial, nevertheless, it demonstrates the concept only, since over time electrolytes are mixed and usage of cation exchange membrane would be necessary [59]. Another strategy aims at electrode treatment and for instance enriching the positive one in acidic functional groups (e.g., lactone, carboxyl, phenol), whereas the negative one with basic surface groups (e.g., ether, carbonyl, pyrone) [23]. Recently, it was shown that ammonia seems to be a good candidate since it reveals amphoteric character, ensures pH gradient and finally ECs voltage extension up to 1.8 V with 1 mol L^{-1} Li_2SO_4 electrolyte [41]. Another approach for voltage extension covers water content decrease and usage of highly concentrated electrolytes called “water-in-salt” electrolytes. The idea is a promising alternative to organic electrolytes, ensuring a perfect compromise applied voltage and system stability however, it still suffers from many issues such as: high viscosity and low electrode wettability [60-64].

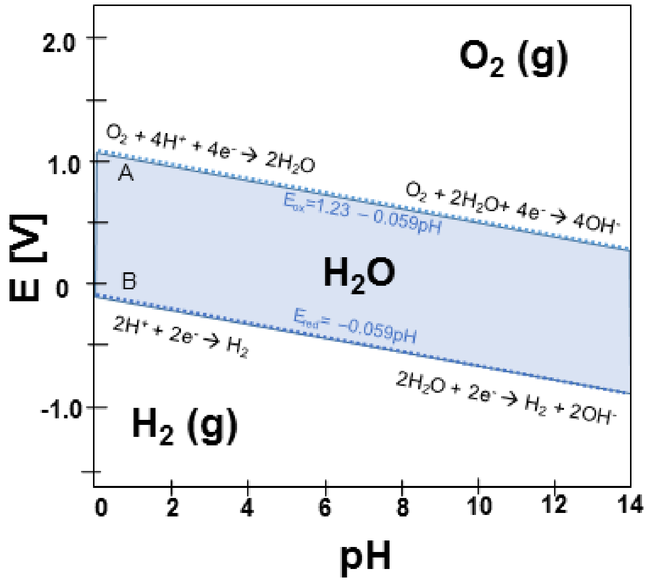

Fig. 4 Water stability presented on Pourbaix diagram [54].

2.6. Redox-active aqueous electrolytes

As shown in Eq. 4, to improve ECs energy and power values, one attempts to increase the capacitance (C). This can be realized *via* introduction of the redox-active species to capacitor system as the source of additional capacitance [65, 66]. One may consider different electrolytic species such as: bromides, iodides, hydroxyquinones, selenocyanates or thiocyanates [44, 67-69]. Depending on redox pair selection, one of EC side (either positive or negative) is characterized by battery-like behavior, while the second one is based on purely capacitive performance. Such situation occurs when 1 mol L^{-1} potassium iodide (KI) was used as the neutral medium (pH = 7) electrolyte for ECs application. It was demonstrated that iodide species are specifically adsorbed on carbon interface ensuring a stable, reversible reaction on the positive side as well as good conductivity [70-73].

The electrochemical activity of iodides is based on following reactions [70, 74]:

$$3I^- \leftrightarrow I_3^{-1} + 2e^- \tag{6}$$

$$2I^- \leftrightarrow I_2 + 2e^- \tag{7}$$

$$2I_3^{-1} \leftrightarrow 3I_2 + 2e^- \tag{8}$$

$$I_2 + 6H_2O \leftrightarrow 2IO_3^{-1} + 12H^+ + 10e^- \tag{9}$$

Very often redox active species selected for ECs are inspired from different types of batteries. Following this trend, a hybrid capacitor with vanadium species was investigated employing V^{2+}/V^{3+} redox pair from vanadium redox flow batteries (VRFB) [75]. Herein, two conjugated redox pairs were used on separate EC compartments. Iodides were the pseudocapacitance source on the positive side of EC, while on the negative one vanadium species were used. Experimentally, 1 mol L^{-1} electrolytic solutions of KI and $VOSO_4$ were utilized. The concept is schematically presented in Fig. 5.

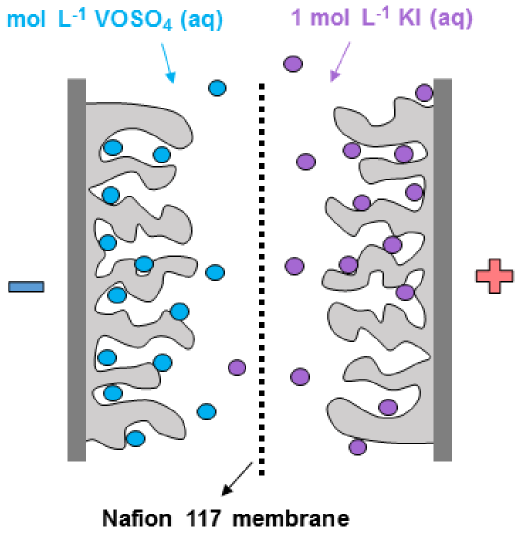

Fig. 5 The concept of hybrid capacitor based on iodide and vanadium redox active species.

Initially, system suffered from relatively high capacitance fade rate. It turned out that typical glass fiber separator (Whatmann GF/A) is the source of capacitor failure. Similarly, as in redox flow batteries (RFBs), Nafion^{TM} cation exchange membrane was applied to inhibit cross-mixing of used electrolytes. Using this configuration, the stability over 5,000 cycles was recorded.

2.7. Lifespan of the electrochemical capacitors

The lifespan of EC is defined as the time of the system in which it loses its initial properties. In other words, some of the components do not fulfil its expected function. This state, in case of ECs, is usually monitored as the specific capacitance loss or resistance increase over time [76, 77]. Generally, it is estimated that capacitor end-of-life criterion is reached when the relative capacitance value decreased to 80% of the initial one or the resistance increased by 2-fold [77-79].

Electrochemical capacitor long-term performance is usually monitored by two types of tests, i.e., galvanostatic cycling or voltage-holding test. In case of galvanostatic cycling, the cell is charged/discharged repeatedly using constant current density. At least 12,000 cycles are required to reliably determine capacitor durability [80, 81]. One may notice that galvanostatic cycling is highly time-consuming and requires more testing equipment. Therefore, an accelerating ageing methodology has been proposed. Such test (named as a *voltage-holding* or *floating test*) is based on potentiostatic hold at maximum ECs operation voltage what directly reflects the application of capacitor as the emergency devices [80]. Due to the fact that the cell is most of the time stressed with the highest voltage (normally it reaches this level only for the few seconds), its behaviour can be monitored at the accelerated pace. Other ageing acceleration factors are the temperature and voltage according with Arrhenius and inverse power laws, respectively. The voltage values close to the decomposition voltage is particularly detrimental [82]. During, the voltage-holding test, cell is firstly charged/discharged galvanostatically 3 times, held at the maximum voltage for 2 hours and finally discharged. Such one sequence is named as one *floating* cycle. The relative capacitance is calculated from the discharge curve after the potentiostatic mode. One may periodically include other techniques (e.g., cyclic voltammetry or electrochemical impedance spectroscopy) between *cycling/floating* cycles to monitor additional parameters during ECs failure. Both ageing tests are schematically presented in Fig. 6.

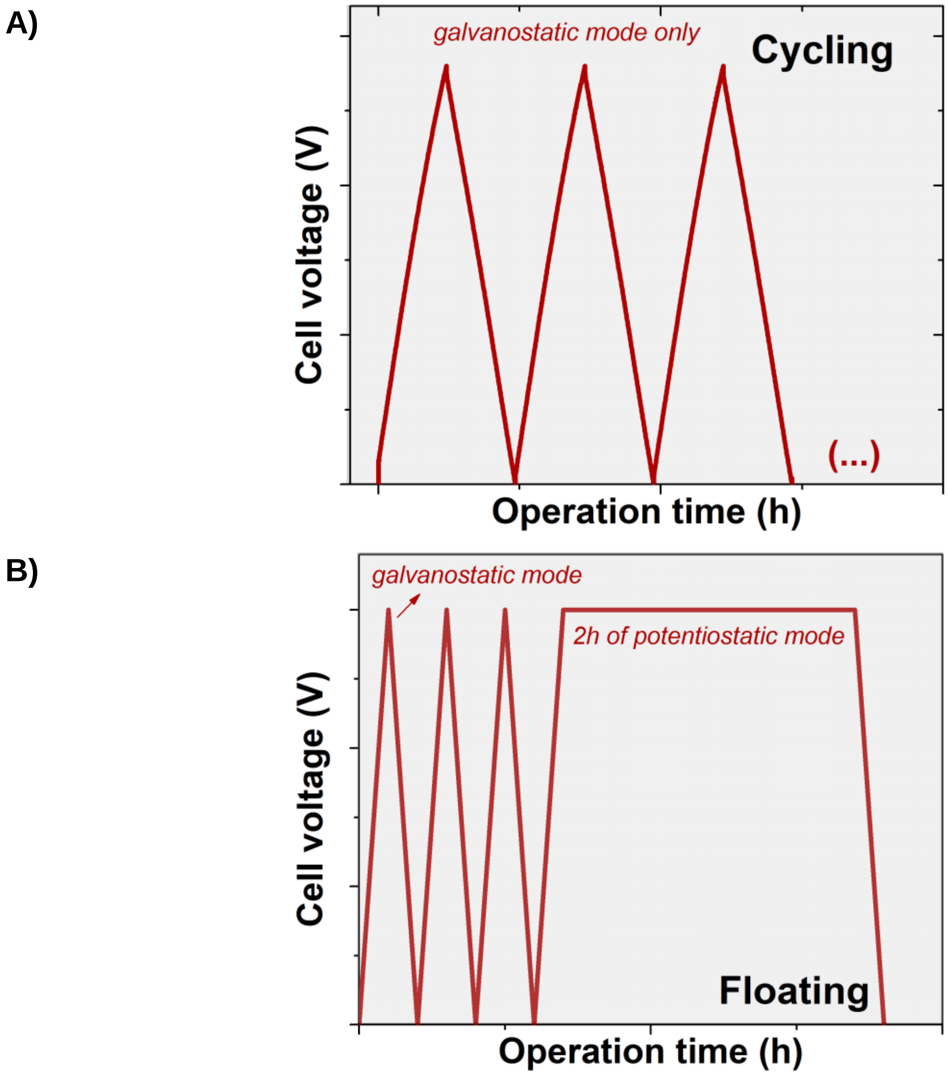

Fig. 6 Schemes of the ageing tests: A) galvanostatic cycling; B) floating.

It is noteworthy that the capacitance decrease is usually not linear and may be divided into three steps. The first step relates to charge redistribution effect; fresh cell with highly porous electrodes needs few cycles to be in the steady-state conditions. In practice, prior to ageing test, cell should be conditioned by galvanostatic charge/discharge or cyclic voltammetry. In the second step, capacitance drops exponentially, and it is usually connected with potential window shift due to the components ageing. Third step is linear and occurs at the relative capacitance value below 15-20% [82].

Analysis of the failure mode in aqueous electrochemical capacitors is particularly interesting; water-based ECs are a promising alternative to organic systems due to their environmental benign and simple construction (no requirements of components drying, water- and oxygen-free assembly environment). However, due to relatively low thermodynamic decomposition of water at 1.23 V, aqueous systems still suffer from many long-term performance problems at high voltages (above 1.23 V) [83]. Therefore, determination of long-term performance fading reasons is an essential step for further improvement of aqueous EC systems.

Various modes are used for ECs lifetime testing, i.e., *post-mortem* or *in-situ* measurements [51, 84-89]. The *post-mortem* approach relies on full device testing. This can be realized in 2-electrode setup with/without the reference electrode. Herein, the cell is aged up to the desired relative capacitance/resistance level and then the cell is disassembled. The properties of the individual components (electrodes) are tested and then compared to their pristine properties. Different kinds of physico-chemical measurements can be applied. Usually, the electrode properties are determined by N_2/CO_2 sorption, Raman spectroscopy, TPD-MS or XPS measurements.

In-situ measurements offer physico-chemical parameters control at the same time (online) with capacitor cell testing. This approach ensures an insightful view into capacitor failure mode. This may include gas evolution monitoring, cell pressure measurements or Raman spectra collection during repeatable charge/discharge cycles of the electrochemical device. However, one should mention that usually *in-situ* measurements are realized in 3-electrode setup (with electrolyte excess) and only one electrode is monitored, not a full device [73, 88]. Nevertheless, one cannot distinguish which ageing-control method is a better one. Each one has its distinctive features, and the best knowledge can be obtained when the information from both approaches are gathered. As it can be concluded from all the research provided, few typical failure reasons for water-based electrochemical capacitors can be listed [76, 80, 90-92]:

i. electrolyte decomposition, especially when the operation voltage is close to the voltage limit;
ii. internal pressure increase; the effect is enhanced at the higher voltage and may lead to cell explosion. Therefore, some pressure relief valve should be placed on the device. One should add that cell overpressure may lead to electrolyte leakage;
iii. electrode oxidation; usually oxygen functional groups appear on activated carbon surface. The ions adsorption process is therefore reduced due to

the pores clogging effect. Mainly the positive electrode oxidizes over *cycling/floating*;

iv. current collectors' corrosion; therefore, collector material should be selected with the regard of used electrolyte and working potentials. Usually, when the equivalent series resistance increased significantly, one may assume that electrode adhesion to the current collector is weakened.

Often all the failure modes are simultaneously present in the studied EC system. Positive electrode oxidation is one of the main effects observed during capacitor long-term performance. On-line mass spectroscopy combined with pressure analysis has shown that carbon surface/electrolyte interactions lead to the gas evolution. Predominantly, harmless CO and CO_2 gas evolution occurs due to oxygen surface group oxidation at 0.6 V when 1 mol L^{-1} Li_2SO_4 is an electrolytic solution. It has been observed that after reaching the cell voltage of 1.6 V, water decomposition causes hydrogen evolution on the negative electrode and carbon corrosion on the positive one [88, 93]. Moreover, short-term cycling causes the reversible gas evolution reactions monitored simultaneously with cell pressure fluctuations. When a long-term performance is applied an irreversible processes undergo and gaseous products evolve [93]. Additionally, type of the evolved gases depends on electrolyte origin; it was proven that with nitrate (NO_3^-) electrolyte, carbon surface groups evacuate as NO_2, NO, CO and CO_2 gases; H_2 evolution was mainly found with sulfate electrolyte [91].

2.8. Summary

Summarizing, electrochemical capacitors are widely developed power devices able to operate for thousands of cycles. Nevertheless, their commercial forms are mainly based on organic electrolytes which are flammable and toxic. Therefore, neutral electrolytes are promising candidates for sustainable, green ECs systems. The research about ECs lifespan is facing nowadays a significant upturn. Until now, it has been noticed that in high voltages, water decomposes producing various gases and oxidizing electrode. It seems there is a destructive role of oxygen in ECs system. Therefore, further, in-depth explanation of ageing failure mechanisms in aqueous medium ECs is an imperative step to provide long-term operation of future devices.

3. Redox flow batteries – state of art

The current research about the redox flow batteries is growing constantly, especially when sustainably generated electrical energy sources are still being sought [4, 94]. Unlike the conventional batteries, RFBs employ two redox pairs dissolved in a supporting electrolyte that are stored in the external reservoirs [95, 96]. Therefore, redox flow batteries are the perfect candidates for scalable application especially when integrated with solar or wind farms [97-100]. This chapter provides with the introduction to the RFBs topic, taking into account their basic properties as well as more advanced technologies or applications. Furthermore, available research solutions will be discussed concerning RFB advantages and limitations in terms of economy, environmental benign and possible future applications. The core of this chapter discusses a metal-based RFB, i.e., vanadium redox flow battery since most of the research studies are focused on this technology. Herein, highlight will be put on the electrode material (carbon felt) in terms of its surface properties and its influence of VRFB performance. The chapter finishes with a summary and gives a future overlook to RFB world.

3.1. Working mechanism and basic principles

Redox flow batteries (RFB) are the secondary batteries which operation principle is based on reversible reactions of two redox couples as schematically summarized below [4]:

$$A^{x} \leftrightarrow A^{x+n} + ne^{-} \qquad E^{0}_{A} \qquad (10)$$

$$B^{y} + ne^{-} \leftrightarrow B^{y-n} \qquad E^{0}_{B} \qquad (11)$$

$$\text{Overall: } A^{x} + B^{y} \leftrightarrow A^{x+n} + B^{y-n} \qquad U_{cell} = E^{0}_{B} - E^{0}_{A} \qquad (12)$$

During the charging process one of the redox couples undergoes the oxidation reaction, while the second one reduction reaction. The reversible process takes place during the discharge. Typically, RFB is composed of two external tanks, where the electrolytic solutions are stored as well as the battery stack, where the electrochemical reactions undergo. The tanks and electrochemical cells are connected through mechanically driven pumping system which allows the electrolyte from the tanks to be transferred in and back to reservoirs. The electrolytes consist of redox-soluble species dissolved in a supporting electrolyte (usually strong acids or bases) [4, 96, 97, 101]. Some additives to the electrolyte are sometimes added for stability or solubility improvement [102, 103]. The electrochemical cell is usually comprised of two flow-through electrodes placed on current collectors which are separated by an ion-conducting membrane which serves as the ionic conductor simultaneously blocking the mixing of two sides of RFB. The electrodes are connected to the electrical load during discharging or to power supply *via* external circuit during charging. Fig. 7 presents the scheme of redox flow battery construction [97].

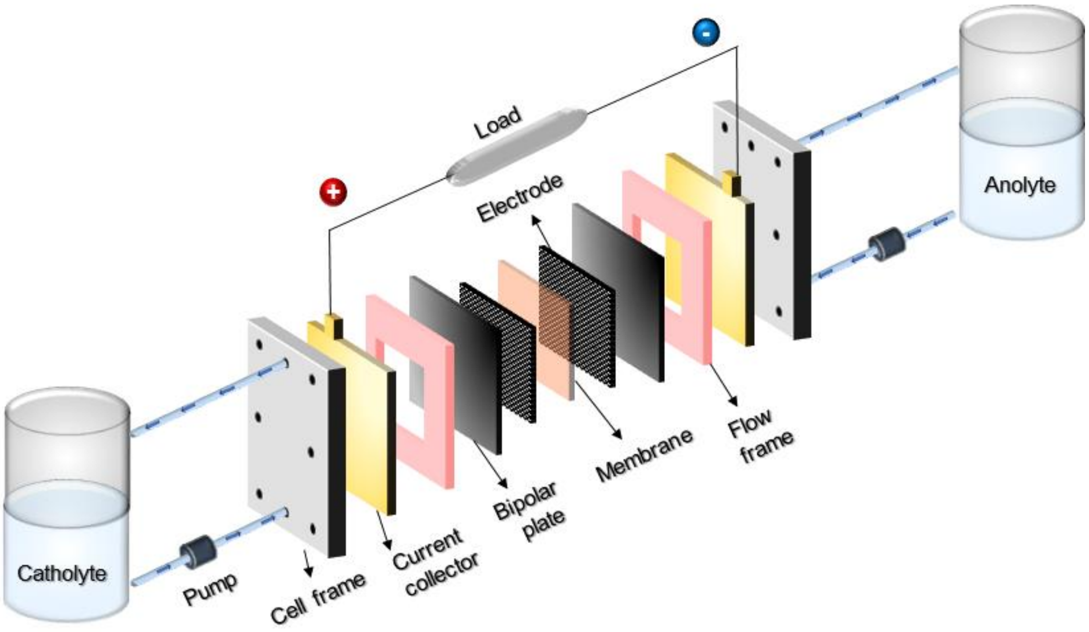

Fig. 7 Scheme of redox flow battery construction. Sourced from [104].

Unlike the conventional batteries (lead-acid, lithium-ion etc.) that apply redox active material in a solid form [105, 106], RFBs usually confine redox material in electrolyte by dissolving the individual redox couple in supporting solution [94]. Therefore, RFBs are sometimes named as reversible fuel cells since the energy is stored in electrolyte which is pumped from external tanks to the electrochemical cell where the electrodes and current collectors are placed. Such untypical spatial separation of electrolyte reservoirs and electrodes allows the energy (kWh) and power (kW) to be decoupled; the energy density is controlled by tank volume and the concentration of redox active species dissolved in a supporting electrolyte [4]. Nevertheless, one should mention that the solubility of the redox species is one of the energy capacity limitations [94, 107]. The power rating is governed by total electrode size (e.g., number of the cells in the stack). Since the energy rating is the function of tank volume, enlargement of battery capacity requires only electrolyte volume increase and in total creates very low incremental costs. Therefore, one should remark that the battery costs per kWh are reduced significantly for large-storage application especially in extended time of RFB exploitation as presented in Fig. 8 [108].

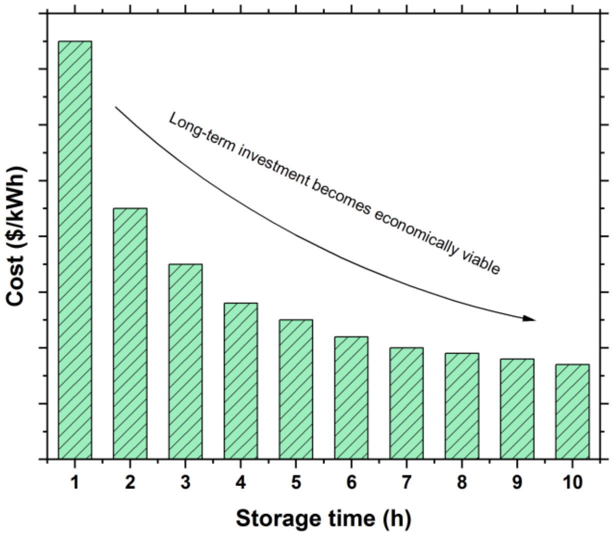

Fig. 8 Capital costs of RFB design per kWh. Based on [108].

On the basis of techno-economic model, one should mention that the total costs of RFB depend not only on the cost of electrolyte (active materials, solvent, additives), tanks and stack (electrode material, membrane, current collectors, bipolar plates, stack assembling or gaskets), but also on many other things such as: pumps, valves, piping, sensors, actuator and eventual thermal regulation [109]. As seen in Fig. 9, cost distribution varies depending on size of the RFB device. Two different vanadium redox flow battery systems were collated together, i.e., 0.25 MWh *vs.* 5 MWh. In both cases, an ion conducting membrane (usually Nafion^{TM}) is the most expensive component of a total system [110]. Therefore, there are currently many attempts to elucidate the cost-effective replacement for Nafion^{TM} membrane [111]. Nowadays, 1 m^2 costs around 1500$ [112]. However, in scaled up system the membrane price decreases significantly (from 44 to 27%). Similar situation is observed for carbon felt electrodes which are 2-fold cheaper in 4 MWh system. Interestingly, as seen, cost of chemicals (vanadium) increases drastically for a larger application. Worth highlighting is the fact that in case of 4 MWh system, there is still room for overall price improvement by battery efficiency enhancement and as a result it lowers electrolyte and stack costs (Fig. 9) [113]. To summarize, due to the unique feature of customizable design of power/energy output makes RFB inherently well-suited for large storage applications.

