Review Report on the PhD Dissertation by Ms. Sylwia Ślesińska

Title: Research on the electrode charging and carbon degradation on electrochemical capacitors

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Overall assessment

This dissertation is **outstanding**. It integrates operando and in-situ electrochemical diagnostics with multi-modal post-mortem characterization to reveal how local interfacial conditions and carbon surface chemistry govern performance and degradation in electrochemical capacitors (ECs) and lithium-ion hybrid capacitors (LICs). The work delivers (i) the first operando, electrode-resolved mapping of pH gradients in neutral sulfate electrolytes under realistic polarization, (ii) a principled re-definition and measurement protocol for the *point of zero charge* (PZC) in porous carbons—advocating a *range of zero charge* (RZC) and introducing the SPECS method—and (iii) a mechanistic map of voltage-directed aging pathways in LIC positive electrodes with concrete chemical fingerprints (phenol/ether growth, carbonate by-products) and their textural/electrical consequences. Together, these findings form a coherent framework that is both conceptually original and practically actionable for device optimization.

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1) Assessment of general theoretical knowledge

Ms. Ślesińska demonstrates a **broad and deep command of electrochemical theory and materials chemistry** across aqueous and organic systems:

- **Electrode/electrolyte interfacial thermodynamics and transport.** The operando pH study shows clear understanding of potential-dependent interfacial reactions, buffering, diffusion/mixing and their impact on the *true* operating window of neutral electrolytes. The candidate resolves asymmetric local pH drifts (≈4 at the positive, ≈8.5 at the negative) during cycling, and interprets consequences for gas evolution and stability—an analysis that requires fluent use of Nernstian concepts, water activity, and local overpotential.

- **Charge storage physics in porous carbons.** In the PZC monograph, she reframes PZC for real carbons as a **potential range** (RZC) rather than a single value (typically spanning ~100–200 mV), and ties this to realistic EQCM measurements and cell architecture. This shows mastery of double-layer formation, ion correlations, and how experimental boundary conditions (e.g., reference placement, geometry) perturb perceived PZC.
- **Advanced electroanalytical methods.** The thesis employs in-situ EQCM to quantify ionic/solvent fluxes; operando micro-pH probing and GC-MS to read out dynamic chemistry; and rigorous post-mortem toolsets (XPS, TPD-MS, porosimetry, Raman). The supporting information and figures reflect a sophisticated command of each technique's strengths and limitations (e.g., surface sensitivity of XPS, the need for Ar-etching to probe depth).
- **Battery-vs-capacitor contrasts and hybrid devices.** The LIC aging paper situates mechanisms in the broader context (floating protocols, electrolyte decomposition routes in EC/DMC + $LiPF_6$, and the limited role of battery-type aging given a Li counter electrode), showing accurate theoretical positioning of the hybrid system.
- **Synthesis to conclusions.** The General Conclusion weaves these themes into a unified view (local pH control, proper PZC/RZC determination in the exact measurement cell, and voltage-programmed aging chemistry), evidencing a global theoretical understanding rather than isolated case studies.

Verdict on criterion 1: The dissertation convincingly demonstrates the theoretical knowledge expected for a doctoral degree in chemical sciences.

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2) Assessment of the candidate's ability to conduct scientific research

The dissertation exhibits **methodological rigor, originality in experimental design, and advanced data interpretation**:

- **Operando/in-situ experimental design.** The candidate devised an electrode-resolved pH micro-probe setup to capture spatially distinct interfacial chemistry in real time—an approach that goes beyond bulk measurements common in EC research.
- **Hypothesis-driven protocols.** Controlled *floating* at graded voltages (4.0–4.6 V)

isolates voltage-dependent aging modes in LICs, then ties mechanistic outcomes to end-