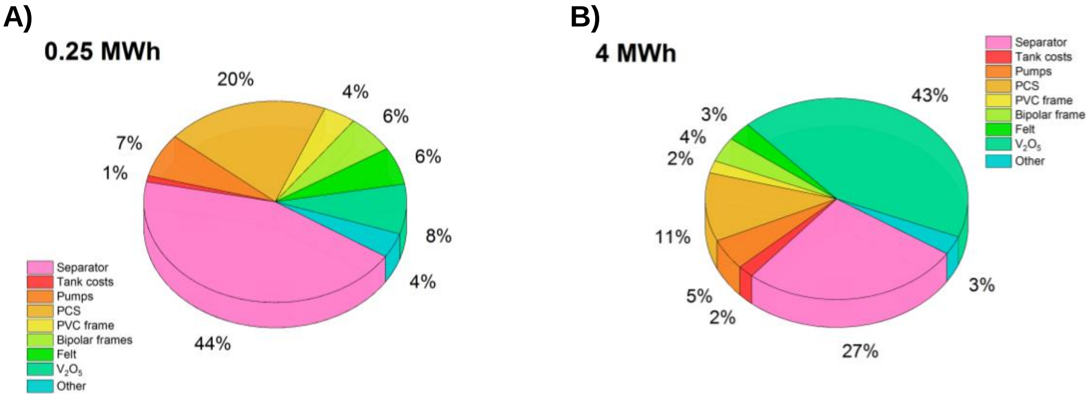

Fig. 9 All-vanadium redox flow battery component cost distribution for: A) 0.25 MWh; B) 4 MWh system. Based on [113].

The general features of redox flow batteries include [108, 114]:

i) the costs per kWh decreases significantly with capacity enhancement. Therefore, RFBs are the perfect solution for stationary, long-term application;

ii) power rating depends on cell stacks (which determines system voltage) or electrode available area (which determines system current density);

iii) energy rating is set by redox-active materials concentration and its volume;

iv) no solid-phases changes during charge/discharge process – lack of short-circuit;

v) easiness of state-of-charge controlling by electrolyte potential measurements;

vi) possibility of deep discharge without destructive effects (capacity loss or lifespan shortening);

vii) capability to withstand fluctuating, irregular power supply, i.e., solar, wind power;

viii) relatively long calendar life;

ix) very negligible self-discharge rate during RFB stand-by or complete break in operation due to positive and negative electrolyte separate storage from the electrochemical cell;
x) pumping system is necessary for electrolyte circulation;
xi) need for acid or base resistant construction (piping, collectors, connections etc.);
xii) relatively low energy to volume ratio in comparison to other types of batteries;
xiii) can be mechanically charged (refueled) by replacement of discharged electrolyte with a charged one;
xiv) harmless components eventual replacement;
xv) safe systems – thermal management is not required since flowing electrolyte plays as a cooling agent.

3.2. Basic parameters of RFB

The volumetric capacity (C_{RFB} in Ah L^{-1}) of redox flow battery informs about the charge stored in a given volume:

$$C_{RFB} = \frac{m \cdot n \cdot F}{M \cdot V} \tag{13}$$

where: m – mass [g]; n – number of electrons which takes part in redox reaction [-]; F – Faraday constant - 26.8 [Ah mol^{-1}]; M – molar mass [g mol^{-1}]; volume [L].

The energy density (E_{RFB} in Wh L^{-1}) can be calculated according to the equation:

$$E_{RFB} = C \cdot U \tag{14}$$

where: C_{RFB} – volumetric capacity [Ah L^{-1}]; U – voltage [V].

Worth mentioning, energy density is usually calculated considering the total volume of two reservoirs; however, one should mention that it should be calculated taking into account the real volume of whole RFB system (electrochemical cell, pumps). Therefore, comparison between different RFB technologies is usually inaccurate [108].

The power density (P_{RFB} in W L^{-1}) depends on the battery discharge time ($t_{discharge}$):

$$P_{RFB} = \frac{E_{RFB}}{t_{discharge}} \tag{15}$$

The current density (A cm^{-2}) strongly influences the charging/discharging time and it is usually referred to the electrode geometric mass. Very often battery power density is expressed in W cm^{-2} [115].

The battery performance is verified by three characteristic parameters, i.e., coulombic, voltage and energetic efficiencies. Coulombic efficiency (CE) is the ratio between the retained charge during the discharging process ($Q_{discharge}$) to the charge required during the charging process (Q_{charge}):

$$CE = \frac{Q_{discharge}}{Q_{charge}} = \eta_c \tag{16}$$

Worth highlighting, CE indicates the possible cross-over or presence of side-reaction [4, 116].

Voltage efficiency (VE) refers to variety of overpotentials (ohmic, diffusion and charge transfer polarization). It is calculated by dividing the mean discharging voltage by charging one at constant current. VE decreases with a current density rise.

$$VE = \eta_v = \frac{\frac{\int_0^{T_D} E_D(t)dt}{T_D}}{\frac{\int_0^{T_C} E_C(t)dt}{T_C}} = \frac{E_D}{E_C} \tag{17}$$

where: D – discharge; C – charge; T- time; E – mean potential.

Energetic efficiency (EE) is the multiplication of coulombic and the voltage efficiency. Depending on the used RFB technology and applied current density, EE usually fluctuates between 60-90% [117].

$$EE = \eta_E = \eta_C \cdot \eta_V \tag{18}$$

3.3. Redox flow battery chemistry and a brief history behind

As it can be seen from Fig. 10, the first RFB concept appeared in 1880 and was based on zinc-bromium chemistry [108]. Almost 100 year later, National Aeronautics and Space Administration (NASA) presented the prototype of iron-chromium flow battery (ICB) which can theoretically operate up to 1.2 V [107, 108]. Even if a 1 kW/13 kWh prototype was constructed, the idea faced the intrinsic problems i.e., cross-contamination of active materials through an anion-exchange membrane resulting in capacity loss [118]. Moreover, Cr^{3+}/Cr^{2+} redox couple suffers from a sluggish kinetics (catalysts or higher temperature required) and due to the low chromium electrochemical potential (E^0 = -0.41 *vs.* SHE), hydrogen evolution was a side reaction decreasing significantly the coulombic efficiency of ICB [119].

Just 10 years after, a cross-contamination issue was successfully solved at the University of South Wales in Australia with all-vanadium redox flow battery concept, based on four oxidation states of vanadium metal, i.e., V^{2+}/V^{3+} and VO^{2+}/VO_2^+ redox pairs [120]. Until now, the system is under a spotlight of RFB development and still there are research studies concerning VRFB performance enhancement [111, 121]. Many derivatives of VRFB were investigated including vanadium-cerium, vanadium-polyhalide or iron-vanadium flow battery [122-124]. In the latter case, VO^{2+}/VO_2^+ pair from VRFB was replaced by Fe^{2+}/Fe^{3+} pair due to lower corrosiveness of iron couple and wider temperature range (0-50°C). Nevertheless, the vanadium-iron flow battery (IVB) operates at a lower voltage than fully vanadium-based flow battery (1.02 V for IVB and 1.26 V for VRFB), therefore, to compensate energy loss a higher concentration of active materials or operation at higher state of charge (SOC) are necessary in IVB.

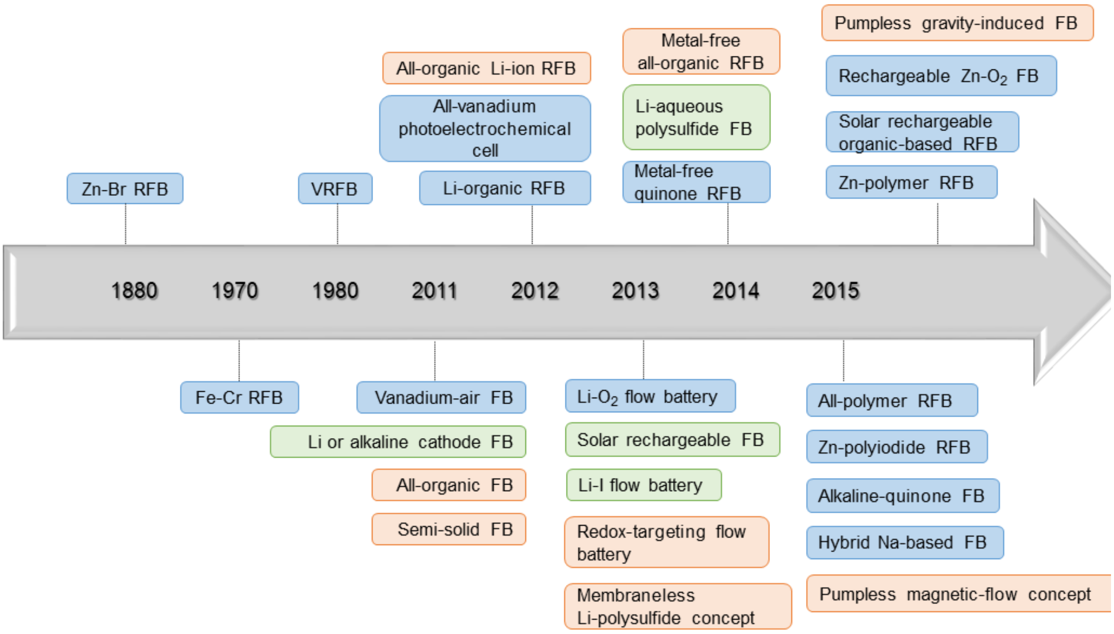

Fig. 10 Timeline of redox flow battery development. Adapted from [108].

RFB concepts are not only based on the metal salts dissolved in aqueous solutions. One of the main drawback of these systems is a low operating voltage due to the thermodynamic decomposition of water starting at 1.23 V [54]. Water electrolysis not only limits the energy stored but also creates some side reactions

(H_2 and O_2 evolution) resulting in pH electrolyte changes and sometimes even the precipitation of metal in supporting electrolyte [125-127]. Therefore, as presented in timeline of RFB development (Fig. 10), a new trend of replacement of aqueous electrolytes with organic ones started to appear [128]. It covers application of tetraethylammonium tetrafluoroborate ($TEABF_4$) and acetonitrile (AN) solvent in all-vanadium, chromium acetylacetonate [107, 129]. Such solution allowed for more flexibility and a wider voltage range to be applied. Contrary, one should mention that conductivity (higher ohmic losses) and solubility of metal ions in organic media is much lower than in case of aqueous system. In addition, the battery system needs a tightly closed, oxygen-free system, since its behavior is sensitive to air. Other general idea of further RFB development concerns organic redox-active materials due to their structural diversity, rich designable chemistry and relatively low price [130]. Currently, the pioneer works concern quinone-based, nitroxide radical compounds ((2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO), 2-phenyl-4,4,5,5-tetramethylimidazoline-loxyl 3-oxide (PTIO)) or dialkoxybenzene (2,5-di-tert-butyl-1,4bis(2-methoxyethoxy)benzene (DBBB), 2,3,6-trimethylquinoxaline (TMQ)) flow chemistry [131, 132]. The general comparison of organic and aqueous RFBs is presented in Tab. 1.

Tab. 1 Basic features of aqueous and organic redox flow batteries.

	Aqueous RFB	***Organic RFB***
Solvent choice	+	+++
Ions solubility	+++	+
Electrolyte conductivity	+++	+
Voltage range	<1.23 V	>3 V
Temperature range	0-100°C	<0°C
Electrolyte viscosity	+	+++

3.4. Criterion of redox pair selection for RFB

One of the selecting criteria of redox active species for RFB is their solubility in a supporting electrolyte. Higher concentration of redox active species means higher energy density. The second criterion concerns the reversibility of a given redox pair under charging/discharging conditions. In addition, chemical stability plays an important role; the solution has to be stable in the operating condition (temperature, pressure). Some salt precipitations can block the piping connections and as the effect breakdown the RFB system. Last, but not least, one should mention that the main driving force for choice of two final redox pairs is the difference between their standard potentials – the higher difference, the higher battery voltage is. Fig. 11 graphically shows the possible choices for pairing the redox couples for RFB applications. Nevertheless, cross-mixing of positive and negative electrolytes is one of the main drawbacks limiting RFB lifetime. There are also other disadvantages shortly summarized in Tab. 2.

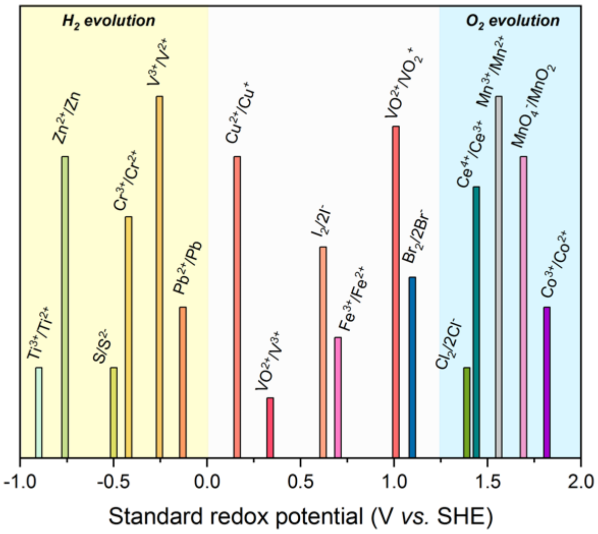

Fig. 11 Standard potential of redox couples. Sourced from [133].

Tab. 2 List of the main redox pairs couples for RFB application. Based on [133, 134].

CATHODIC			***ANODIC***		
Redox couple	***E^0 vs SHE***	***Problems***	***Redox couple***	***E^0 vs SHE***	***Problems***
V^{2+}/V^{3+}	-0.26 V	oxidation in air	**VO^{2+}/VO_2^+**	1.00 V	slow kinetics, precipitation
Cr^{2+}/Cr^{3+}	-0.41 V	slow kinetics	**Fe^{2+}/Fe^{3+}**	0.77 V	quite corrosive
Zn^{2+}/Zn	*-0.76 V*	*precipitation, dendrites formation*	***$Br_2/2Br^-$***	*1.09 V*	*sensitive to temperature, $Br_{2(g)}$ is hazardous and corrosive*
S_2^{2-}/S_4^{2-}	*-0.27 V*	*tight pH control to prevent $H_2S_{(g)}$ emissions*	***Ce^{3+}/Ce^{4+}***	*1.75 V*	*low solubility*

Up to date, a wide library of various RFB types was reported including various redox couples (iodine, polysulfide, metal oxides), technologies (membrane- or pump-free RFB) and interconnections (photochemical flow batteries) [114, 133, 135-137]. Nevertheless, many of proposed solutions are still in their infancy and require more advancements to satisfy large-scale energy needs (costs, safety, energy/power density, lifetime). Despite the high cost of vanadium and many other drawbacks, VRFB system is currently the most adapted for commercial reality and developed one. Therefore, the next section of this thesis will be mainly devoted to VRFB technology.

3.5. Vanadium redox flow batteries

3.5.1. Concept and basic principles of VRFB

Vanadium exists in four oxidation states having a different color at each one as presented in the Tab. 3. Such property is utilized in vanadium redox flow battery (VRFB) which is a rechargeable battery that utilizes all vanadium oxidation states. V^{2+}/V^{3+} and VO^{2+}/VO_2^+ redox pairs are used for the negative and positive side, respectively [138, 139]. In VRFB, vanadium is dissolved in a supporting electrolyte (usually 1-3 mol L^{-1} sulfuric acid) having a maximum concentration of 1-2 mol L^{-1} [95]. The vanadium solubility in H_2SO_4 is one of the limitation of energy density in VRFB [138]. The concept of vanadium redox flow battery is presented in Fig. 12.

Tab. 3 Vanadium oxidation states [138].

Oxidation state	***Symbol***	***Color***
+II	V^{2+}	violet
+III	V^{3+}	green
+IV	VO^{2+}	blue
+V	VO_2^+	yellow

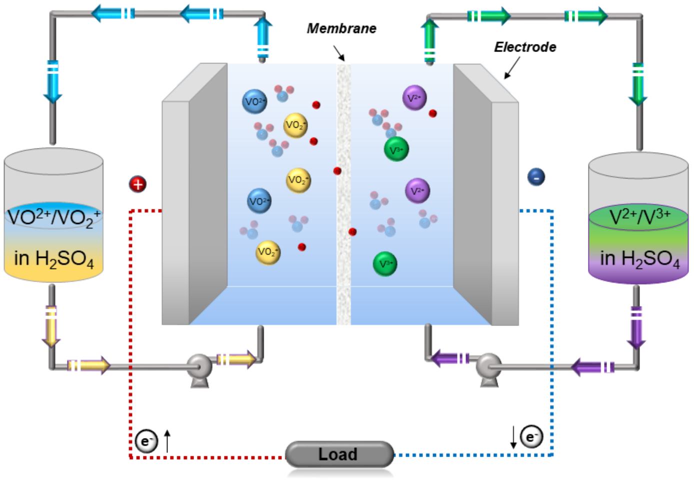

Fig. 12 Vanadium redox flow battery scheme.

During the discharging, there is a reduction of VO_2^+ to VO^{2+} on the positive side of VRFB:

$$VO_2^+ + e^- + 2H^+ \leftrightarrow VO^{2+} + H_2O \qquad E^0 = 1.004\ V \qquad (19)$$

Simultaneously, oxidation of V^{2+} to V^{3+} occurs on the negative side of the battery:

$$V^{2+} \leftrightarrow V^{3+} + e^- \qquad E^0 = -0.255\ V \qquad (20)$$

The overall reaction is as follows:

$$VO_2^+ + 2H^+ + V^{2+} \leftrightarrow VO^{2+} + H_2O + V^{3+} \qquad U_{cell} = 1.259\ V \qquad (21)$$

The standard battery voltage (at 25ºC and 1 mol L^{-1} concentration) equals to 1.259 V and stands as the difference between positive and negative half-cells.

3.5.2. Vanadium redox flow battery properties

The main characteristic of VRFB is the utilization of vanadium ions with four different valences in the electrolyte. This feature creates a unique advantage in easy design and operation of vanadium species in RFB system; practically the same electrolyte can be stored in the positive and negative reservoirs. Therefore, VRFB is characterized by relatively long lifespan [140, 141]. The main reason of capacity fade in VRFB is the imbalance in volume or ion valence on positive and negative tanks. Contrary to the other battery types, the capacity fade can be recovered through chemical (addition of oxidizing or reducing agents or remixing of both reservoirs) and/or electrochemical methods (reversible polarization). One should also mention about the role of electrodes in VRFB degradation process. In fact, carbon electrodes do not go through mechanical, thermal or phase changes; they merely ensure the active sites for electron transfer during the charging/discharging processes. Therefore, generally carbon-based electrodes provide a stable cycle life for VRFB. Nevertheless, carbon oxidation/corrosion over time cannot be also omitted [127]. With these particular features (especially latitude in energy/power tailoring), VRFB are believed one of the most promising stationary energy storage technology in the last decades [142]. Nonetheless, still some of the issues require a whole series of improvements; this covers a high price of vanadium chemicals and Nafion^{TM} membrane [110].

3.5.3. Key components of vanadium redox flow battery

3.5.3.1. Electrolytes

The electrolyte in VRFB acts as the medium to store the vanadium species in a supporting electrolyte. Its volume and concentration influence the energy density. Typically, it is composed of vanadium salt dissolved in a sulfuric acid. The role of sulfuric acid is to increase the ionic conductivity and ensure proton (hydrogen ion) for the redox reaction of VO^{2+}/VO_2^+ species. However, the traditional solution suffers from many issues originating from vanadium solubility and temperature stability [143, 144]. It has been proven that VO_2^+ ions are only stable in the temperature range between 0-40ºC and precipitation occurs when heated/cooled. This feature significantly hampers the widespread utilization of VRFB, since only low energy density of < 25 Wh L^{-1} for vanadium concentration <1.7 mol L^{-1} can be obtained [145]. Therefore, many scientists put attention towards optimization of the electrolyte composition [146]. It was found out that red vanadium pentoxide precipitation occurs on the positive electrode. However, the amount of V_2O_5 deposit depends on SOC, temperature and electrolyte concentration [147]. Increase of acid concentration seemed to be a good solution for vanadium (V) stabilization [146, 148]. It has been discovered that ca. 3 mol L^{-1} solution of vanadium can withstand up to 30ºC in 6 mol L^{-1} sulfuric acid. However, at the improved vanadium concentration, the diffusion coefficient and electrochemical activity dropped [125, 148]. Given that, 1.5-2 mol L^{-1} in 3 mol L^{-1} sulfuric acid was claimed as the compromise [125]. The negative electrode composition suffers also from many issues, however, the magnitude is much smaller than in the case of the positive side of VRFB system. Firstly, V^{2+} solubility diminishes with increase of acid concentration and drop of the temperature [144]. In addition, it has to be mentioned that V^{2+} form oxidizes to V^{3+} when exposed to the air. This can practically affect battery discharge on one of the half-cell and created an imbalance between both compartments. Therefore, VRFB has to be closed or N_2 purge is necessary [149].

To enhance energy density of VRFB other supporting electrolytes for vanadium species have been studied. The most breakthrough effect was achieved by the scientist from Pacific Northwest National Laboratory (PNNL) who used a mixed-acid vanadium redox flow battery, well known as generation 3 (G3) VRFB battery

[98]. The inspiration has been taken from the studies of M. Skyllas-Kazacos who investigated G2 V-Br flow battery using HCl as a supporting electrolyte [150]. PNNL revisited this concept showing that chloride-based electrolyte can stabilize vanadium and as the effect all vanadium forms are stable with the concentration of 2.5 mol L^{-1} between -5ºC and 50ºC. This idea has led to ca. 70% energy density enhancement in much extended temperature range as compared in Tab. 4 [108].

Tab. 4 Various types of VRFB battery. Based on [108].

Generation	***Type***	***Electrolyte***	***$V_{concentration}$ mol L^{-1}***	***Specific energy***		***Thermal stability ºC***
				Wh kg^{-1}	***Wh L^{-1}***	
G1	VRFB	V/H_2SO_4	1.5-3	15-40	20-55	10-40
G2	V-Br RFB	V/HBr/HCl	2-3.5	25-50	35-70	0-50
G3	VRFB	V/H_2SO_4	2-2.7	25-35	35-55	-5-50

Mixed acid solution idea was also successfully realized using methanesulfonic acid (MSA) addition. An enhanced energy density of VRFB was achieved with 2 mol L^{-1} vanadium solution in 1.5 mol L^{-1} CH_3SO_3H and 1.5 mol L^{-1} H_2SO_4 mixture [144]. Other organic and inorganic additives have been comprehensively studied. Much slower capacity fade rate was monitored with phosphate salt ($NH_4H_2PO_4$) [151]. Moreover, it has been proven that addition of metal ions to the electrolyte enhances energetic efficiency through catalytic effect. As the example, Bi^{3+} nanoparticles dissolved in the negative electrolyte improve significantly the sluggish kinetics of V^{2+}/V^{3+} redox pair [152]. Other metal-based additives cover Mn^{2+}, In^{3+} or Cr^{3+} ions [153, 154]. The stability of V(V) solution was ameliorated *via* addition of d-sorbitol to electrolyte; its –OH groups provide the active sites for transfer of electron [155]. Similar effect for VO^{2+}/VO_2^+ pair was achieved by Wang *et al*. who proposed several compounds for the electrolyte, such as methyl orange, Triton X-100 surfactant, sodium lignin sulfonate or polyvinyl alcohol (PVA) [156]. Summarizing, series of different additives have been investigated. However, inorganic additives seem to be more stable. Mostly organic compounds oxidize to CO_2 form simultaneously reducing VO_2^+ to VO^{2+} [144].

3.5.3.2. Membrane

The membrane in VRFB plays the main role; firstly, it physically separates the electrodes from short-circuiting. Secondly, it prevents cross-mixing of electrolytes for positive and negative electrode. Last, but not least, it facilitates the ions transport to complete the circuit during the current flow [110, 111]. Therefore, usually cation exchange membrane is used for VRFB since it provides H^+ transport necessary for the VO^{2+}/VO_2^+ reaction [110, 157].

The key requirements for the ideal membrane:

i) *high chemical stability* over the battery operation temperatures, strong oxidizers and supporting electrolytes (strong acids or bases); no biological fouling is essential

ii) *high mechanical endurance* against pumping, pressure or breakage

iii) *low-cost*

iv) *high ionic conductivity* – the higher conductivity, the smaller ohmic drop and higher voltage efficiency

v) *high ionic selectivity* to minimize cross-mixing or cross-over

The last two requirements are essential. Nevertheless, they compete between each other; therefore, the compromise for each RFB needs to be adjusted to obtain the most satisfactory battery behavior [110].

Generally, ion-exchange membranes (either cation or anion-exchange) are usually used for RFB application [139]. Nevertheless, some studies investigated amphoteric membranes or non-ionic ones [158, 159]. There are only few types of RFB that do not require membrane usage [135].

Currently, perfluorinated polymer membrane, i.e., Nafion™ seems to have the perfect characteristic for VRFB. Its thickness impact was in detail studied by J. Xi using N-112 (50µm), N-1135 (88 µm), N-115 (125 µm) and N-117 (175 µm) membranes [160]. The result showed that the thicker membrane, the lower vanadium permeability and the higher ohmic drop. Therefore, N-115 seemed to be the most appropriate one for VRFB application since the balance between ionic conductivity and selectivity is maintained. However, N-212 was found to be a perfect solution for high current density application. Beside Nafion™

advantages (stability in acidic, highly oxidative environment), its costs forced the scientist to find novel, low-cost alternatives. Nafion-modified membranes have been recently extensively studied including SiO_2, TiO_2, sulfonated polyether ether ketone (SPEEK)/WO_3 composites) [161-163]. Additionally, non-fluorinated membranes such as polyether ketone (PEK), polyether sulfones (PES), polybenzimidazoles (PBI) revealed good performance to act as the replacement for Nafion^{TM}. It is also worth mentioning that considerable attention was put on anion exchange membranes, since they can reduce vanadium cross-over. In practice, however, they block also proton transfer and reveal higher resistances [158, 164, 165].

3.5.3.3. Electrodes

The electrodes for redox flow batteries have a different role than in the conventional secondary batteries. Most importantly, they do not undergo through any reaction by itself, however, they provide a platform for vanadium redox reaction that happens on electrode surface. Secondly, the electrodes should serve as channels for electrolyte that has to flow through electrode. Therefore, porous, three-dimensional structure is an essential requirement for RFB electrodes to provide a uniform distribution of the electrolyte [108].

Additionally, an ideal electrode should possess following properties:

i) *chemical stability* – an inertness towards strong acids (supporting electrolyte) and oxidative or reductive environment (VO_2^+ or V^{2+}, respectively) is essential;

ii) *low-cost and availability* – inexpensive and easily manufactured electrodes can promote a wider RFB application. Therefore, simple carbon electrodes seem to have a better future than metal-based ones;

iii) *good compression rate* – it has been proven that compressible electrodes can reduce ohmic resistance. One should mention that an optimal compression rate (25-50%) has to be kept to ensure electrolyte permeability and no pressure changes [166];

iv) *good mechanical stability* against constantly pumped electrolyte;

v) *wide potential range* – the electrodes should resist much wider electrochemical window as the RFB operates; some side reactions, e.g., oxygen or hydrogen evolution must not damage them;

vi) *good electrochemical reaction activity* which ensures reaction reversibility;

vii) *good electrical conductivity* in order to minimize the resistance in RFB; very often excellent conductivity compete with favorable electrode reactivity since, e.g., oxygen-containing groups are the active-sites which also decrease electrode conductivity;

viii) *high effective surface area* – porous structure is necessary to ensure active sites for redox reaction; materials functionalization ensures a higher number of active sites at the expense of conductivity [167-169].

3.5.3.3.1. Types of electrodes

Development of the ideal electrode for redox flow battery application is one of the current research challenge. To meet above-mentioned requirements intensive studies has been carried out. Up to now, various electrode materials have been developed including carbon-based materials, conductive plastics (carbon-polymer composites), metals and metallic oxides [108, 120, 170]. Tab. 5 summarizes the advantages and disadvantages of various types of electrode materials for RFB application. It was found out that carbon-polymer composites suffer from poor electrochemical activity due to low conductivity and low surface area [171]. Some of composites with high-carbon loadings are quite acceptable; however, results of Skyllas-Kazacos *et al.* indicate that carbon-impregnated current collectors can improve energetic efficiency of VRFB [172]. Higher electrochemical activity exhibits all the metallic materials usually based on precious metals (Au, Ir, Pt, Ru) or their oxides. Yet, their high costs, short-term stability and electrocatalytic activity towards oxygen/hydrogen evolution reaction (e.g., dimensionally stable anode (DSA) with IrO_2 nanoparticles) exclude them from practical applications [108].

Tab. 5 Comparison of electrode materials for VRFB. Adapted from [108].

Material		**Electrochemical activity**	**Conductivity**	**Active surface area**	**Electrochemical window**	**Cost**
Carbon-based	**CF**	++	+++	++	+++	+++
	GF	++	+++	++	+++	+++
	CP	++	+++	+	+++	+++
	CNTs	+++	+++	+++	++	+
	GO	+++	++	++	++	+
	graphite, graphene	+	+	+	+++	+
Condu ctivve	**carbon-polymer**	++	++	+	+++	+++
Metal-based	**noble metals**	+++	+++	+	+	+
	DSA	+++	++	+	+	+
	other metallic oxides	++	+++	+++	++	++

3.5.3.3.2. Carbon materials and their treatment methods

It seems that carbon-based materials are one of the best candidates for RFB electrodes. Among carbonaceous materials, different types can be distinguished including carbon felts (CF), graphite felts (GF), carbon papers (CP), carbon nanotubes (CNTs) or graphite [108]. CF and GF are mostly used for VRFB. Skyllas-Kazacos demonstrated that polyacrylonitrile (PAN)-based GF performance has much suitable characteristics than rayon-based one [170]. CP as a flat fiber-sheet possesses slightly too small surface area, therefore to correct this issue usage of three layers of CP was proposed by M.M. Mench e*t al.* [173]. Beside many disadvantages, carbon-based electrodes are still materials with tunable properties of low-cost and good electrical conductivity. In fact, their poor electrochemical activity, influencing sluggish reaction rate and poor kinetics, forced the scientists to implement corrective actions. This implies to heat, chemical and electrochemical treatments [108].

Thermal treatment

Heat-treatment stands for the easiest, inexpensive, low-demand surface modification method. Already in 1992 the group of Skyllas-Kazacos *et al.* scanned the properties of GFs treated in various temperatures and times [174]. 400ºC was found to be the optimal temperature allowing wettability and conductivity of GF to be significantly improved. Such sacrificial GF properties were obtained due to oxygen-functional groups incorporation (C=O and C-OH), which are the active-sites for vanadium oxidation/reduction reaction. XPS studied showed that mostly phenolic groups (C-OH) impact the electrochemical performance of VRFB. The role of oxygen-abundant groups on carbon surface is essential for reversible vanadium redox reaction [127, 175]. Skyllas-Kazacos *et al.* proposed the mechanism which clarifies the significance and role of oxygen in VRFB [167, 176]. The process was divided into 3 steps as seen in Fig. 13. Firstly, there is an ion exchange process between vanadium ions from electrolyte and H^+ ions from phenolic groups on carbon surface. Secondly, O atom from C-OH group is transferred to VO^{2+} (when the positive side for VRFB is considered) *via* C-O-V bond. Third step involves ion exchange between vanadium formed on electrode surface and hydrogen ions in the electrolyte. Finally, VO_2^+ diffuses back to the electrolyte. The similar mechanism is presented for the negative side of the battery, and it is reversible according to the process direction (charging or discharging).

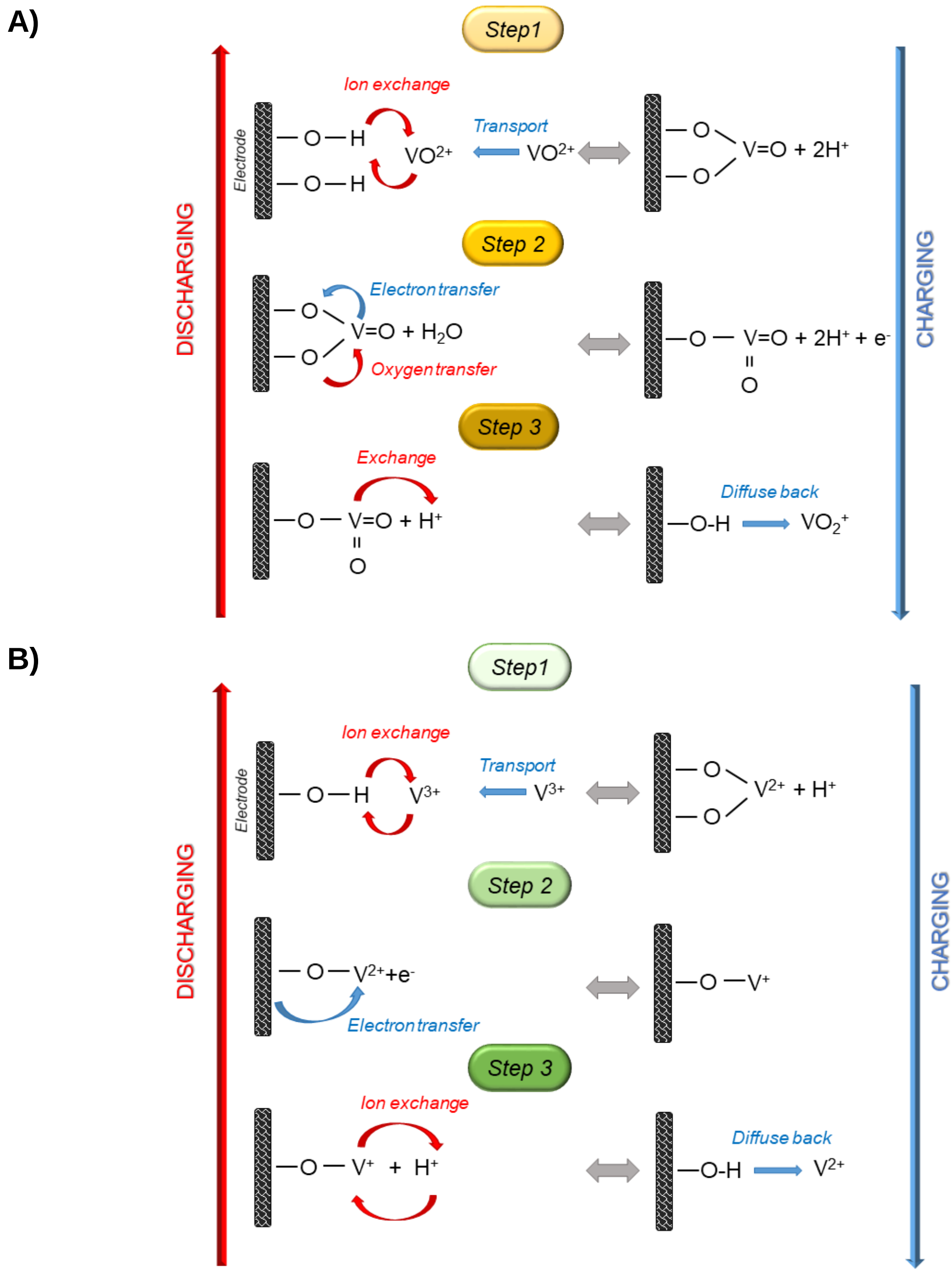

Fig. 13 Schematic illustration of vanadium reaction on oxygen-rich carbon surface for A) the positive; B) the negative side of VRFB. Based on [176].

Different studies about GF thermal treatment were indicated. Park *et al.* reported that mild oxidation of CF (500ºC for 5 h) can improve VRFB energetic efficiency even for 500 cycles. The studies highlighted the relationship between electrochemical performance of VRFB and the nature of reaction sites (types and quantity). Independently on the modification method used, vanadium reactivity relies on active surface area, which increases with surface-functionalization; however, the conductivity is also crucial. Therefore, the number of surface groups needs to be optimized; the compromise between conductivity and oxygen-containing groups is always being found [175, 176].

Not only the surface treatment was carried out in the air atmosphere; some studies reported that ammonia or its mixture with oxygen forms an interestingly functionalized carbon surface. Nitrogen and oxygen content of PAN-based graphite electrodes treated in 1:1 NH_3:O_2 for 5 h at 700ºC equal to 8% and 32%, respectively [177]. It was found that nitrogen-doped electrodes usually enhance electrochemical activity of VO^{2+}/VO_2^+ redox pair [178].

Chemical treatment

An important role of oxygen for vanadium redox reaction was also confirmed by wet chemical methods. Different solutions such as acids, bases, H_2O_2 or $KMnO_4$ were reported [167, 168, 179, 180]. It was found that chemical treatment removes all the impurities present on electrode surface; however, its etching force is slightly smaller than in the case of thermal treatment. During oxidation, C=C bond break takes place, forming a various types of surface group (hydroxyl, carbonyl or carboxyl) [108].

A large concentration of oxygen on CF surface was obtained *via* application of nitric and sulfuric acid [167]. Some of the research showed synergetic effect of thermal and chemical approach; an increased surface area and –COOH groups incorporation was obtained by 98 wt.% H_2SO_4 immersion (5 h) followed by oxidation at 450ºC at 2h [108]. Mixed acid treatment (HNO_3 and H_3PO_4 with ratio of 3:1) improved energetic efficiency (EE = 83%) of VRFB [104, 168]. Pre-treatment importance for effective CF modification was highlighted by Kim *et al.* showing that corona-discharge method can induce free-radicals on carbon surface; afterwards CF was sonicated in H_2O_2 solution forming a great amount of hydroxyl, carboxyl groups leading to the improved vanadium reactivity [181]. Similarly, to heat treatment, not only oxygen surface functionalities can be introduced to carbon matrix. It was found out that nitrogen-functional groups obtained *via* ammonia solution treatment can enhance energetic efficiency of VRFB up to 85% [182]. Other N-doping method employed *in-situ* polymerization of polypyrrole (PPy) with subsequent carbonization in $Co(NO_3)_2$ solution. Nitrogenous GF exhibited an improved electrochemical kinetics of vanadium reaction [183].

Other treatment methods

Electrochemical treatment was estimated as one of the most effective, controllable modification method for carbon oxidation [108]; it employs carbon as the anode while, e.g., platinum as the counter electrode. The anode is positively polarized (using galvanostatic or potentiostatic method) inducing oxyanions migration from applied electrolyte (e.g., acid) towards CF surface [167, 175, 184]. Some other novel techniques for functional groups formation were demonstrated; it includes plasma [176, 185, 186] or microwave treatment [186]. Additionally, it was demonstrated that the carbon nanotubes (CNTs) exhibit an electroactive properties allowing vanadium kinetics to be improved [183, 187].

3.6. Concept of “dual-circuit redox flow battery”

3.6.1. Energy density of redox flow batteries

The concept of RFB relies on energy storage in the electrolyte. The higher the difference between the Nernst potential of redox pairs, the higher the battery voltage and the higher the energy and power. Energy density is one of the limitations of RFB technology, since it strongly depends on the amount (practically on the concentration) of the electroactive substance dissolved in the supporting electrolyte. The energy density of RFB oscillates between 21-35 Wh L^{-1} and it is relatively lower than for other battery system [4]. In order to improve the redox active species solubility, one may increase the temperature or modify the electrolyte composition utilizing, e.g., „common ion effect” principle or mixture of different substances [144]. Moreover, the energy density depends on the electron transfer at the electrode surface and the number of moles of the species which can be converted during charging/discharging reaction.

3.6.2. Concept of “dual-circuit redox vanadium redox flow battery” for indirect water splitting

The relatively low energy density of RFB forced the current research interest to the development of the solution for this limitation. Primarily, it has been noticed that due to the low potential of V^{2+}/V^{3+} redox pair ($E^0 = -0.255$ V *vs.* SHE), hydrogen evolution is often present on the negative side of the VRFB [188]. However, for pristine VRFB, this reaction is a side effect limiting battery performance, since during the hydrogen evolution, hydrogen ions are consumed changing the pH of the electrolyte and finally the concentration of dissolved vanadium species [188]. The idea of “dual circuit redox flow battery” took the advantage of conventional VRFB and the feature of hydrogen evolution feasibility on the negative side of VRFB. Since, hydrogen is one of the most seeking energy resources, both ideas were connected forming so-called “dual-circuit vanadium redox flow battery” [189-192]. This system is a hybrid between VRFB and electrolyzer, where the electrochemical energy from battery can be converted into hydrogen with the idea of “indirect water splitting”. In the “dual-circuit flow battery” a conventional VRFB is combined with catalytic reactor placed in the separate unit on the negative side of the battery. The energy can be stored in two various ways. Firstly, VRFB can be conventionally charged/discharged *via* load. Secondly, on demand or in the presence of the energy surplus, VRFB can be chemically discharged producing at the same time hydrogen gas according to the equation:

$$2H^+ + 2V^{2+} \rightarrow H_2 + 2V^{3+} \tag{22}$$

Herein, it has to be highlighted that the hydrogen evolution takes place only on the negative side of VRFB (with V^{2+}/V^{3+} pair). Practically, the redox-active pair plays the role of mediator for chemical O_2 and H_2 evolution on respective compartments. The idea of indirect water splitting is depicted in Fig. 14 with vanadium-cerium RFB as the example.

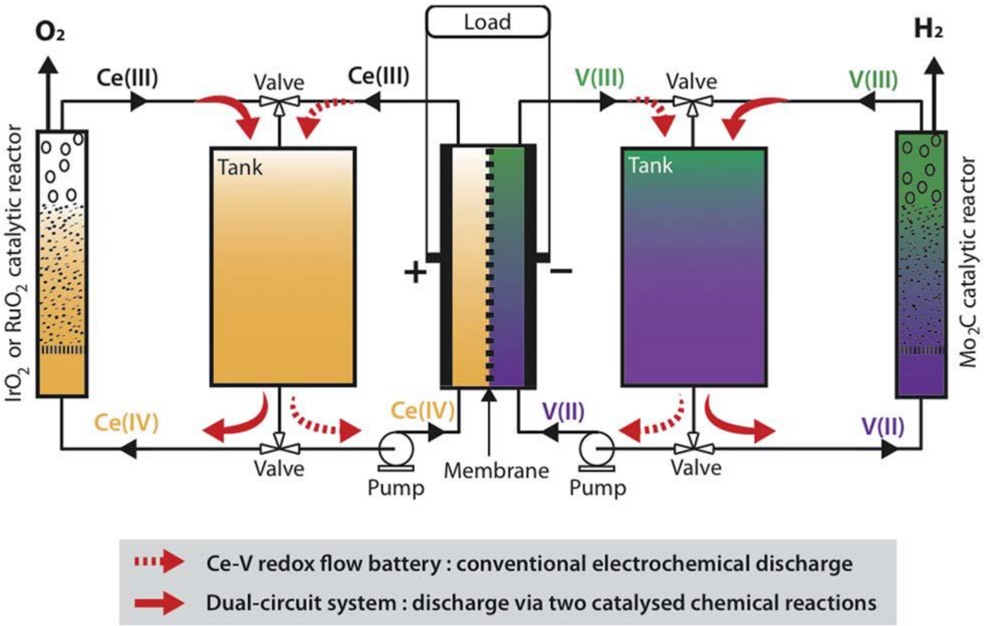

Fig. 14 The principle of “dual-circuit redox flow battery” with V-Ce system. Adapted from [191].

The charging reaction for V-Ce cell:

$$Ce^{3+} \leftrightarrow Ce^{4+} + e^- \qquad E^0 = 1.720 \text{ V vs SHE} \qquad (23)$$

$$V^{3+} + e^- \leftrightarrow V^{2+} \qquad E^0 = -0.255 \text{ V vs SHE} \qquad (24)$$

Once the V-Ce battery is charged, V^{2+} species can be transported into external reactor to be chemically oxidized to V^{3+} species (with the help of catalyst) and return to V-Ce cell. Similar process is proceeded on the cerium side with simultaneous oxygen evolution. This step is essential since to balance the “dual-circuit system” one should consider discharging of the cerium side (Ce^{4+} reduction). Moreover, as seen in Eq. 22, during the hydrogen evolution, protons are consumed and the pH of the electrolyte solution changes. Therefore, water oxidation is inevitable to deliver equal number of protons and charge balance of the positive side of V-Ce battery according to the equation:

$$2H_2O + 4Ce^{4+} \rightarrow O_2 + 4H^+ + 4Ce^{3+} \qquad (25)$$

Both hydrogen and oxygen evolution reactions require the catalyst presence to lower the overpotential of respective reaction [193-195]. Hydrogen evolution reaction (HER) can undergo with various catalysts (e.g., Ir, Pt, Ru). However, for “dual-circuit RFB system” purpose, it has been demonstrated that molybdenum carbide is sufficiently active and less expensive than precious metals [189-192]. Moreover, in case of V-Ce system, application of cerium is advantageous due to the higher redox potential of cerium ($E^0 = 1.44$ V *vs*. SHE in sulfuric acid) than for water oxidation. The indirect water splitting concept has also another advantage; physical separation of HER and OER allows the required catalyst to be longer active since it works only under reductive or oxidative conditions.

The “dual-circuit flow battery system” was successfully realized with VRFB system. The CellCube VRFB was purchased from Gildemeister Energy Solution and placed in Martingy (Switzerland). The electrolyte contained 1.6 mol L^{-1} vanadium species dissolved in 2 mol L^{-1} H_2SO_4. Its volume was equal to 1000 L of each tank supplying 10 kW/40 kWh. The cell was constructed from 6 stacks of 20 cells (A4 size) connected in series in 3 strings. The hydrogen catalytic reactor (Fig. 15) was designed to fit the battery; it comprises of 8 stages filled with 800 g of Mo_2C catalyst which is supported on Denstone beds to facilitate the HER by ensuring higher available surface area.

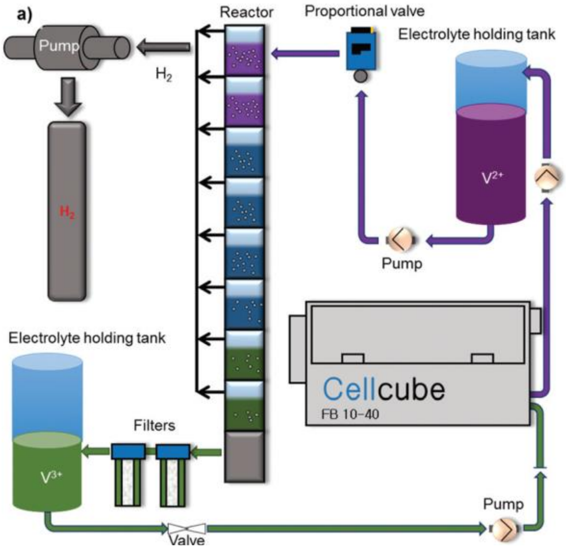

Fig. 15 The scheme of hydrogen reactor fitted to VRFB. Adapted from [191].

Despite high potential of cerium, the system suffers from corrosion issues on the positive electrode, cross-mixing of electrolyte and low solubility of cerium in sulfuric acid (ca. 0.1 mol L^{-1}). Therefore, in the scaled up “dual circuit VRFB” construction, reduction of positive electrolyte is realized by application of hydrazine. The hydrazine is oxidized to nitrogen according to the Eq. 26.

$$N_2H_4 + 4VO_2^+ + 4H^+ \rightarrow N_2 + 4VO^{2+} + 4H_2O \qquad (26)$$

Hydrazine was found out to be a good solution (100% conversion to N_2), although there are many maintenance problems (e.g., exothermic reaction with VO_2^+ species) and it is environmental unfriendly impact. There were other strategies proposed, e.g., sulfur dioxide (Eq. 27) or hydrogen sulfide (Eq. 28); however, their implementation would require additional engineering solutions (removal of produced sulfuric acid or solid sulphur).

$$H_2S + 2VO_2^+ + 2H^+ \rightarrow S + 2VO^{2+} + 2H_2O \qquad (27)$$

3.7. Summary

Over the last few years, the interest about the redox flow battery technology significantly increased due to significant activity towards energy storage from renewable sources (wind, sun). Several novel RFB chemistries were presented, however, their improvements are essential for commercial application. Beside many disadvantages (relatively low energy density) and difficulties (low pH environment) vanadium redox flow batteries are mostly commercialized system to date. Nevertheless, the optimization of electron transfer process at the carbon electrode surface is still under intensive development. This requires the oxygen-containing surface functional groups on the electrode surface. The role of oxygen is crucial to achieve the redox reaction reversibility during charging/discharging of the battery. It can be realized *via* adaptation of various carbon electrode oxidation methods while keeping the conductivity control. Additionally, the energy density of VRFB is still relatively low, therefore combination of VRFB with hydrogen generation station may easily increase battery storage capacity, practically without electrolyte volume increase. This VRFB and catalytic reaction circuit connection transforms the battery into a hybrid system which can store the electrical energy and produce the hydrogen on demand. Spatial separation of hydrogen and oxygen evolution in "dual-circuit flow battery" is advantageous since hydrogen gas produced does not require removal of oxygen as in typical electrolyzer [192, 196]. Moreover, it ensures the way for energy storage (e.g., in case of energy surplus from renewable resource) since the battery can be at the same time charged electrochemically and discharged chemically *via* catalytic tank.

Summarizing, there is an inevitable role of oxygen in VRFB system. Firstly, oxygen surface groups are necessary to play a role of active sites on the carbon electrode. With their support, vanadium oxidation/reduction reaction proceeds efficiently and reversibly. Secondly, when a "dual-circuit redox flow battery" system is considered, one might not neglect oxygen evolution reaction (OER). This process is surely one of the endpoint which completes the entire process of hydrogen production on demand. OER is a source of protons for indirect water splitting and its absence would require other chemicals (e.g., hydrazine) or cause VRFB performance fading in "dual-circuit redox flow battery".

The aim of the work

The aim of the work is the optimization of electrochemical capacitor (ECs) and redox flow batteries (RFBs) devices for future application. The research focuses on **the role of oxygen** in **redox flow battery** and **electrochemical capacitor** as well as evaluation of their long-term performance what is of particular importance for practical use. Since each of these systems is intrinsically based on the different energy storage/conversion principle, an individual approach for each cell was implemented.

In the first part of the thesis, the research work aims at the development of aqueous medium electrochemical capacitors in terms of the energy output and their lifetime. Since water medium ECs still suffer from certain issues at high voltages (water decomposition at U>1.23 V), **the ageing mechanisms** of pH neutral salt-based ECs **at high voltages** are **evaluated**. For this reason, *post-mortem* approach is used with wide-range of physico-chemical measurements (N_2 sorption at 77K, elemental analysis, XPS and Raman spectroscopy). Thereby, an insightful comparison between ECs with various capacitive ($LiNO_3$, Li_2SO_4) and faradaic (KI) electrolytes was made.

The detailed studies of oxygen content changes on the individual electrodes allowed ECs ageing reasons for individual system to be elucidated. Therefore, various **improvement strategies for aqueous medium ECs at high voltages** were proposed. The evaluated concepts aim at environmental friendliness and cost-free technologies which significantly extend ECs lifespan at high voltages.

High oxygen content significantly reduces carbon electrode conductivity, however, its presence is inevitable for vanadium redox reaction in RFB. Hence, the next part of the thesis aims at development of oxidation method for carbon felt electrodes. Herein, mild oxidant ($LiNO_3$ salt) was proposed and its influence on physico-chemistry of carbon at different conditions is elucidated. These studies allowed **the influence of carbon felt oxidation on vanadium reactions reversibility** to be determined.

Another research goal is the improvement of “dual-circuit vanadium redox flow battery”. This system operates beyond RFB limitation (low energy density) producing hydrogen on demand in the separate catalytic tank *via* indirect water splitting. However, to ensure protons for hydrogen production, complementary process is necessary. Electrochemical water oxidation performed in vanadium-oxygen cell is therefore considered. Different cell *configurations* are proposed to obtain the most **efficient** and **long-term operating "dual-circuit vanadium redox flow battery"**. Summarizing, oxygen presence is not only necessary in the form of surface groups on carbon felt for improved VRFB performance. Oxygen evolution is indispensable for efficient operation of "dual-circuit vanadium redox flow battery" realized with vanadium-oxygen cell. In this way, such unique concept additionally allows a pure source of hydrogen and oxygen to be obtained.

Chapter II

Ageing process of water-based electrochemical capacitor elucidated via post-mortem analysis

Publications:

P1: *Mechanism of the performance fading of carbon-based electrochemical capacitors operating in a* $LiNO_3$ *electrolyte*

P2: *Ageing mechanisms in electrochemical capacitors with aqueous redox-active electrolytes*

P3: *Revisited insights into charge storage mechanisms in electrochemical capacitors with* Li_2SO_4*-based electrolyte*

1. Summary of publications

Electrochemical capacitors (ECs) have attracted the worldwide research interest over the last decades mainly due to their excellent power capabilities (up to 10 kW kg^{-1}) and relatively long lifespan (up to 10^6 cycles) [5]. However, besides many advantages, ECs still suffer from moderate energy density (ca. 2-10 Wh kg^{-1}) compared to batteries (ca. 100-200 Wh kg^{-1} for Li-ion technology) [197]. It is especially evident in aqueous medium ECs where maximum operation voltage is limited by water decomposition voltage to $U = 1.23$ V [41, 55, 83, 198]. Water-based ECs are preferred due to electrolyte environmental friendliness and relatively high conductivity (e.g., 1 mol L^{-1} Li_2SO_4 - 60 mS cm^{-1}) which influences the higher power densities [55]. In this context, it is of particular importance to improve the energy density (E) values *via* specific capacitance (C) or cell voltage (U) increase according to equation $E = 0.5CU^2$ but still retaining a sufficient cycle life. Therefore, the main issue addressed in Chapter II is to identify the ageing phenomenon of carbon/carbon symmetric ECs operating in water-based medium at high voltages or with redox-based electrolyte. It is assumed that *via* performance fade mechanism elucidation, it is possible to counteract the ageing reasons. This knowledge allows the energy density value to be boosted with simultaneous long-term performance retention.

Chapter II summarizes the work included in three different publications which are based on the same research methodology, i.e., capacitor ageing phenomenon analysis using *post-mortem* approach. However, different aspects were considered in each individual paper. The research concerns the studies about pseudocapacitive and capacitive electrolytes operating in pH neutral medium. The influence of applied voltage on ECs lifespan was studied in paper **P1** entitled *Mechanisms of the performance fading of carbon electrodes operating in a $LiNO_3$ electrolyte* (Journal of Power Sources 438, 227029, 2019). Secondly, ECs failure reason of sulfate-based electrolyte was evaluated in **P3** entitled *Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4-based electrolyte* (Energy Storage Materials 22, 1-14, 2019). Last, but not least, redox-based electrolyte (1 mol L^{-1} KI) long-term behaviour was observed in **P2** entitled *Ageing mechanisms in electrochemical capacitors with aqueous redox-active electrolytes* (Electrochimica Acta 311, 211-220, 2019).

Herein, the impact of electrochemical lifetime test (*floating vs. cycling*) was insightfully compared. All the studies gathered allowed the influence of electrolyte type to be fully observed.

The same research methodology was applied for the different EC systems. In order to elucidate the capacitor failure causes so-called *post-mortem* method was applied (Fig. 16). Firstly, all the systems were assembled in Swagelok® cell with stainless steel (316L) current collectors and selected water-based electrolyte. For those studies highly porous (S_{BET} = 1841 m^2 g^{-1}) carbon cloth electrode (Kynol 507-20) has been chosen. It is a self-standing material; therefore, a binder presence is herein eliminated. Secondly, the assembled system was electrochemically aged until end-of-life criterion, i.e., 20% of initial capacitance loss recommended by International Standard IEC 62391-1 [77-79, 81]. For the electrochemical studies, two various electrochemical protocols (*cycling* or *floating*) were used. *Cycling* procedure consists of repeatable charging/discharging cycles performed at constant current density, i.e., 1 A g^{-1}. Contrary, each *floating* sequence included three charging/discharging cycles (at 1 A g^{-1}) followed by 2 h voltage hold at elevated voltage. Since the ECs system is exposed for a longer time to harsh condition (maximum voltage), *floating* test is well-known as accelerated ageing procedure [80]. After electrochemical studies, the aged electrodes were extracted from Swagelok® system and cleaned with distilled water to remove the salt residues from electrolyte. Next, the comprehensive *post-mortem* physico-chemical analyses were performed on the aged carbon cloth electrodes (separately for positive and negative one) and the obtained properties were compared to the pristine electrode properties (before any electrochemical protocol). The research included various techniques such as: N_2 sorption at 77K, scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), elemental analysis (EA), Raman and X-ray Photoelectron Spectroscopy (XPS).

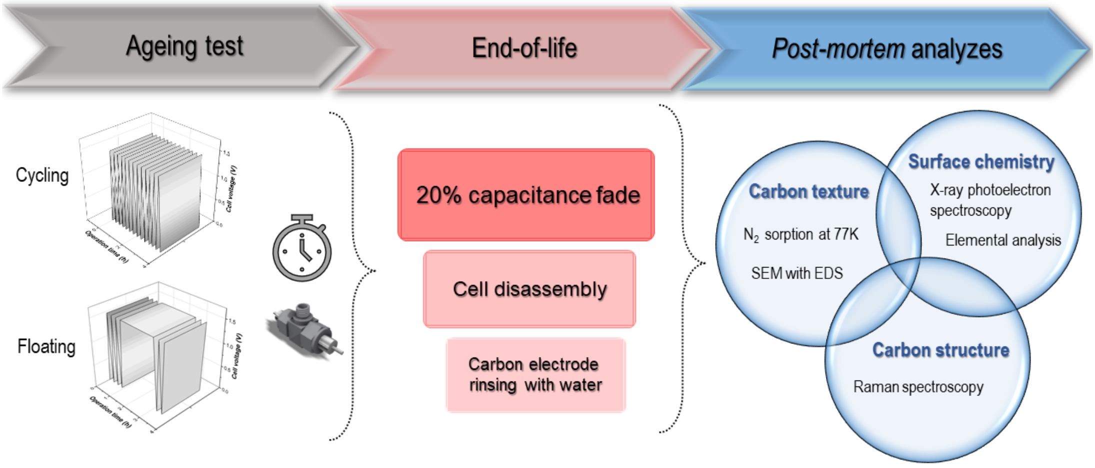

Fig. 16 The scheme presenting post-mortem protocol applied for ECs lifespan investigations.

The entire research performed in frame of this capacitor ageing topic has a broad character since it involves many electrochemical techniques linked with physico-chemical results. On this basis, electrodes microstructure, chemical composition and porosity changes of capacitor electrodes after long-term performance were estimated. Moreover, it is worth highlighting that *post-mortem* approach was chosen for ageing phenomenon elucidation since it allows real symmetric capacitor system to be fully investigated. Indeed, *in-situ* measurements are currently up to date, however, one should keep in mind that quite often only one electrode is investigated (not a full ECs system) with an excess of electrolyte [93, 199, 200]. Therefore, *post-mortem* studies better reflect the commercial capacitor behaviour.

Based on performed research, it cannot be directly estimated which is the maximum operating voltage for electrochemical capacitor. This value should be always verified by long-term performance studies, when two end-of-life criteria (2-fold resistance increase and 20% of initial capacitance fade) are reached simultaneously. However, depending on user demand, ECs can operate longer at lower voltages or for a shorter time with much higher energy density. Interestingly, based on S_{BET} values interpretations, two different ageing mechanisms (voltage dependent) with $LiNO_3$ electrolytic solution were identified. It seems that up to 1.5 V, there is a reversible NO_3^- ions reduction on the positive electrode and the carbon electrode is progressively oxidized. However, the reversibility of this reaction decreases over time resulting in a decreased S_{BET} value for about 20-30% after the ageing test (80% of relative specific capacitance fade). When U>1.5 V, it is estimated that carbon oxidation and carbon corrosion occur. Moreover, electrolyte decomposition with evolution of various gases (e.g., CO_2, CO) takes place.

The electrochemical and physico-chemical data proved that the main ECs ageing reason is related to the oxidation of the positive electrode. A notable contribution of this parameter is detrimental to capacitor system. The oxygen content increased almost 5 times (from 7 wt.% to 32 wt.%) for the positive electrode after the *floating* tests at 1.6 V (Fig. 17). However, when the capacitor is stopped at the same relative capacitance value, independently on voltage applied, all the electrodes reveal same qualitative and quantitative changes (proven by XPS and EA).

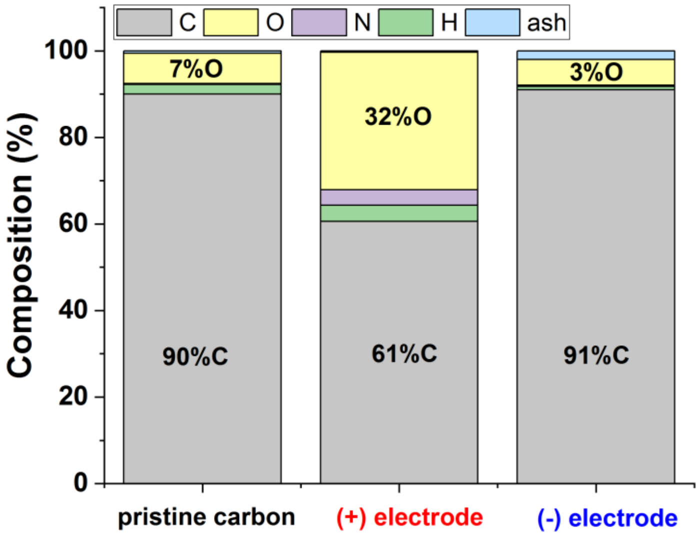

Fig. 17 Elemental composition of electrodes (positive and negative) after the floating test (1.6V) in comparison to the pristine one.

The oxidation of positive electrode is harmful for the system. Moreover, a solid-state deposit which can originate from CO and CO_2 evolution is attached to the electrode surface after the *floating* test. It is postulated that it partially blocks carbon porosity and induces capacitance drop. It is worth highlighting that solid-state deposit presence was also observed by SEM on the negative electrode. However, the negative electrode does not contribute to ageing phenomenon in ECs with nitrate-based salt. S_{BET} values for the negative electrode do not differ much from the pristine one. The difference of max. 100 m^2 g^{-1} could imply the carbon porosity clogging due to deposit presence.

A similar observation (positive electrode oxidation) has been drawn for sulphate- and iodide-based electrolytes. Since, the positive electrode is always exposed to oxidative conditions during capacitor charging, the oxygen content increases independently on electrolyte applied, introduces surface groups and affects the electrode conductivity. Moreover, this process is more pronounced with *floating* protocol than with *cycling*. *Floating* test triggers an accelerated ECs fade observed as much more pronounced resistance increases. Nevertheless, carbon structure changed more after galvanostatic cycling due to reversible ionic fluxes during repeatable charging/discharging cycles. Additionally, it has been observed that when redox-electrolyte (1 mol L^{-1} KI solution) played a role of electrolyte in ECs, there is a hindered access to carbon porosity (observed as S_{BET} fade) both on the negative and positive capacitor compartment. It was estimated that iodide species migrate towards the negative electrode during long-term performance. Therefore, to block this process, cation-exchange membrane (Nafion^{TM}) application is inevitable.

Summarizing, it was found out that ageing mechanisms of ECs strongly depend on the electrolyte type and electrochemical protocol applied (*floating vs. cycling* test*,* applied voltage*).* The positive electrode oxidation is present in each case, whatever the system is. However, it does not stand for one reason of capacitor failure. Additionally, one can observe solid-state deposit formation or electrolyte decomposition. Nevertheless, it can be concluded that there is a detrimental role of oxygen in electrochemical capacitors. In all the systems tested, oxygen functionalities on carbon surface are detected during long-term operation. This effect blocks the specific surface area of porous carbon which is a key component taking part in electric double-layer formation. It affects energy storage mechanism of electrochemical capacitors.

Chapter III

Possible methods for capacitor lifetime extension

P4: *Enhancing capacitor lifetime by alternate constant polarization*

1. Summary of publication and unpublished data

The studies presented in the previous chapter allowed the failure mechanisms of symmetric water-based capacitor to be fully identified. The key findings show that each system has to be optimized individually and to inhibit capacitor failure, it is imperative to counteract its cause. The studies presented in this chapter are fully focused on such target. Two preventive approaches to meet the challenge of ECs long durability with nitrate-based electrolyte can be distinguished:

i. development of novel exploitation protocol, i.e., *alternate floating*
ii. reuse of the negative electrode

Alternate constant polarization exploitation protocol (P4)

The previous studies presented in Chapter II proved that symmetric ECs system based on lithium nitrate aqueous solution is affected by positive electrode oxidation and solid-state deposit formation during the ageing test. Interestingly, the negative electrode structural or textural properties does not change significantly. Taking into account such information, a novel exploitation protocol, i.e., *alternate floating*, has been developed (Fig 18). A significant increase of time (from 210 to 384 h) operation is observed. The research is presented in **P4** entitled *Enhancing capacitor lifetime by alternate constant polarization (Journal of Power Sources, 506, 230131, 2021).*

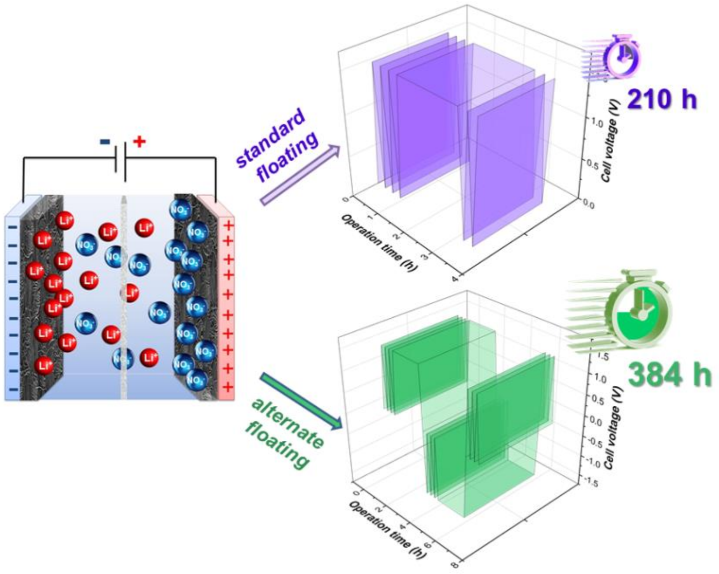

Fig. 18 Scheme of beneficial alternate floating vs. standard floating.

The idea is based on alternate use of positive and negative electrodes. In other words, during one *floating* cycle, the positive electrode is a positive pole. Then, it is repolarized and play the role of the negative one (in practice connection of the capacitor would be reversed). This idea is applicable only for the symmetric capacitive-based capacitors which form electric double-layer (EDL) during charging process. In case of redox-active species, repolarization would be detrimental since redox couple operate in narrow potential range only [6, 65, 201]. The scheme of different *floating* protocol is shown in the attached paper. *Standard floating* protocol has been compared with *alternate* (repolarization after each *floating* cycle) and *reversed* (one repolarization after $C/C_0 = 0.8$) ones. The research includes not only the electrochemical testing but also *post-mortem* analysis of carbon electrodes *via* N_2 sorption at 77K, SEM and XPS analysis. Various electrolytic solution concentrations were studied (0.2 to 5.0 mol L^{-1} $LiNO_3$). It was observed that conductivity of solutions affects the capacitance values. The lowest metrics has been obtained for 0.2 mol L^{-1} $LiNO_3$, however, the specific capacitance for the concentration of 0.5 - 5.0 mol L^{-1} differs only in few F g^{-1}. Interestingly, when the *alternate* polarization protocol is applied, it can be observed that the higher electrolyte concentration, the smaller lifespan improvement. It has been proven that ECs operation time can be almost doubled with 0.2 mol L^{-1} $LiNO_3$ solution, however, not much difference is observed for 5.0 mol L^{-1} $LiNO_3$. It is assumed that at higher electrolyte concentration, there is a hindered ions movement due to a higher solution viscosity. Therefore, when polarization is inversed, the ions exchange process (reorganization and movement) is much slower as in the case of lower electrolyte concentrations. In addition, it was observed that in case of organic based capacitors *alternate floating* has practically no impact. Therefore, it is believed that during polarization change with aqueous systems, some corrosion products/solid-state deposits can be partially dissolved. Therefore, in case of highly concentrated electrolytes (5 mol L^{-1} $LiNO_3$), there is not much improvement in ECs lifespan due to reduced number of water molecules. Taking into account few factors, it seems that moderate electrolyte concentration (0.5 mol L^{-1}) would be the best choice for *alternate floating* application. Firstly, there is still a significant improvement in ECs lifetime (ca. +50%). Secondly, a smaller electrolyte concentration reduces the expenses of capacitor assembly simultaneously showing almost identical operation time as 5.0 mol L^{-1}. Herein, it has to be mentioned that one of the main drawbacks of *alternate polarization* is the fact that the positive electrode is much more damaged as in the case of *standard floating.* Mainly, the higher oxygen content was detected by XPS as well as slightly smaller specific surface area is analyzed in the attached manuscript. Nevertheless, in contrast to *standard floating,* both electrodes (positive and negative) are equally damaged after *alternate floating* which proves that the assumed concept of full exploitation of the negative electrode is successfully achieved.

Re-use of the negative electrode

The second approach of capacitors lifetime improvement overlaps “zero waste” principle. It has been noticed that with nitrate-based electrolyte, the negative electrode after long-term operation does not change its structural and textural properties remarkably. Since the symmetric system is considered, the trial of negative electrode reuse has been performed.

Initially, as presented in Fig. 19, four identical capacitor systems were assembled with 1 mol L^{-1} $LiNO_3$ electrolytic solution. Carbon cloth (Kynol 507-20) was utilized as the electrode material for capacitor system. The systems were aged using *floating* protocol in relatively harsh voltage condition, i.e., at 1.8 V presented as *Configuration 1*. After reaching the end-of-life criterion ($C/C_0 = 0.8$), four ECs systems were disassembled, and the negative electrodes were recovered from the aged cells. The electrodes were washed out using the distilled water to remove all the residues from the aged electrolyte from *Configuration 1* and avoid salt crystallization on its external surface. Otherwise, skipping this step may cause pore clogging or a higher electrolyte concentration and incomparable conditions during *Configuration 2*. Therefore, washing is an essential step for negative electrode recovery. Afterwards, the electrodes were dried at 50^{o}C and further used to build the new cells shown as *Configuration 2*. Such combination allowed two already aged negative electrodes (from *Configuration 1*) to be reused in a new capacitor system. In other words, one of the negative electrodes from *Configuration 1* (e.g., A’) becomes the positive electrode in *Configuration 2*. However, the negative electrode from *system 2* (B’) still works as the negative in *system 5. Configuration 3* in the recycle process is analogous to the previous one. Such reuse process can be repeated as long as there are two negative electrodes (not affected by ageing process) available for new system assembly.

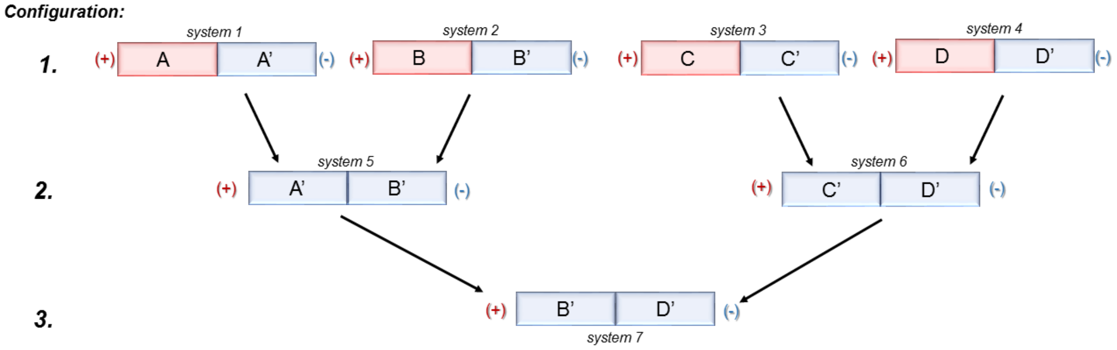

Fig. 19 The concept of the negative electrode reuse in the subsequent capacitor systems.

The capacitance fade curves recorded during subsequent *Configurations* are presented in Fig. 20 A-C. The capacitor cells with a 1 mol L^{-1} $LiNO_3$ electrolytic solution can generally operate ca. 40 h during voltage-holding ageing protocol at high voltage stress (1.8 V). As it can be noticed, the lifetime of the systems (5-7) with the reused electrodes is very comparable to the fresh one. Similar course of curve is recorded with the average *floating* time of 40 h. Interestingly, even if the system in the previous *configuration* was stopped at the relative capacitance value below 80%, there is still a proper response of the cell at the subsequent configuration. This observation directly confirms that negative electrode is not affected by ageing process and its structural/textural features are similar to the non-aged carbon (pristine one).

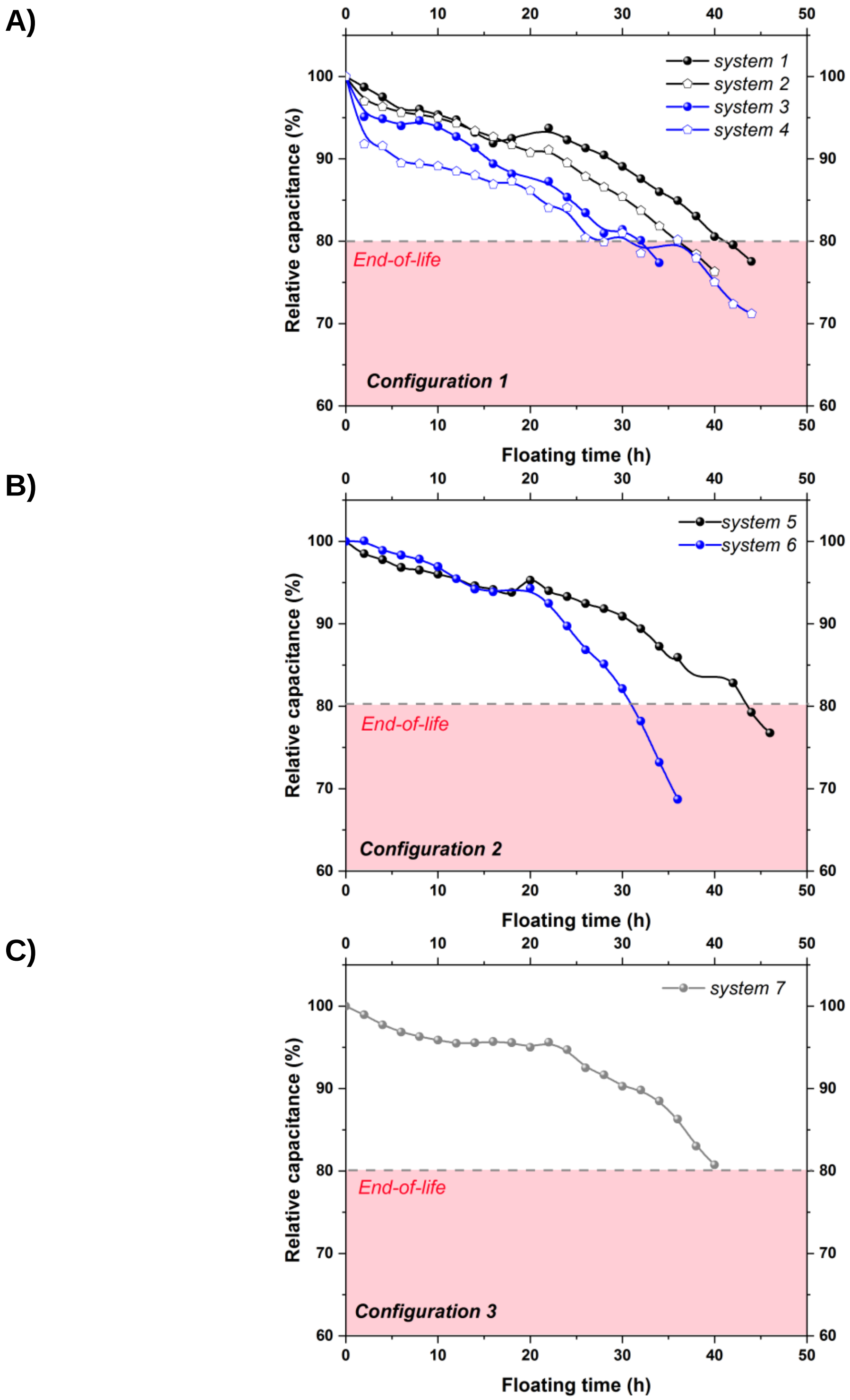

Fig. 20 Relative capacitance vs. floating time for the capacitors with a 1 mol L^{-1} LiNO$_3$ tested at 1.8 V: A) configuration 1; B) configuration 2; C) configuration 3.

The concept of the negative electrode reuse is additionally confirmed by other electrochemical techniques. Cyclic voltammograms (Fig. 21) were recorded at each *Configuration* before and after the ageing protocol described as 100% and 80%, respectively. The relatively low scan rate of 5 mV s^{-1} was used to monitor every change at each testing *Configuration*. However, the shape of the curves both before and after ageing at each *Configuration* are practically identical. This suggests that the failure mechanisms for each system even with the reused electrodes is the same.

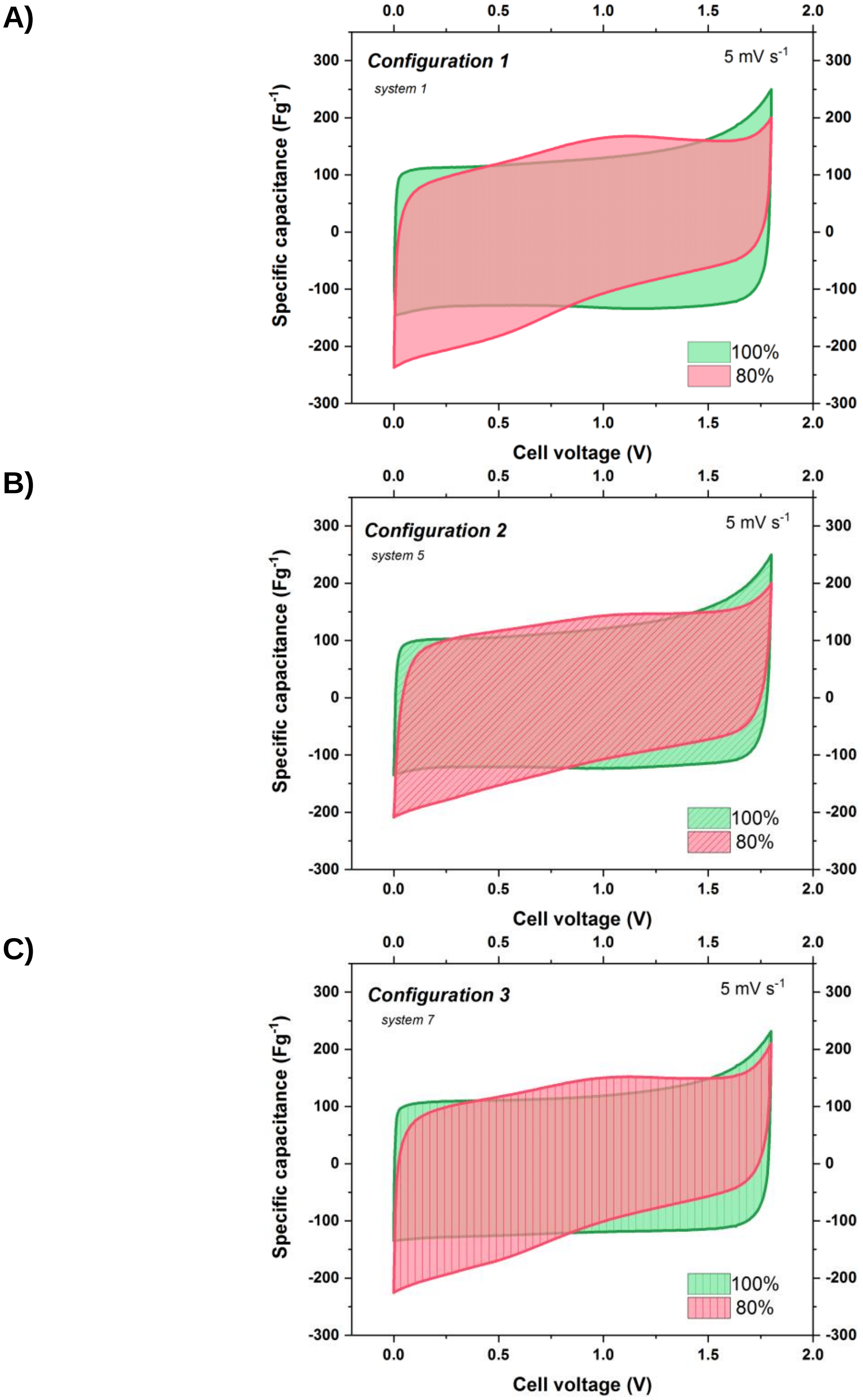

Fig. 21 Cyclic voltammograms (5 mV s^{-1}) recorded before and after ageing test with 1 mol L^{-1} $LiNO_3$ tested at 1.8 V: A) configuration 1; B) configuration 2; C) configuration 3.

Since the resistance is the second important factor determining capacitor state-of-health [77, 85, 202], impedance spectra were recorded before and after *floating* test during each reuse step. As remarked in Fig. 22A, the equivalent series resistance (ERS) values before ageing for *Configurations 1-3* practically overlap each other. The small increase (from 0.76 to 0.90 Ohm) might be affected by difference in system assembly or suggest negligible wear-out of the negative electrode during the previous *Configurations*. Similar trend is observed in Nyquist spectra after the ageing protocol (Fig. 22B). The ESR increases with each *Configuration*. Interestingly, when ESR percentage change is compared, 76% increase is recorded for the non-used (pristine electrodes). However, for reused electrodes, only ca. 50% of ESR is observed. Such observation might suggest that the reused electrodes are already “pre-tested” and reached the steady-state. Therefore, the ESR change is slightly reduced.

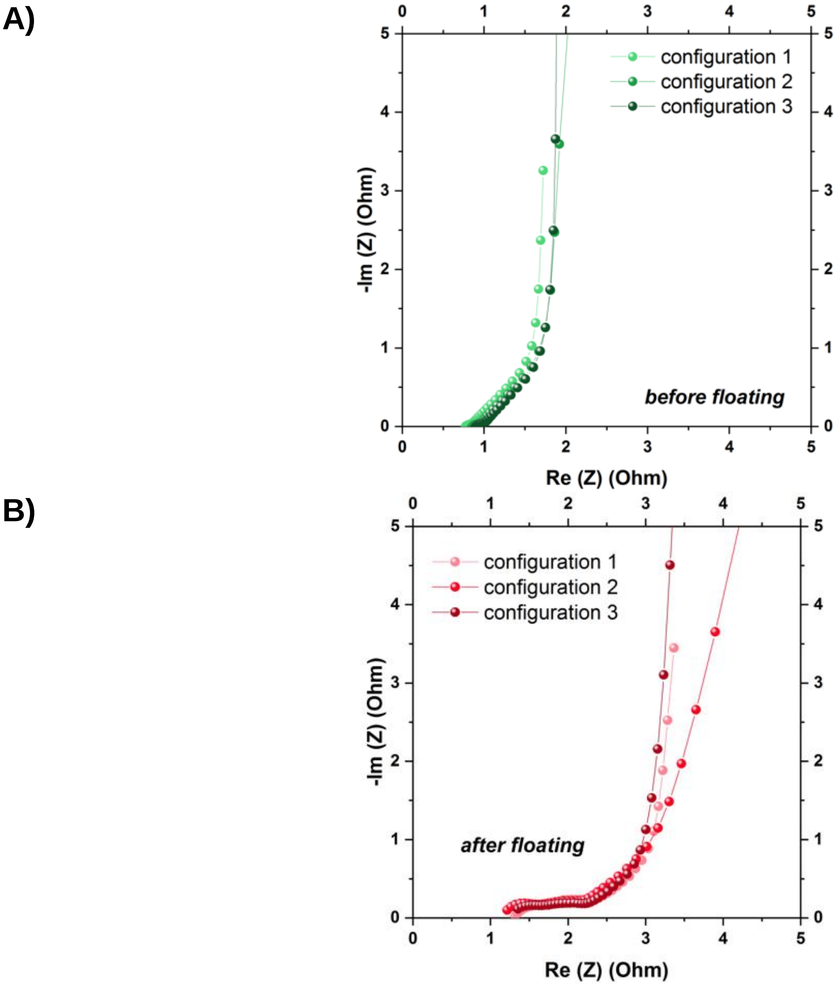

Fig. 22 Comparison of the impedance spectra recorded at 0 V for various configurations: A) before ageing; B) after ageing.

Summarizing, it has been demonstrated that both approaches (*alternate floating* and reuse of the negative electrode) allow the properties of the negative electrodes to be fully utilized resulting in capacitor lifetime improvement. Both solutions ensure eco-friendly, cost-free solutions for prolongation of capacitor usage according to the trend „less waste, more repairs". Therefore, not only the research should focus on completely novel technologies, which are often too expensive for real application, but also on the improvement of already existing solutions *via* in-depth understanding of their full performance and trials of their reapplication. Such actions of reuse/recycle/repairs would be beneficial for the environment, which currently suffers from pollution due to constant waste growth.

Chapter IV

Vanadium-oxygen cell studies

P5: *Vanadium-oxygen cell for positive electrolyte discharge in dual-circuit vanadium redox flow battery*

1. *Summary of publication*

"Dual-circuit vanadium redox flow battery" is a vanadium redox flow battery (VRFB) connected with a separate catalytic tank (a catalytic reactor placed in a secondary circuit) intended for hydrogen production [189-192]. Depending on user demand VRFB can be repeatedly charged/discharged without use of "dual-circuit" system or hydrogen evolution reaction ($E^0 = 0.000$ V *vs.* SHE) can be exploited in an external tank attached to the negative compartment of VRFB. This process can be proceeded due to low potential of V^{2+}/V^{3+} couple which is equal to $E^0 = -0.255$ V *vs.* SHE as it is presented in Fig. 23. It is worth highlighting that in the standard VRFB operation mode, eventual hydrogen evolution is a harmful process and can cause the complete failure of VRFB since it consumes protons while simultaneously changing pH and the concentration of the pristine electrolyte [126, 188, 203, 204].

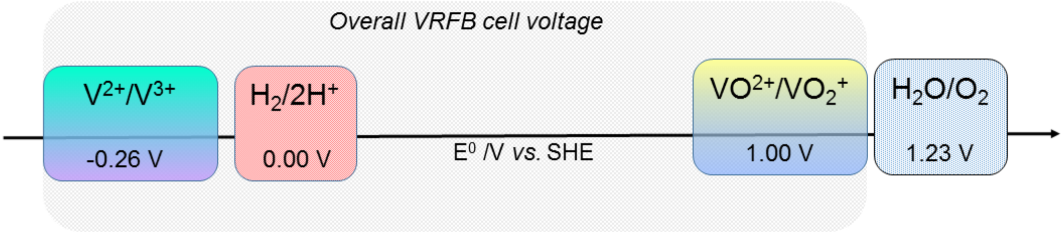

Fig. 23 Standard reduction/oxidation potentials of the reactions that might be expected during VRFB operation.

However, in "dual-circuit redox flow battery" low potential gap between $2H^+/H_2$ and V^{2+}/V^{3+} redox pair (Fig. 23) was exploited as an advantage giving the energy boost of VRFB through pure hydrogen evolution on the negative side of VRFB using a direct chemical reaction on Mo_2C catalyst [189-192]. In other words, when the VRFB is in a charged state, two processes can be driven, i.e., typical battery discharge or hydrogen generation in the external catalytic tank according to equation:

$$2H^+ + 2V^{2+} \rightarrow H_2 + 2V^{3+} \tag{29}$$

However, when the second mode is chosen (i.e., HER) protons are consumed and charge imbalance in VRFB is observed. In other words, during hydrogen generation the negative side of the battery is discharged from V^{2+} to V^{3}, while the positive one still remains in a charged state. Therefore, a similar process, i.e., discharge of positive compartment (reduction of VO_2^+ to VO^{2+}) is necessary to maintain proton and charge balance of the whole “dual-circuit VRFB” system. Electrochemical water oxidation on the positive side is a suitable reaction for this purpose since it can produce equal number of protons with simultaneous regeneration of positive electrode (reduction of VO_2^+ to VO^{2+}).

Nevertheless, due to the fact VO_2^+/VO^{2+} does not provide sufficient potential to produce O_2 spontaneously, the additional energy input is required. The idea was based on development of V-O_2 electrolyzer which can be coupled with “dual circuit RFB” presented in **P5** entitled *Vanadium-oxygen cell for positive electrolyte discharge in dual-circuit vanadium redox flow battery* (Journal of Power Sources, 439, 227075, 2019). Since generation of H_2 from VRFB requires additional energy input (VRFB must be firstly charged and when H_2 is generated the positive side of VRFB must be balanced), the main aim of V-O_2 cell is the minimum power input with high conversion rate (good performance at high current density).

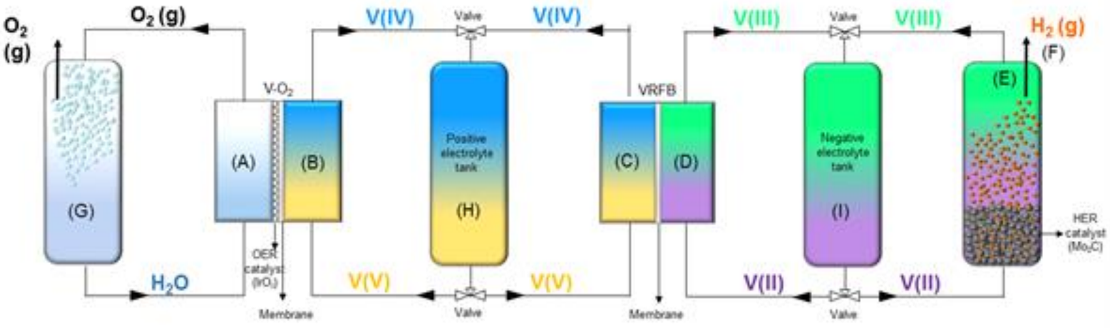

Fig.24 Dual-circuit vanadium redox flow battery with V-O_2 cell [205].

The system was constructed as it is presented in Fig. 24. The following reactions take place with corresponding indication of each compartment:

V-O_2

(A) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E^0 = 1.23$ V *vs.* SHE (30)

(B) $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$ $E^0 = 1.00$ V *vs.* SHE (31)

VRFB

(C) $VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^-$ $E^0 = 1.00$ V *vs.* SHE (32)

(D) $V^{3+} + e^- \rightarrow V^{2+}$ $E^0 = -0.255$ V *vs.* SHE (33)

<u>Dual-circuit</u>

(E) $V^{2+} \rightarrow V^{3+} + e^-$ $E^0 = -0.255$ V *vs.* SHE (34)

(F) $2H^+ + 2e^- \rightarrow H_2$ $E^0 = 0.00$ V *vs.* SHE (35)

V-O_2 cell was successfully integrated with “dual-circuit redox flow battery” and tested in various configurations to find the optimal solution. All the details concerning the electrochemical measurements, cells assembly and their connections are included in the attached paper and supplementary information.

First advantage of developed cell is that the system does not use any other chemical species, e.g. Ce that can poison the whole VRFB battery (as it was in the case of V-Ce cell [191, 192]). It simply consists of vanadium solution of both sides, so any cross-mixing can be quickly balanced by mixing all the tanks together and start the process from the beginning. Additionally, V-O_2 by itself (without “dual-circuit”) can be used for the adjustment of eventual VRFB state-of-charge imbalance. Moreover, water oxidation reaction was proceeded with the support of commercially available, dimensionally stable anode (DSA) with iridium-based catalyst (Fig. 25) which ensured a good stability of “dual-circuit system”. For hydrogen evolution, an inexpensive molybdenum carbide catalyst was utilized. This is a key feature of “dual-circuit” because in a typical electrolyzer two expensive catalysts would be required, e.g., Pt for H_2 and Ir/Ru for O_2 [206, 207]. Moreover, hydrogen produced from electrolyzer would require an additional purification while in “dual-circuit” VRFB system O_2 and H_2 are locally separated as presented in Fig. 24.

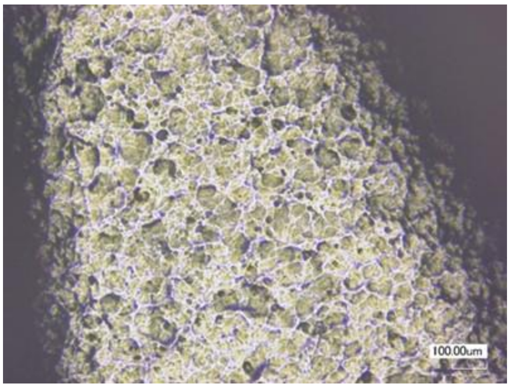

Fig. 25 Dimensionally stable anode mesh with iridium oxide as the catalyst for oxygen evolution reaction used in V-O_2 approach.

The idea of V-O_2 approach has been tested in various cell configurations in order to obtain the most promising results (the lowest voltage of V-O_2 cell). It has been proven that usage of VO_2^+ solution in 2 mol L^{-1} H_2SO_4 instead of sulfuric acid only as electrolyte on the positive side of V-O_2 cell (compartment A in Fig. 24) does not significantly change the performance of V-O_2 (Fig. S2 in the supplementary information of the paper). This approach allows the stability of the system to be maintained, since no vanadium concentration gradient is present in the system between compartment A and B. Moreover, vanadium solution in compartment A does not influence the stability of DSA. It has been found that replacement of carbon felt (CF) electrode into multiple layers of carbon paper (CP) can significantly improve VO_2^+ /VO^{2+} kinetics [173, 208]. Three-layers of CP were estimated as the most promising solution (Fig. S3 in the supplementary information of the paper). The total “dual-circuit RFB” efficiency with V-O_2 fluctuates between 43-65%, depending on the current density. An excellent system stability was obtained during the ageing test performed for 120 h at harsh conditions (high current density).

Therefore, it can be concluded that the investigated cell (V-O_2) can be proposed as a novel way for the discharge of the positive compartment of the battery. Taking into account all the previous solutions proposed for the positive electrolyte discharge, V-O_2 approach performs better still maintaining the idea of indirect water splitting where pure hydrogen is generated (it is locally separated from oxygen evolution) and no additional species are introduced to the system (hydrazine or cerium [94, 189-192]).

Chapter V

Alkali metal salt carbon felt oxidation on VRFB performance

1. Motivation of the work

As described in the literature review part of this PhD thesis, carbon felts are the commonly used electrodes for VRFBs. They are of low cost, highly available and acid-resistant flow-through electrodes which stand as the host for vanadium redox reaction [95, 120, 209]. Even though VRFBs are already commercialized, there are still some issues which could be improved. It was observed that some side reactions may lead to VRFB performance fading. Since, V^{2+}/V^{3+} redox pair operates at $E^0 = -0.255$ V *vs.* SHE, H_2 evolution is a competitive reaction on the negative side of VRFB which leads to electrolyte pH and concentration change [126, 188]. Moreover, carbon corrosion and oxygen evolution reaction on the positive side of VRFB cause the battery performance losses over time [127, 210-212]. To mitigate this effect, carbon felt surface modification is necessary [213-216]. It includes various oxidation methods with the most recognized and used industrially one – heat-treatment [170, 175, 217]. Some other studies include utilization of CF electrodes with noble metals, carbon nanotubes and many other cost-effective oxidation methods [217-219]. There is still a particular need to elaborate low-cost carbon-based material with good conductivity and sufficient activity to enhance VRFB properties. The studies carried out in the frame of electrochemical capacitor topic showed that nitrate salts may oxidize carbon material [220, 221]. Therefore, the research presented in the frame of this chapter aims at the development of relatively cheap and facile oxidation method for carbon felt surface oxidation using sodium nitrate salt. Both physico-chemical and electrochemical studies allow CF surface properties with the vanadium redox reaction behavior to be correlated.

2. Experimental

Two various carbon felt electrodes (GFD 4.6 and KFD 2.5) from SGL Carbon company (Germany) were used for the studies. Carbon felt electrodes were firstly pre-activated chemically in concentrated nitric acid (HNO_3). Afterwards, the materials were cleaned with distilled water, ethanol and dried in 60°C. As prepared electrodes were further treated with alkali metal salt in a molten state. Potassium nitrate was used. The melting temperature of KNO_3 salt equals to 334°C [222]. The samples were heat-treated with the presence of KNO_3 salt in various conditions (380-440°C) for 10 min in oxygen atmosphere (named e.g., GFD/KFD-380). Moreover, the two samples treated at 500ºC for 12 h with and without salt were compared (GFD-500 and GFD-500HT). In addition, samples treated in acid or in salt only were prepared. Tube furnace (Shinko company) was applied for those studies. After the treatment, all the CFs were washed extensively with distilled water in ultrasonic bath and dried again. The samples were tested electrochemically in three-electrode cell setup. Carbon felt electrodes played a role of the positive electrode with the diameter of 10 mm. Pt mesh was applied as the counter electrodes, whereas Hg/Hg_2SO_4 in 2 mol L^{-1} H_2SO_4 was a reference electrode with $E^0 = 0.674$ *vs.* SHE. Titanium current collectors were used. 0.1 mol L^{-1} $VOSO_4$ solution in 2 mol L^{-1} H_2SO_4 was the electrolytic solution. The samples were tested using cyclic voltammetry at 2 mV s^{-1}. Both vanadium redox pairs, i.e., V^{2+}/V^{3+} and VO^{2+}/VO_2^+ were studied in the separate electrochemical system. Additionally, physico-chemical properties of carbon materials were studied using X-ray photoelectron spectroscopy (XPS) and contact angle measurements. For water uptake measurements, carbon felt samples were soaked with 0.1 mol L^{-1} $VOSO_4$ in 2 mol L^{-1} H_2SO_4 for 30 s at room temperature. The water uptake (WU) was calculated according to the formula:

$$\mathrm{WU} = \frac{\mathrm{W_w} - \mathrm{W_D}}{\mathrm{W_D}} \tag{36}$$

where: W_w - sample weight after absorption [g]; W_D - sample weight before absorption [g].

3. Results and discussion

The properties of carbon materials are presented in Tab. 6, while their preparation scheme is shown in Fig. 26. Both CFs are made from the same precursor, i.e., PAN (polyacrylonitrile). The details about their preparation are not accessible since it covers company ‘know-how’. However, as indicated in brochure, thermal activation for pristine material is necessary [223]. KFD carbon felt is a carbonized material while GFD is a graphitized one. Therefore, GFD chemical resistivity is higher compared to KFD.

Tab. 6 Properties of studied carbon felts. Adapted from [223].

Properties	***Carbonized felt KFD 2.5EA***	***Graphitized felt GFD 4.6EA***
Fiber precursor	PAN	PAN
Nominal thickness, mm	2.5	4.6
Chemical resistivity	+	+++
Compressibility	+	+
Bulk density, g cm^{-3}	0.1	0.09
Area weight, g cm^{-3}	250	465
Open porosity, %	>90	94
S_{BET}, m^2 g^{-1}	0.6	0.4
Total impurities, %	<0.6	<0.05
Costs	+++	+

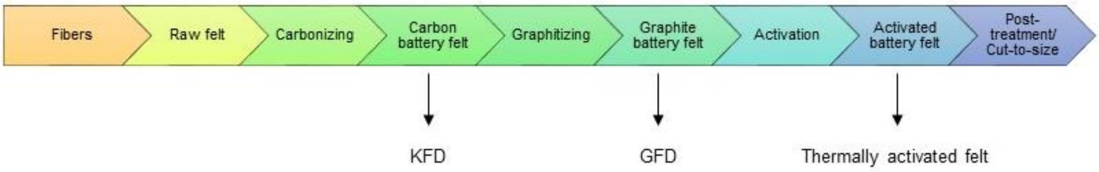

Fig. 26 Scheme of carbon felt preparation method. Based on [223].

The comparison between two various CFs is presented in Fig. 27. Cyclic voltammetry for the full scan (2 mV s^{-1}) clearly shows that KFD carbon felt reveals more capacitive character than graphitized one, which may relate to a slightly higher specific surface area than GFD (Tab. 6). Moreover, when the acid-treatment was applied, both cyclic voltammograms become narrower, suggesting CFs oxidation and therefore, slightly more resistive character. Herein, for performance comparison, the CV scans were carried out in full range of vanadium working potential. However, in the real RFB system only two vanadium redox pairs are used and operate separately (V^{2+}/V^{3+} and VO^{2+}/VO_2^+). Usually, reduction of VO^{2+} to V^{3+} is not visible due to its poor reversibility [175, 224].

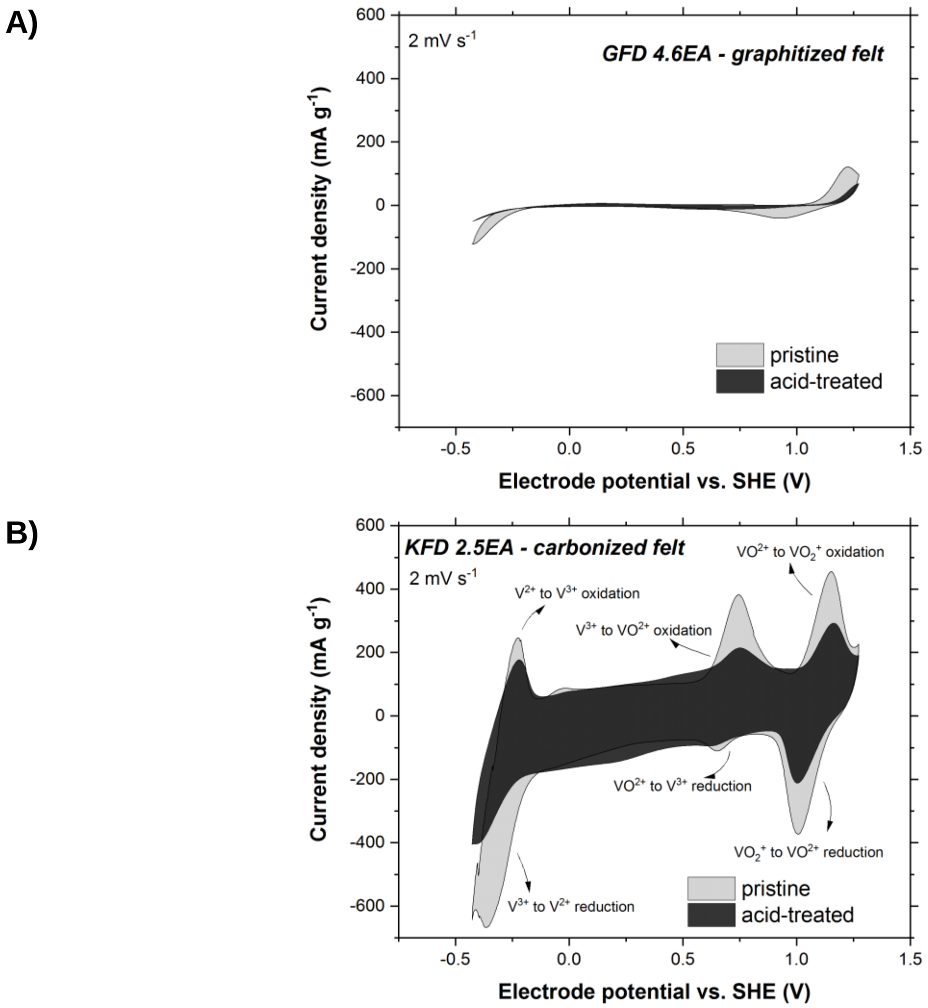

Fig. 27 Cyclic voltammetry profiles (2 mV s^{-1}) for pristine and acid-treated carbon felts A) GFD; B) KFD.

To prove the necessity of carbon felt-surface pretreatment with HNO_3, further electrochemical measurements coupled with XPS studies were carried out (Fig. 28). As seen from Fig. 28A, vanadium reactions are almost inactive for pristine CF. When the oxidation is applied, one can observe respective oxidation/reduction peaks of vanadium species. However, when both acid and salt were used, the peak separation is smaller and more reversible processes are recorded. Pristine GFD carbon possess 2.1 at.% of oxygen and 97.9 at.% of carbon. When both salt and acid treatment were carried out, oxygen content doubled (5 at.%), whereas 3 at.% is obtained for salt-treated only sample. Therefore, it is proven by XPS studies that enhancement of oxidation is obtained with acid pre-treatment. As shown in deconvoluted XPS spectra, two types of oxygen groups can be distinguished and salt treatment only enhances already present surface groups without introducing the novel ones.

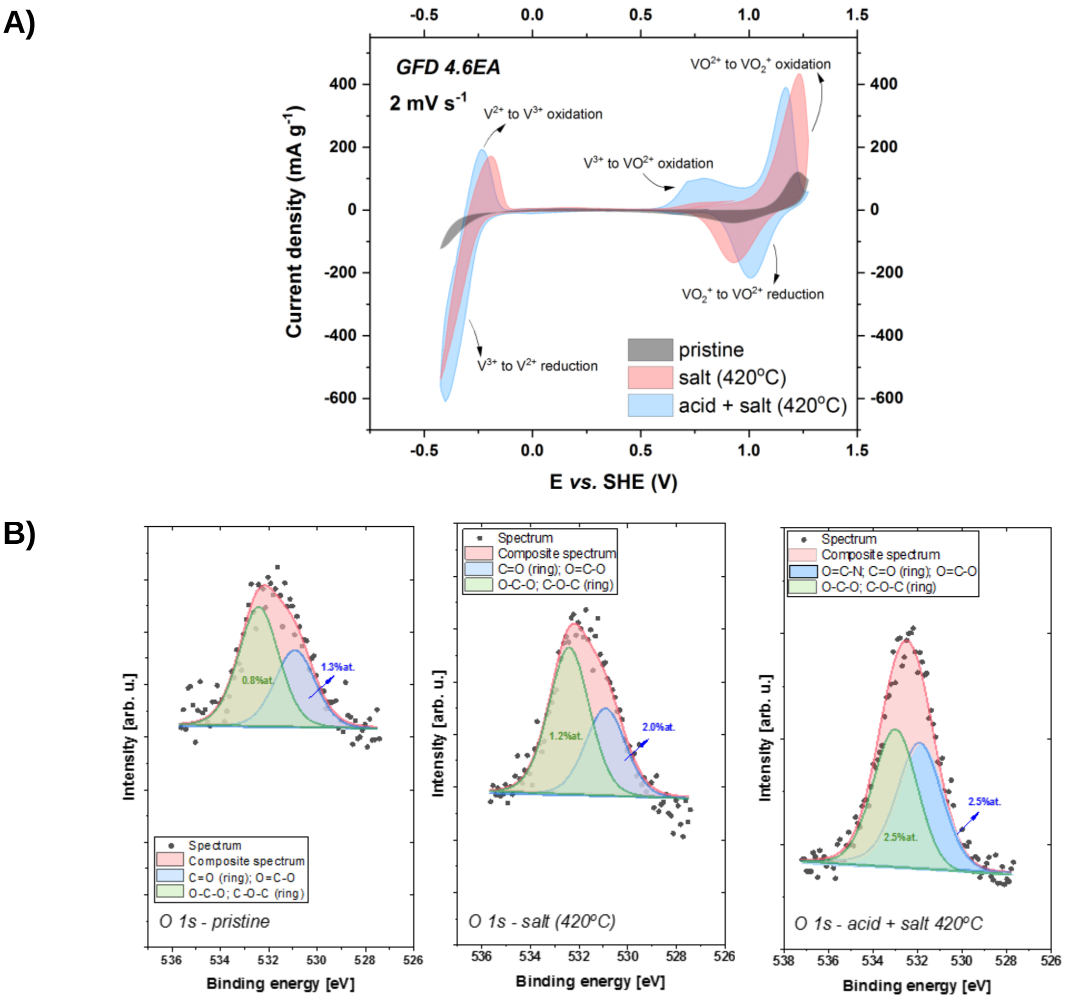

Fig. 28 Influence of carbon acid pre-treatment: A) cyclic voltammetry (2 mV s^{-1}) in the potential range -0.4-1.2 V vs. SHE; B) O1s XPS spectra.

Fig. 29 presents SEM micrographs of differently prepared GFD samples. One can observe that carbon felt consists of individual fibers. Oxidation process adapted for these studies does not significantly influence the texture of studied samples; slight thickness reduction is visible for the samples in the salt presence. It can be therefore assumed that non-aggressive conditions are used; mild oxidation *via* salt treatment is assumed.

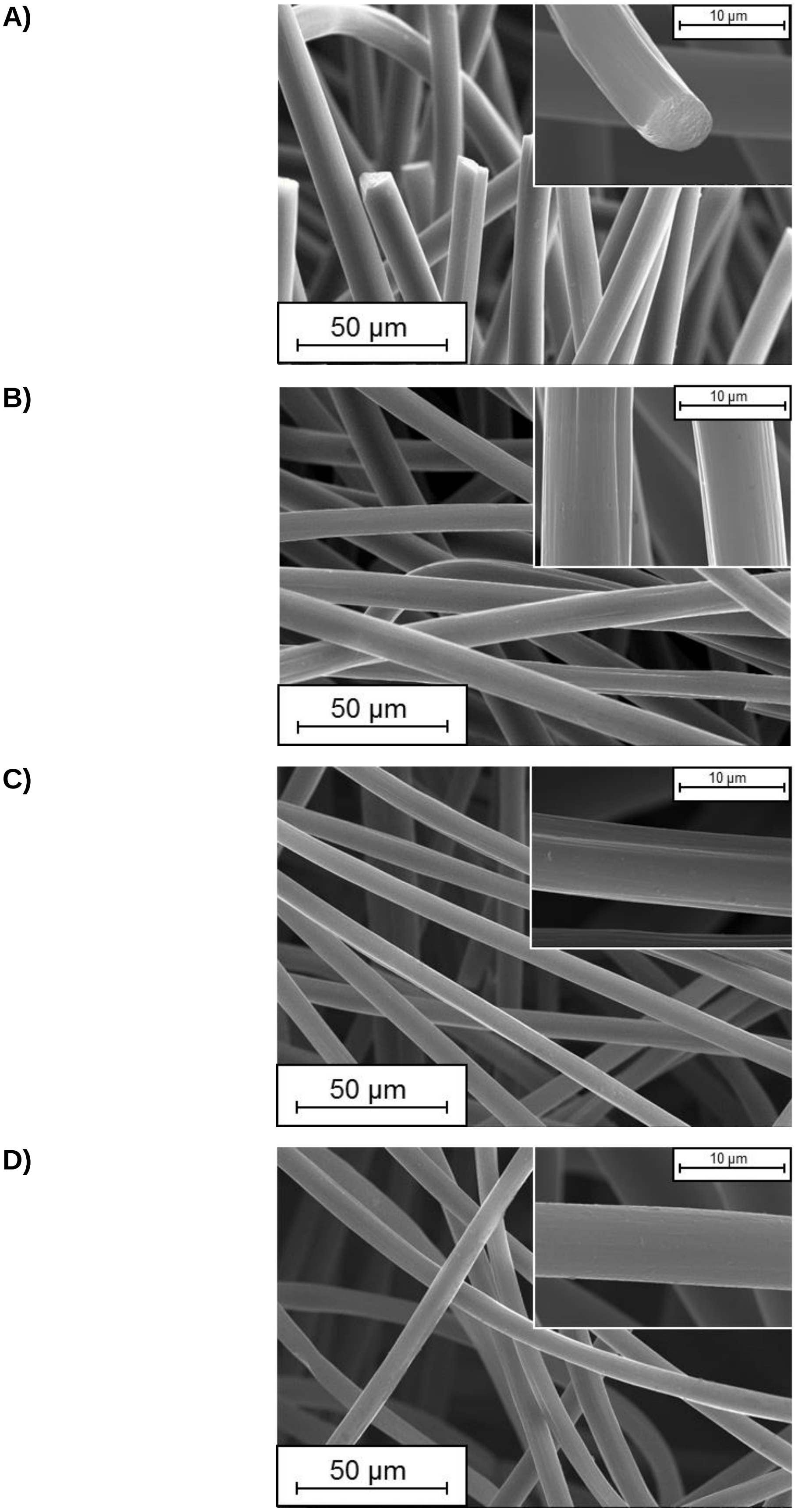

Fig. 29 SEM micrographs of GFD carbon felt: A) pristine; B) acid-treated; C) salt-treated; D) acid & salt-treated.

The carbon felt treatment was carried out in the various temperatures (380-440^{o}C) for 10 minutes. Herein, two redox couples (V^{2+}/V^{3+} and VO^{2+}/VO_2^+) were studied separately to simulate VRFB performance. Cyclic voltammetry profile (2 mV s^{-1}) was recorded at two various potential ranges (Fig. 30A). When the negative side (V^{2+}/V^{3+}) is considered, one can observe that GFD-380 and GFD-400 are almost inactive and cyclic voltammograms resemble the shape of the pristine sample. Treatment in 380^{o}C does not ensure a homogenous salt distribution. When 400^{o}C was used, the CF response is quite good for positive side (VO^{2+}/VO_2^+), however, there is still a problem for the negative side. It can be also observed that with an increase of temperature, a higher vanadium reversibility is obtained. To observe the surface changes over various treatment conditions, XPS spectra were collected. As observed in Fig. 30B, none of the samples except GFD-380 contains nitrogen on its surface. Moreover, higher oxygen content than expected (not in trend) was detected for GFD-380. These facts prove that GFD-380 was not enough washed and some traces of NO_3^- left. Moreover, it was observed empirically that the salt at 380^{o}C is scattered in points on CF surface causing there a higher oxidation state. For all other samples the trend is linear – oxygen content increases with the temperature rise. The highest oxygen content is obtained for GFD-440 (6.8 at.%). Water uptake value increases with temperature meaning that a higher wettability is obtained for treated samples (Fig. 30C).

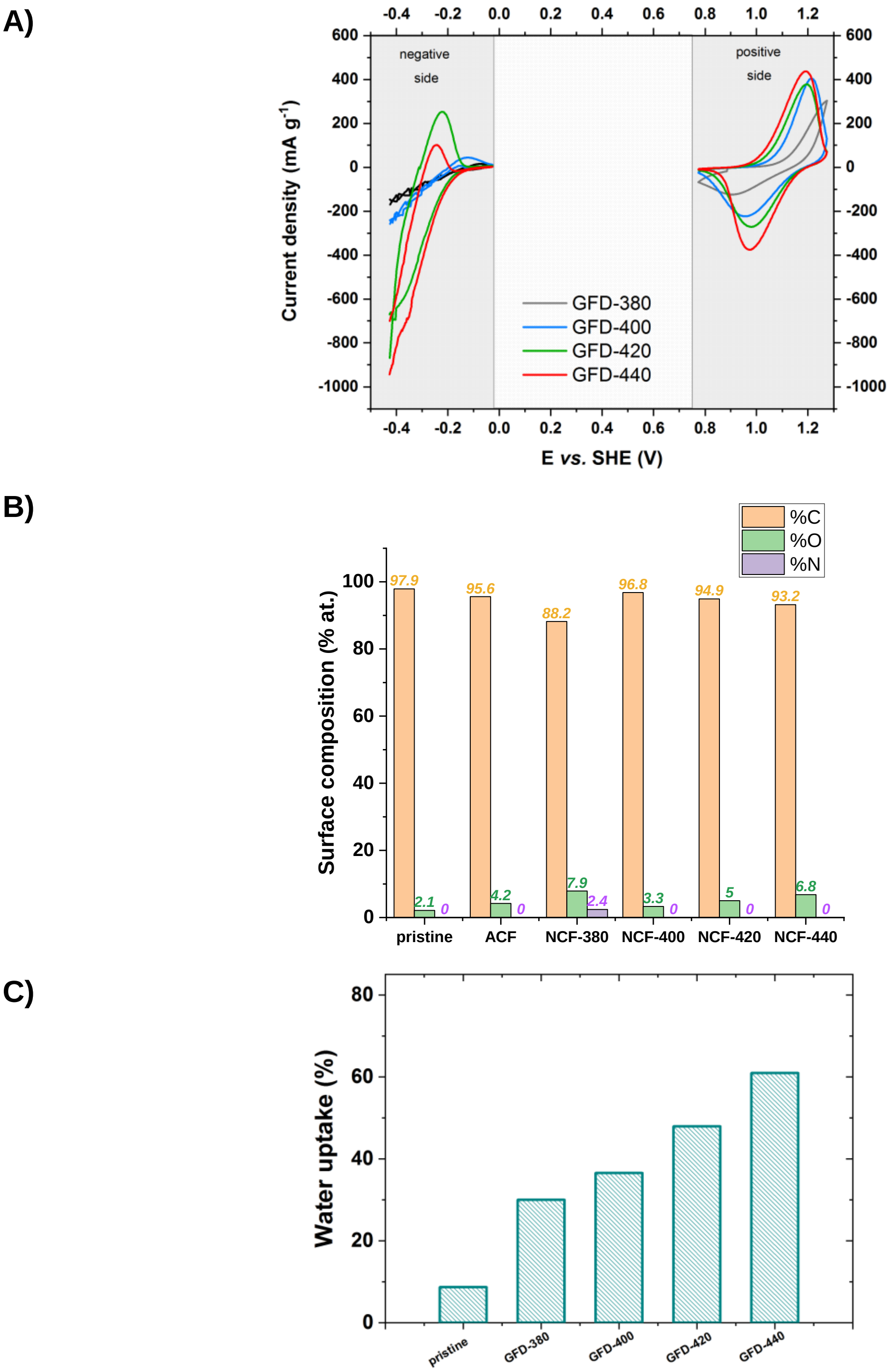

Fig. 30 GFD-based samples: A) cyclic voltammograms at 2 mV s^{-1}; B) surface composition for XPS measurements; C) water uptake.

Based on obtained electrochemical data, vanadium peak analysis was carried out. Basically, two factors were elucidated, i.e., peak potential (ΔE) and peak current (ΔI). Both parameters allow the redox reaction reversibility to be analysed. When ΔE is smaller and ΔI is closer to 1 a higher reversibility can be assumed. Fig. 31 presents the data for differently treated GFD samples. When the negative side (V^{2+}/V^{3+}) is considered, one may notice that GFD-380 performs practically as the pristine sample. The reversibility increases dramatically from 400°C and the best one is obtained for GFD-420 (ΔE = 0.19 V; ΔI = 2.8). It is worth highlighting that the negative side of VRFB is always more problematic, since V^{2+} is sensitive to oxygen presence and the reaction compete with hydrogen evolution. Therefore, the results presented for the positive side (Fig. 31C-D) have better ΔE and ΔI parameters. Herein, the vanadium reaction reversibility increases linearly with temperature rise. It seems that GFD-440 is the most appropriate for VO^{2+}/VO_2^+ side revealing ΔE = 0.22 V and ΔI = 0.86. These results can be directly connected with oxygen content increase above presented in Fig. 30B. All the electrochemical and physico- chemical data are also consistent with water uptake values (Fig. 30C), which refer to the ratio of absorbed water weight to dry material weight.

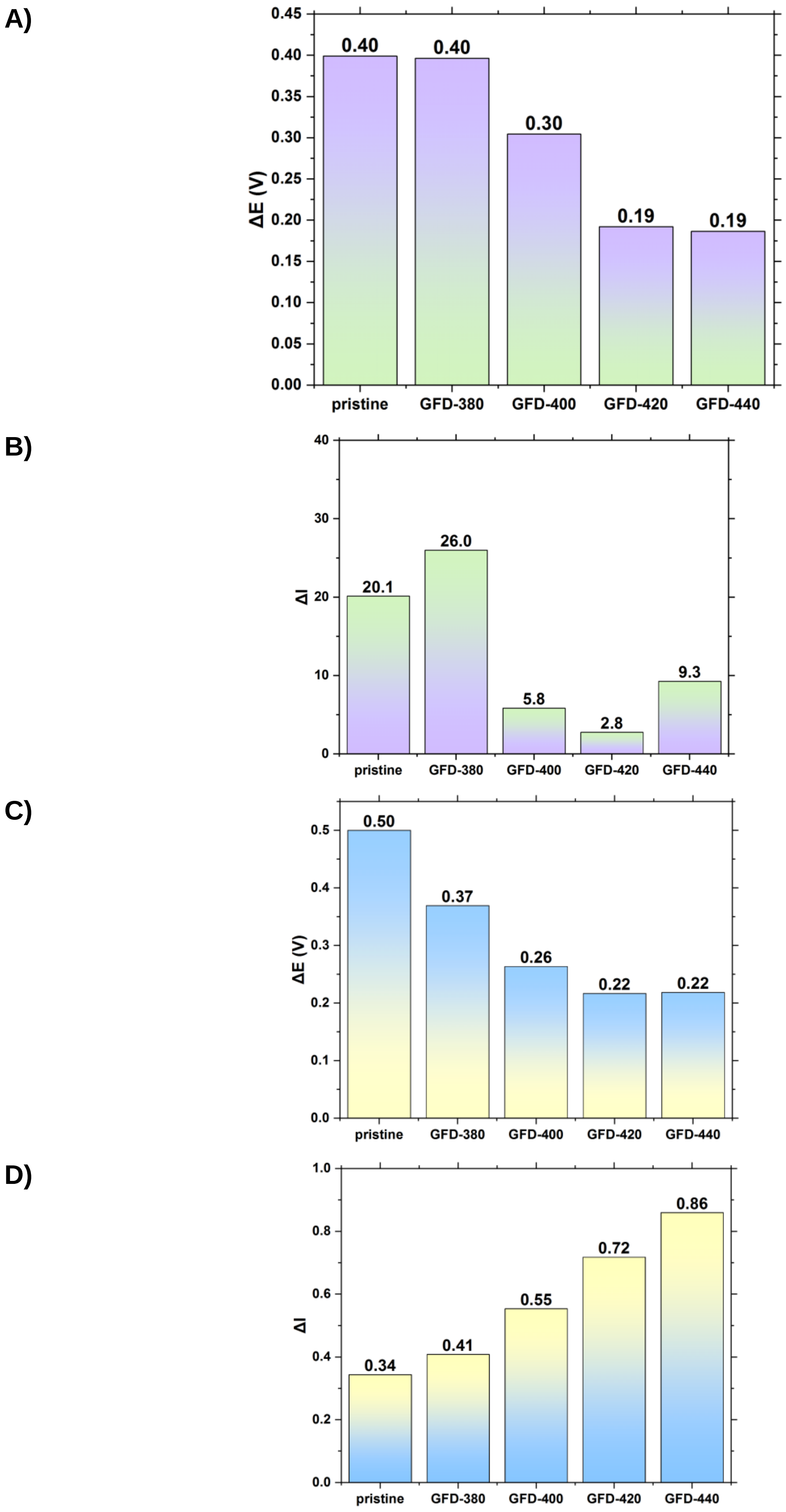

Fig. 31 Peak analysis data for GFD samples: A) and B) V^{2+}/V^{3+}; C) and D) VO^{2+}/VO_2^+ pair.

Similar analysis of peak response was performed for KFD carbon felt. As above-mentioned, KFD carbon felt is not rigid and as stable as GFD one and its thermal stability is lower. Therefore, the molten salt treatment was only performed at 380ºC and 400ºC. 420ºC is already beyond KFD stability limit. Fig. 32 presents cyclic voltammograms and surface composition from XPS measurements recorded for KFD samples. It can be observed that the trend is opposite to GFD; higher current response is recorded for KFD-380 and only slight improvement for KFD-400 is noticed when compared to pristine carbon. This observation is confirmed during peak analysis (Tab. 7). An excellent reversibility of KFD-treated samples may be also connected with its surface composition (Fig. 32B). Contrary to GFD felt, KFD contains pristine nitrogen and higher oxygen content. Therefore, KFD sample is more hydrophilic and more sensitive to molten-salt treatment. As seen in Fig. 32B, the treatment with KNO_3 salt may enhance nitrogen content in KFD sample from 3.7 at.% (pristine) to 6.1 at.% (KFD-380 and KFD-400). Interestingly, slightly higher oxygen content is obtained for KFD-380 than for KFD-400 and therefore it is assumed that KFD-380 reveals better peak parameters (ΔE and ΔI).

Tab. 7 Peak analysis for KFD carbon felt: A) V^{2+}/V^{3+}; B) VO^{2+}/VO_2^+ side.

Sample	**V^{2+}/V^{3+}**		**VO^{2+}/VO_2^+**	
	ΔE	ΔI	ΔE	ΔI
pristine	0.22	3.72	0.12	0.96
KFD-380	0.08	1.76	0.22	1.00
KFD-400	0.19	3.25	0.21	0.90

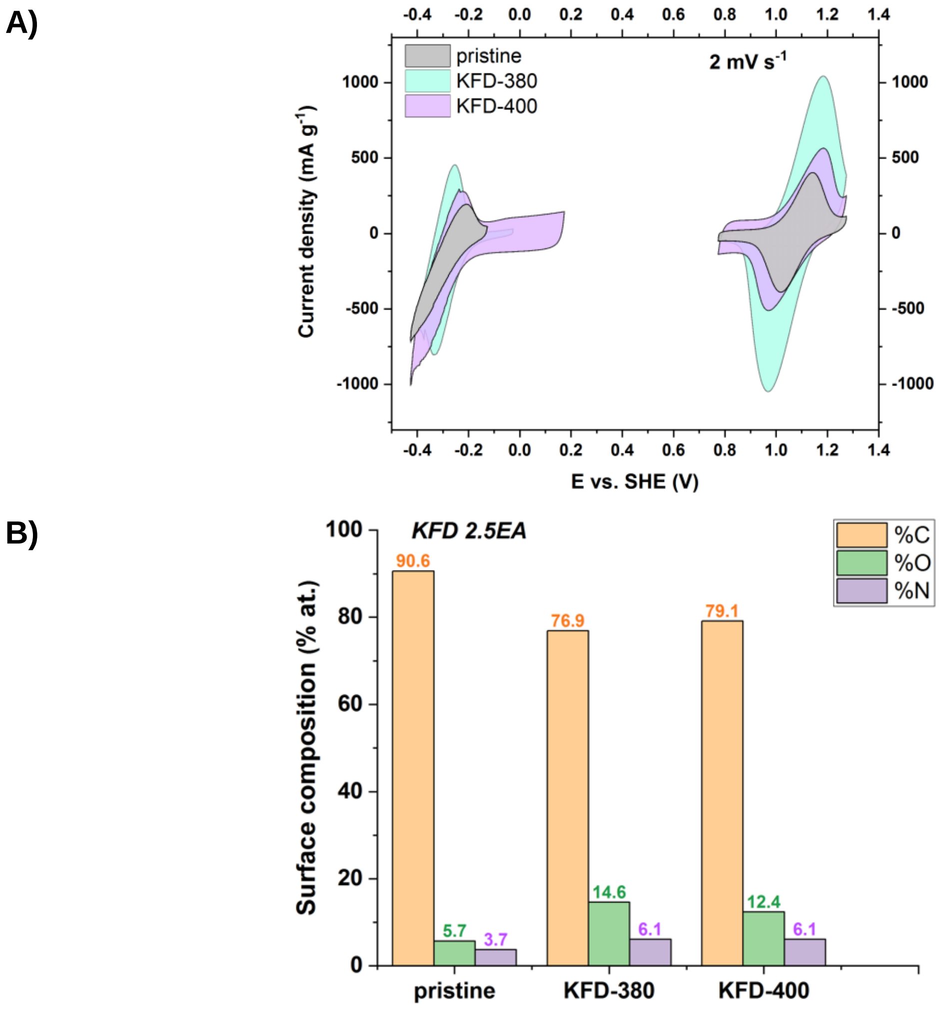

Fig. 32 KFD carbon felt: A) cyclic voltammograms at 2 mV s^{-1}; B) XPS data.

The results recorded for KFD series proved a positive influence of nitrogen presence on vanadium redox reaction behavior. Moreover, temperature has a crucial influence on CF final performance. Since it seems that for GFD carbon felt there is still a room for improvement, the next part of the research concerns GFD further treatment. Samples were heated with and without salt at 500^{o}C for 12 h. Their electrochemical response is presented in Fig. 33A-B. As seen, when VO^{2+}/VO$_2^+$ redox pair is considered both CFs behave almost similar. Therefore, it can be assumed that for the positive side, rather the temperature and extended treatment time has a main impact. Worth highlighting, CV profiles overlap each other over the cycles. Interestingly, when the negative side is considered, one may firstly notice that the current response is almost 4-fold smaller for heated sample than for heat & salt treated one. Secondly, CV profiles recorded for the negative side with the commonly known heat-treatment (Fig. 33A) cannot operate efficiently upon cycles. Over time, hydrogen evolution becomes a dominant reaction leading to the pH change and performance loss over time for heat-treated sample. When the sample was oxidized in the presence of KNO_3 salt, the stability problem is solved and there is a negligible change of CV shape over time. Such behavior may be explained when XPS data are considered (Fig. 33C). One may observe that oxygen is more than doubled with the salt presence (4.5 at.% *vs.* 9.8 at.%) Moreover, for the first time in GFD carbon felt, nitrogen was detected on CF surface. Its presence significantly influences vanadium redox reaction behavior due to the improved hydrophilicity of the sample. It was measured that contact angle decreased from 126º for heat-treated sample to 60º for heat & salt treated one. As seen, with an extended time and a higher temperature GFD carbon felt is more sensitive to KNO_3. It is herein assumed that nitrate salt is reduced while carbon undergoes oxidation what fits to the data presented in Chapter II and III, when it was proven that activated carbon electrodes become oxidized after ageing test with lithium nitrate electrolyte. Nitrogen was also found on carbon surface. Nevertheless, graphitized carbon felt (GFD) has more rigid structure and its modification required more aggressive conditions than activated carbon which operated electrochemically for a long time with nitrate salt electrolyte.

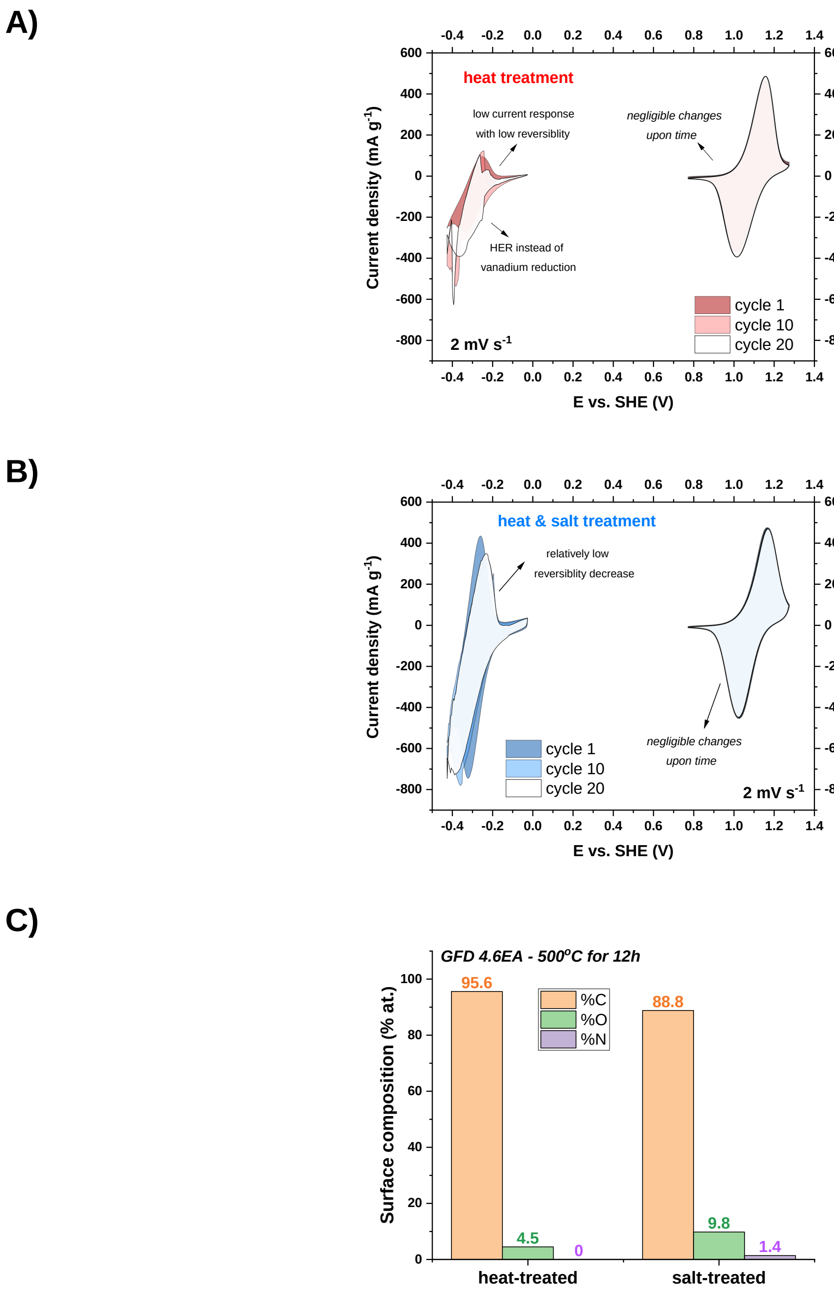

Fig. 33 GFD carbon felt (500°C 12h): A) CV (2 mV s^{-1}) for heat-treated sample; B) CV voltammograms (2 mV s^{-1}) for heat & salt treated sample; C) XPS data.

Summarizing, a simple molten salt oxidation method was elaborated for carbon felt treatment. The properties of differently prepared materials were broadly studied considering their electrochemical properties correlated with carbon surface properties. It was proven that application of relatively cheap, mild oxidizing agent, i.e., alkali metal salt (nitrate) can be competitive to other proposed methods.

General conclusions

Considering the current world discrepancy between energy/power requirements and its generation, constant improvement of energy storage devices is the essential step towards future energy development. The research studies presented in this PhD dissertation contribute to the optimization of faradaic and capacitive based energy storage devices, i.e., redox flow batteries and electrochemical capacitors.

It has been elucidated that the positive electrode in water-based ECs is a main limiting component. Regardless the cell voltage, electrolyte and lifespan test, positive electrode oxidizes over time what causes pore clogging and solid-state deposit presence on its surface. Moreover, from practical point of view aqueous ECs can operate at higher voltages for a shorter time or at lower voltages for thousands of cycles. Therefore, the maximum voltage window cannot be directly estimated since this aspect is user- and application dependent.

It was additionally observed that for purely capacitive EC systems (with sulphates and nitrates in electrolytic solution), the properties of the negative electrode remain practically unchanged after the ageing tests. On this basis, two various anti-ageing actions were successfully implemented for nitrate-based ECs. Firstly, an electrochemical protocol (*alternate floating*) was proposed allowing the capacitor operation time to be almost doubled. Secondly, it has been proven that the negative electrode from ECs can be recovered and reused for the newly constructed system. This approach opens a novel trend considering the environmental issues of the great importance for future sustainable world.

Additionally, it was estimated that the main ageing cause for redox-based ECs relies on active species transfer towards the opposite compartment. It has been proven that application of cation exchange membrane can partially block iodides transfer to the negative ECs side Therefore, the long-term performance of iodide-based system is improved and inhibits the wear-out of carbon-based electrodes, both affected by ageing phenomena in redox-based EC systems.

It can be also concluded that each electrochemical system should be studied individually to elucidate its main ageing reasons. On this basis, anti-ageing actions can be implemented according to the principle of preventing the cause. Summarizing, high oxygen content has rather a negative role in electrochemical capacitors when the lifespan performance is considered.

Contrary to that, oxygen is evitable for efficient vanadium reduction/oxidation reaction on respective VRFB sides. Oxygen functional groups play a role of active sites for reversible redox reaction. Since it was estimated that nitrate salt can effectively oxidize carbon surface, a simple oxidation method with use of potassium nitrate in the molten state was successfully demonstrated allowing an improved vanadium reaction behaviour to be recorded. An optimal treatment conditions were found for this purpose.

Finally, it was proven that not only oxygen on carbon surface is necessary for VRFB reversible performance; oxygen evolution reaction is a perfect solution for “dual circuit redox flow battery”. The reaction of water decomposition plays as the source of protons, which are necessary for hydrogen production in “dual circuit VRFB”. To balance this system vanadium-oxygen cell was proposed. It was shown that V-O_2 cell is a stable, sustainable alternative to discharge the positive side of VRFB in “dual circuit system”. Such procedure does not introduce any additional chemical species to “dual circuit RFB” and ensures relatively high efficiency during extended operation time.

Key findings:

The role of oxygen in ECs and RFB system was insightfully evaluated:

- **Oxygen content increases** ca. 3 times (to ca. 30%) for the positive electrodes **during ECs long-term performance** (with nitrates and sulphates); when redox-active electrolyte (iodide) is used both electrodes oxidize upon ageing process; this causes clogging the pores and carbon conductivity deterioration
- **Solid-state deposit** (carbonate) was found on carbon surface
- In order to extend ECs lifetime **an individual approach is necessary** for each system; ECs lifetime depends on electrolyte type, applied voltage and ageing protocol applied
- **Alternate polarization improves** nitrate-based **ECs lifetime** (up to +80%) causing an equal oxidation of both electrodes during ageing
- Oxygen evolution reaction is not always a detrimental reaction in electrochemical systems. In fact, **water decomposition** is one of the failure reasons in ECs, however, **for “dual-circuit redox flow battery” is essential** for its stable operation (charge and proton balance);

- Extremely **pure H_2 and O_2** can be produced **in “dual-circuit redox flow battery” with vanadium-oxygen cell**; a stable performance of whole system is proven
- **Oxygen surface groups** improve the wettability of CF electrode and enhance the efficiency of vanadium reaction in VRFB
- **Alkali metal salt** in molten state (nitrate) can be used as cheap and easily available **oxidizing agent for carbon felt** electrodes in VRFB
- There is a **crucial role of oxygen surface groups both in ECs and RFB.** However, due to the different character of electrodes (activated carbon *vs.* carbon felt) **various oxygen/carbon ratio is needed.**

Symbols and abbreviations

AC	activated carbon
AC/DC	alternating current / direct current
ACF	activated carbon fibers
AN	acetonitrile
C	charge
C	total capacitance [F]
C_-	capacitance of the negative electrode [F]
C_+	capacitance of the positive electrode [F]
CB	carbon black
CDC	carbide derived carbons
C_e	electrode capacitance [F]
CE; η_c	coulombic efficiency [%]
C_{EDL}	capacitance of electric double-layer [F]
CF	carbon felt
CNT	carbon nanotube
CP	carbon paper
C_{RFB}	volumetric capacity of redox flow battery [Ah L^{-1}]
D	discharge
d	EDL thickness [m]
DBBB	2,5-di-tert-butyl-1,4bis(2-methoxyethoxy)benzene
DSA	dimensionally stable anode
E	mean potential [V]
E^0	standard potential [V]
EA	elemental analysis
EC	electrochemical capacitor
E_c	capacitor energy [Wh]
E_{cell}	standard battery voltage [V]
EDL	electric double-layer
EDS	energy dispersive spectrscopy
EE; η_E	energetic efficiency [%]
EES	electrical energy storage systems
E_{RFB}	energy density [Wh L^{-1}] or [Wh kg^{-1}]
ε_0	vacuum permittivity [F m^{-1}]
ε_r	relative electrolyte permittivity [-]
F	Faraday constant - 26.8 Ah mol^{-1}
FB	flow battery
FTIR	Fourier Transform Infrared Spectroscopy
GF	graphite felt
HER	hydrogen evolution reaction

ICB	iron-chromium flow battery
IVB	iron-vanadium flow battery
j	current density [A cm^{-2}]
m	mass [g]
M	molar mass [g mol^{-1}]
MS	mass spectrometry
MSA	methanesulfonic acid
n	number of electrons [-]
OER	oxygen evolution reaction
OLC	onion-like carbon
PAN	polyacrylonitrile
PBI	polybenzimidazole
P_c	capacitor power [W]
PC	propylene carbonate
PCS	power conversion system
PEK	polyether ketone
PES	polyether sulfone
PNNL	Pacific Northwest National Laboratory
PPy	polypyrrole
P_{RFB}	power density of redox flow battery [W L^{-1} or W kg^{-1}]
PTFE	polytetrafluoroethylene
PTIO	2-phenyl-4,4,5,5-tetramethylimidazoline-loxyl 3-oxide
PVA	polyvinyl alcohol
PVDF	poly(vinylidene fluoride)
Q_{charge}	charge during the charging process
$Q_{discharge}$	charge retained during the discharging process
R	system resistance [Ω]
RFB	redox flow battery
S	surface area of electrodes [m^2]
S_{BET}	specific surface area [m^2 g^{-1}]
SEM	scanning electron microscopy
SOC	state of charge
SPEEK	sulfonated polyether ether ketone
T	time [s]
$t_{discharge}$	time of discharge [s]
$TEABF_4$	tetraethylammonium tetrafluoroborate
TEM	transmission electron microscopy
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl) oxyl
TMQ	2,3,6-trimethylquinoxaline
TPD	temperature-programmed desorption
U or U_{cell}	voltage [V]

V	volume [L]
VE; η_v	voltage efficiency [%]
VRFB	vanadium redox flow battery
W_D	sample weight before absorption [g]
WU	water uptake (%)
W_w	sample weight after absorption [g]
XPS	X-ray photoelectron spectroscopy

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Scientific achievements

1.1 Publications (7)

1. **Piwek J.,** Płatek A., Fic K., Frąckowiak E.,
   Carbon-based electrochemical capacitors with acetate aqueous electrolytes
   Electrochimica Acta 215, 179-186 (2016); ***IF: 6.215***

2. Płatek A., **Piwek J.,** Fic K., Schubert T., Gentile P., Bidan G., Frąckowiak E.,
   Electrochemical performance of silicon nanostructures in low-temperature ionic liquids for microelectronic applications
   Journal of Materials Chemistry A 5, 22708-22716 (2017); ***IF: 11.301***

3. Fic K., Płatek A., **Piwek J.,** Frąckowiak E.,
   Sustainable materials for electrochemical capacitors
   Materials Today 21, 437-454 (2018); ***IF: 26.416***

4. **Piwek J.,** Dennison C.R., Frąckowiak E., Girault H., Battistel A.,
   Vanadium-oxygen cell for positive electrolyte discharge in dual-circuit vanadium redox flow battery
   Journal of Power Sources 439, 227075 (2019); ***IF: 8.247***

5. **Piwek J.,** Płatek A., Frąckowiak E., Fic K.,
   Mechanisms of the performance fading of carbon electrodes operating in a $LiNO_3$ electrolyte
   Journal of Power Sources 438, 227029 (2019); ***IF:8.247***

6. Płatek A., **Piwek J.,** Fic K., Frąckowiak E.,
   Ageing mechanisms in electrochemical capacitors with aqueous redox-active electrolytes
   Electrochimica Acta 311, 211-220 (2019); ***IF:6.215***

7. Fic K., Płatek A., **Piwek J.,** Menzel J., Ślesiński A., Bujewska P., Galek P., Frąckowiak E.,
   Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4-based electrolyte
   Energy Storage Materials 22, 1-14 (2019); ***IF: 16.280***

8. **Piwek J.,** Płatek A., Frąckowiak E., Fic K.,
   Enhancing capacitor lifetime by alternate constant polarization
   Journal of Power Sources 506, 230131 (2021); ***IF: 8.247***

Total Impact Factor: 91.168

Impact Factor Including Co-authors: 19.111

1.2. Publications of the results in conference proceedings (2)

1. Frąckowiak E., **Piwek J.**, Płatek A., Ślesiński A., Fic K.,
   Carbon based electrochemical capacitors: beyond capacitive storage
   CARBON 2019, The World Conference on Carbon, Lexington, KY, July 14th-19th 2019
2. **Piwek J.**, Fic K., Płatek A., Ghimbeu C., Frąckowiak E.,
   Post-mortem AC characterization as the insight into ageing process of electrochemical capacitors
   Carbon 2018, The World Conference on Carbon, Madrid, Spain, July 1st – 6th 2018

1.3 Patents and patents applications

Patents (2):

1. Płatek A., **Piwek J.,** Fic K., Frąckowiak E.,
   Kondensator elektrochemiczny operujący w elektrolicie o stałym pH;
   PL 231259
2. **Piwek J.,** Płatek A., Fic K., Frąckowiak E.,
   Kondensator elektrochemiczny operujący w roztworze zawierającym jony octanowe; PL 231260

Patent applications (2):

1. Płatek A., **Piwek J.,** Fic K., Frąckowiak E.,
   Kondensator elektrochemiczny; Application No. 4283532
2. **Piwek J.,** Płatek A., Fic K., Frąckowiak E.,
   Kondensator elektrochemiczny; Application No. 4283533

1.4 Scientific conferences

Oral presentations - international conferences (13):

1. **Piwek J.**, Dennison C.R., Battistel A., Frąckowiak E., Girault H.,
   Vanadium-Oxygen Cell in Dual-Circuit Vanadium Redox Flow Battery
   2019 MRS Spring Meeting & Exhibit, Phoenix, Arizona USA, April 22nd-26th, 2019
2. Frąckowiak E., **Piwek J.**, Płatek A., Ślesiński A., Fic K.,
   Carbon based electrochemical capacitors: beyond capacitive storage
   CARBON 2019, The World Conference on Carbon, Lexington, KY, USA, July 14th-19th 2019
3. Fic K., Płatek A., **Piwek J.**, Menzel J., Frąckowiak E.,
   Insights into carbon electrode/aqueous electrolyte interface from the operando approach

CARBON 2019, The World Conference on Carbon, Lexington, KY, USA, July 14th-19th 2019

4. Fic K., Płatek A., Menzel J., Ślesiński A., Bujewska P., **Piwek J.**, Galek P., Frąckowiak E.,
   Operando exploration of the ionic fluxes at the electrode/electrolyte interface for better electrochemical capacitors
   6th International Conference on Advanced Capacitors (ICAC 2019) Shinshu University, Ueda, Nagano, Japan, September 8th-12th 2019

5. Frąckowiak E., **Piwek J.**, Fic K., Płatek A.,
   Ageing of electrode/electrolyte interface in electrochemical capacitor
   6th International Conference on Advanced Capacitors (ICAC 2019) Shinshu University, Ueda, Nagano, Japan, September 8th-12th 2019 2019

6. Frąckowiak E., **Piwek J.**, Płatek A., Menzel J., Galek P., Fic K.,
   Electrolyte – Important Component of Electrochemical Capacitor
   The Third International Conference on Energy Storage Materials, Shenzhen, China, November 28th – December 1st 2019

7. Frąckowiak E., **Piwek J.**, Płatek A., Fic K.,
   Ageing of carbon based electrochemical capacitors in neutral aqueous electrolyte
   8th International Conference on Carbon for Energy Storage and Environment Protection CESEP'19, Alicante, Spain, October 20th – 24th 2019

8. Płatek A., **Piwek J.,** Fic K., Frąckowiak E.,
   Insight into ageing phenomena of redox active electrolytes in the electrochemical capacitors
   69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2nd – 7th 2018

9. Fic K., **Piwek J.,** Płatek A., Frąckowiak E.,
   Insights into electrochemical capacitors ageing at different voltage/current conditions
   Americas International Meeting on Electrochemistry and Solid State Science AIMES 2018, Cancun, Mexico, September 30th – October 4th 2018

10. Frąckowiak E., Płatek A., **Piwek J.,** Fic K.,
    A key role of oxygen in electrochemical energy storage systems
    IV International Conference OXYGENALIA 2018, Vilnius, Lithuania, October 11th -13th 2018

11. **Piwek J.**, Płatek A., Fic K., Frąckowiak E.,
    The Effect of Ageing Phenomena on the Carbon Porosity in High-Voltage Aqueous Capacitor
    Carbon for Energy Storage and Environment Protection (CESEP'17), Lyon, France, October 23rd – 26th 2017

12. **Piwek J.,** Płatek A., Fic K., Gastoł D., Gentile P., Bidan G., Schubert T., Frąckowiak E.,

Microcapacitors based on silicon silicon nanostructures operating in ionic liquids MRS Spring Meeting, Phoenix, USA, April 2nd – 6th 2016

13. **Piwek J.,** Płatek A., Fic K., Frąckowiak E.,
Silicon nanowires for energy storage in ionic liquids
COST Action MP1004 Winter Seminar „Latest Developments in Electrochemical Capacitors" Poznań, Poland, January 29th – 31st 2015

Oral presentations - national conferences (4):

1. **Piwek J.**, Płatek A., Fic K., Frąckowiak E.,
State-of-health monitoring of carbon electrode for aqueous electrochemical capacitors
XII Konferencja Naukowo-Techniczna „Materiały Węglowe i Kompozyty Polimerowe", Ustroń, Jaszowiec, Poland, April 2nd – 5th 2019

2. Płatek A., **Piwek J.**, Fic K., Frąckowiak E.,
Sulphate-based carbon/carbon electrochemical capacitor analysis supported by EQCM studies
XII Konferencja Naukowo-Techniczna „Materiały Węglowe i Kompozyty Polimerowe", Ustroń, Jaszowiec, Poland, April 2nd – 5th 2019

3. **Piwek J.,** Płatek A., Fic K., Frąckowiak E.,
Post-mortem activated carbon characterization as the insight into ageing of electrochemical capacitors
I Polish Carbon Society Scientific Workshop, Wrocław, Poland, September 21st 2018

4. **Piwek J.,** Płatek A., Fic K., Frąckowiak E.,
Ageing of activated carbon-based electrochemical capacitors on various operating conditions
XI Konferencja Naukowo-Techniczna „Materiały Węglowe i Kompozyty Polimerowe Nauka – Przemysł" 2018, Ustroń – Jaszowiec, Poland, April 17th – 20th 2018

Posters presentations - international conferences (14):

1. **Piwek J.,** Frąckowiak E.,
Influence of carbon felt surface oxidation on vanadium redox flow battery behavior
71st Annual Meeting of International Society of Electrochemistry, Belgrade Online, August 31st –September 4th 2020

2. **Piwek J.,** Płatek A., Frąckowiak E., Fic K.,
Novel approach for lifespan extension of electrochemical capacitors
71st Annual Meeting of International Society of Electrochemistry, Belgrade Online, August 31st –September 4th 2020

3. Płatek A., **Piwek J.,** Frąckowiak E., Fic K.,
Beyond energy storage limitations – long-term operation of sulfate-based electrochemical capacitors
71st Annual Meeting of International Society of Electrochemistry, Belgrade Online, August 31st –September 4th 2020

4. **Piwek J.,** Płatek A., Fic K., Frąckowiak E.,
Comparison of ageing mechanisms in water-based electrochemical capacitors with capacitive and pseudocapacitive contribution
ISEECap 2019, International Symposium on Enhanced Electrochemical Capacitors, Nantes, France, May 6th -10th 2019

5. **Piwek J.**, Fic K., Płatek A., Ghimbeu C., Frąckowiak E.,
Post-mortem AC characterization as the insight into ageing process of electrochemical capacitors
Carbon 2018, The World Conference on Carbon, Madrid, Spain, July 1st – 6th 2018

6. **Piwek J.**, Płatek A., Fic K., Frąckowiak E.,
Boosting the performance of AC/AC electrochemical capacitors by addition of redox active species
69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy, September 2nd – 7th 2018

7. Płatek A., **Piwek J.**, Fic K., Frąckowiak E.,
Effect of electrolyte pH stabilisation on carbon-based capacitor performance
The World Conference on Carbon 2017, Melbourne, Australia, July 23rd – 28th 2017 23-28 2017

8. **Piwek J.**, Dennison C.R., Battistel A., Frąckowiak E., Girault H.,
The alternative for positive electrolyte discharge in dual-circuit vanadium redox flow battery
Carbon for Energy Storage and Environment Protection (CESEP’17), Lyon, France, October 23rd – 26th 2017

9. Płatek A., **Piwek J.**, Fic K., Frąckowiak E.,
Supercapacitor based on potassium acetate electrolyte
The First International Conference on Energy Storage Materials, Shenzen, China, November 18th – 21st 2017

10. **Piwek J.**, Dennison C.R., Battistel A., Frąckowiak E., Girault H.,
The alternative for positive electrolyte discharge in dual-circuit vanadium redox flow battery
The First International Conference on Energy Storage Materials, Shenzen, China, November 18th – 21st 2017

11. **Piwek J.,** Platek A., Frackowiak E.,
Would vinegar-based electrolytes be the sufficient aqueous medium for supercapacitors?
6th International Conference on Carbon for Energy Storage/Conversion and Environment Protection, Poznań, Poland, October 18th – 22nd 2015

12. Platek A., **Piwek J.,** Frackowiak E.,
    How does the capacitor accept buffer solutions as electrolytes?
    6th International Conference on Carbon for Energy Storage/Conversion and Environment Protection, Poznań, Poland, October 18th – 22nd 2015

13. **Piwek J.,** Platek A., Skowron P., Frackowiak E.,
    Study of electrode composition on performance of electrochemical capacitors, 65th Annual Meeting of the International Society of Electrochemistry, Lausanne, Switzerland, August 31st – September 5th 2014

14. Platek A., **Piwek J.,** Frackowiak E.,
    Galvanostatic cycling vs floating for supercapacitor testing,
    65th Annual Meeting of the International Society of Electrochemistry, Lausanne, Switzerland, August 31st – September 5th 2014

Posters presentations - national conferences (3):

1. **Piwek J.**, Płatek A., Fic K., Frąckowiak E.,
   Immortality of electrochemical capacitors – dream or reality?
   Polish Scientific Networks 2019 Conference, Poznań, Poland, September 19th – 21st 2019

2. Platek A., **Piwek J.,** Fic K., Frackowiak E.,
   Capacitor with buffer solutions as electrolyte
   IX Konferencja Naukowo-Techniczna „Materiały Węglowe i Kompozyty Polimerowe”, Ustroń-Jaszowiec, Poland, April 20th – 22nd 2019

3. **Piwek J.,** Platek A., Fic K., Frackowiak E.,
   Vinegar-based electrolytes for supercapacitors
   IX onferencja Naukowo-Techniczna „Materiały Węglowe i Kompozyty Polimerowe”, Ustroń-Jaszowiec, Poland, April 20th – 22nd 2019

1.5 Internships

1. **Swiss Federal Institute of Technology Lausanne** (École Polytechnique Fédérale de Lausanne - EPFL), EPFL Valais, Wallis, Sion, Switzerland
   Laboratory of Physical and Analytical Electrochemistry (LEPA)
   Supervisor: Prof. H. Girault
   September 1st 2016 – August 31st 2017

   Responsibilities:
   - research on the influence of an ion exchange membrane on the electrochemical performance of a vanadium redox flow battery
   - development of an electrochemical system which allows the redox flow cell connected to a catalytic reactor producing hydrogen to be balanced.

2. **Ionic Liquids Technologies (Io-li-tec GmbH)** Heilbronn, Germany
   Laboratory of ionic liquids synthesis
   September 1st – 30th 2014

Responsibilities:
- synthesis of ionic liquids and their physico-chemical analyses
- purification of ionic liquids using activated carbon as the adsorbent

3. **Dalkia ZEC S.A.,** Poznań, Poland
   Heat and power plant - laboratory of analysis and maintenance
   September 1st – 30th 2013

   Responsibilities:
   - physico-chemical analyses of biomaterials and determination their energy value for heat production

4. **Paul Scherrer Institut (PSI)** Villigen, Switzerland
   Fuel Cells Systems and Diagnostics
   Supervisor: Dr. F. Buechi
   June 1st 2012 – August 31st 2012

   Responsibilities:
   - image processing (alignment of tomography data to reference scan with Fiji software package) of *in-situ* PEFC X-ray tomography data
   - programming of a Mathlab-routine for data evaluation from fuel-cell based cleaning vehicle. Calculation of energy produced, hydrogen consumed and efficiency of the system.

1.6 Awards

Poznan City Award (Nagroda Miasta Poznania) in 2019 for the outstanding scientific achievements in the field of chemical technology related to the lifetime of electrochemical capacitors working in the water-based medium.

Poster prize:

1. **Piwek J.**, Płatek A., Fic K., Frąckowiak E.,
   Immortality of electrochemical capacitors – dream or reality?
   Polish Scientific Networks 2019 Conference, Poznań, Poland, September 19th – 21st 2019

2. **Piwek J.**, Fic K., Płatek A., Ghimbeu C., Frąckowiak E.,
   Post-mortem AC characterization as the insight into ageing process of electrochemical capacitors
   Carbon 2018, The World Conference on Carbon, Madrid, Spain, July 1st – 6th 2018

3. **Piwek J.**, Płatek A., Frąckowiak E.,
   Would vinegar-based electrolytes be the sufficient aqueous medium for supercapacitors?
   6th International Conference on Carbon for Energy Storage/Conversion and Environment Protection, Poznań, Poland, October 18th – 22nd 2015

1.7 Research projects

1. **Preludium 15** (2018/29/N/ST4/01055), National Science Centre
   Influence of carbon surface oxidation on vanadium redox reaction mechanism in an acidic medium
   Principal investigator
2. **European Research Council (ERC)** GA 759603
   If immortality unveil…'– development of the novel types of energy storage systems with excellent long-term performance
   Principal investigator: Krzysztof Fic
   Researcher
3. **UNISONO** (2018/30/Z/ST4/00901), National Centre of Science
   Innovative nanostructured electrodes for energy storage concepts
   Principal investigator: Elżbieta Frąckowiak
   Researcher
4. **OPUS 16** (2018/31/B/ST4/01852), National Centre of Science
   Study of electrode/electrolyte interface of high stability and quick charge response
   Principal investigator: Elżbieta Frąckowiak
   Project assistant
5. **OPUS 8** (2014/15/B/ST4/04957), National Centre of Science
   Charging/discharging mechanism at the electrode/electrolyte interface of supercapacitors
   Principal investigator: François Béguin
   Researcher
6. **Swiss Government Excellence Scholarship** Biuro Uznawalności i Wykształcenia Wymiany Narodowej realized at École Polytechnique Fédérale de Lausanne - EPFL), EPFL Valais, Wallis, Sion, Switzerland
   The redox flow batteries as the main player in energy storage game
   Supervisor: Hubert Girault
   Principal investigator
7. **NEST-309143**
   Nanowires for Energy Storage
   Principal investigator: Elżbieta Frąckowiak
   Project assistant
8. **Polish-Swiss project** PSPB 107/2010 INGEC
   In situ investigation of the next generation electrochemical capacitor
   Principal investigator: Elżbieta Frąckowiak
   Researcher

5.8 Memberships in scientific organizations and other functions/trainings

Conference organizing committee:

1. Polish Scientific Networks 2019 Conference, Poznań, Poland, September 19th – 21st 2019
2. II Polish Carbon Society Scientific Workshop, Poznan, Poland, September 27th 2019
3. 6th International Conference on Carbon for Energy Storage/Conversion and Environment Protection, Poznań, Poland, October 18th – 22nd 2015

Other:

1. Origin program training *Basics of data analysis in program environment*
2. Member of International Society of Electrochemistry
3. Member of Polish Carbon Society
4. Finalist of the Unilever Engineer's League 2015 competition

Co-authorship statements

Poznan, July 25th, 2020

Justyna Piwek

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Declaration

As the co-author of the following paper:

Piwek Justyna (50%); Płatek Anetta (25%);Frąckowiak Elżbieta (10%); Fic Krzysztof (15%);

Mechanisms of the performance fading of carbon-based electrochemical capacitors operating in a $LiNO_3$ *electrolyte*

Journal of Power Sources 438, 227029 (2019)
DOI: 10.1016/j.jpowsour.2019.227029

I hereby declare that my contribution to this works was:

50% - by making the electrochemical and physicochemical experiments, preparing and plotting the data and writing the initial draft of the manuscript

Justyna Piwek
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Journal of Power Sources 438, 227029 (2019)
DOI: 10.1016/j.jpowsour.2019.227029

I hereby declare that my contribution to this works was:

25% - by help in making the experiments and discussing the obtained results

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10% - by supervising the research progress and help in manuscript preparation

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Ageing mechanisms in electrochemical capacitors with aqueous redox-active electrolytes

Electrochimica Acta 311, 211-220 (2019)
DOI: 10.1016/j.electacta.2019.04.117

I hereby declare that my contribution to this works was:

50% - by making the electrochemical and physicochemical experiments, preparing and plotting the data and writing the initial draft of the manuscript

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Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4*-based electrolyte*

Energy Storage Materials 22, 1-14 (2019)
DOI: 10.1016/j.ensm.2019.08.005

I hereby declare that my contribution to this works was:

25% - by supervising the research progress and preparation of the manuscript final version

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Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4-based electrolyte

Energy Storage Materials 22, 1-14 (2019)
DOI: 10.1016/j.ensm.2019.08.005

I hereby declare that my contribution to this works was:

10% - by making the experiments and writing the initial draft of publication about energetic and coulombic efficiency in electrochemical capacitor and quartz crystal microbalance studies

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Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4*-based electrolyte*

Energy Storage Materials 22, 1-14 (2019)
DOI: 10.1016/j.ensm.2019.08.005

I hereby declare that my contribution to this works was:

10% - by making the experiments and writing the initial draft of publication about long-term performance of electrochemical capacitor

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Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4-based electrolyte

Energy Storage Materials 22, 1-14 (2019)
DOI: 10.1016/j.ensm.2019.08.005

I hereby declare that my contribution to this works was:

10% - by making the experiments and writing the initial draft of publication about hydrogen sorption, voltage stability region and Raman spectroscopy

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Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4*-based electrolyte*

Energy Storage Materials 22, 1-14 (2019)
DOI: 10.1016/j.ensm.2019.08.005

I hereby declare that my contribution to this works was:

10% - by making the experiments and writing the initial draft of publication about influence of vitamin E on electrochemical capacitor performance, pressure changes and leakage current analysis in electrochemical capacitor

Adam Ślesiński
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Poznan, July 25th, 2020

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Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4-based electrolyte

Energy Storage Materials 22, 1-14 (2019)
DOI: 10.1016/j.ensm.2019.08.005

I hereby declare that my contribution to this works was:

10% - by making the experiments and writing the initial draft of publication about influence of vitamin E on electrochemical capacitor performance

Paulina Bujewska
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Poznan, July 25th, 2020

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Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4-based electrolyte

Energy Storage Materials 22, 1-14 (2019)
DOI: 10.1016/j.ensm.2019.08.005

I hereby declare that my contribution to this works was:

10% - by making the experiments and writing the initial draft of publication about viscosity and conductivity of electrolytic solution

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Revisited insights into charge storage mechanisms in electrochemical capacitors with Li_2SO_4-based electrolyte

Energy Storage Materials 22, 1-14 (2019)
DOI: 10.1016/j.ensm.2019.08.005

I hereby declare that my contribution to this works was:

15% - by supervising the research progress

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Poznan, June 10th, 2021

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Declaration

As the co-author of the following paper:

Piwek Justyna (45%); Płatek-Mielczarek Anetta (25%); Frąckowiak Elżbieta (15%); Fic Krzysztof (15%);

Enhancing the capacitor lifetime by alternate constant polarization

Journal of Power Sources 506, 230131 (2021)
DOI: https://doi.org/10.1016/j.jpowsour.2021.230131

I hereby declare that my contribution to this works was:

45% - Conceptualization, Investigation, data treatment, Writing – original draft

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Poznan, June 10th, 2021

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As the co-author of the following paper:

Piwek Justyna (45%); **Płatek-Mielczarek Anetta (25%);** Frąckowiak Elżbieta (15%); Fic Krzysztof (15%);

Enhancing the capacitor lifetime by alternate constant polarization

Journal of Power Sources 506, 230131 (2021)
DOI: https://doi.org/10.1016/j.jpowsour.2021.230131

I hereby declare that my contribution to this works was:

25% - Data treatment, Formal analysis, Writing – original draft

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Poznan, June 10th, 2021

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DOI: https://doi.org/10.1016/j.jpowsour.2021.230131

I hereby declare that my contribution to this works was:

15% - Supervision, Funding acquisition, Writing – review & editing

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15% - Supervision, Funding acquisition, Writing – review & editing

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Vanadium-oxygen cell for positive electrolyte discharge in dual-circuit vanadium redox flow battery

Journal of Power Sources 439, 227075 (2019)
DOI: 10.1016/j.jpowsour.2019.227075

I hereby declare that my contribution to this works was:

40% - by making the experiments on vanadium-oxygen cell, preparing and plotting the data and writing the draft of the manuscript

Justyna Piwek
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Philadelphia, USA, September 7th, 2020

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École Polytechnique Fédérale de Lausanne (EPFL)
Valais Wallis, Rue de L'Industrie 17
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Vanadium-oxygen cell for positive electrolyte discharge in dual-circuit vanadium redox flow battery

Journal of Power Sources 439, 227075 (2019)
DOI: 10.1016/j.jpowsour.2019.227075

I hereby declare that my contribution to this works was:

20% - by supervising the experimental research, discussing the obtained results

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Declaration

As the co-author of the following paper:

Piwek Justyna (40%); Dennison C.R. (20%); **Frąckowiak Elżbieta (5%);**
Girault Hubert (10%); Battistel Alberto (25%)

Vanadium-oxygen cell for positive electrolyte discharge in dual-circuit vanadium redox flow battery

Journal of Power Sources 439, 227075 (2019)
DOI: 10.1016/j.jpowsour.2019.227075

I hereby declare that my contribution to this works was:

5% - by supervising the research progress

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I hereby declare that my contribution to this works was:

10% - by discussing the concept of the experiments and supervising the research progress

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I hereby declare that my contribution to this works was:

25% - by supervising the experimental research, discussing the obtained results, help in manuscript preparation

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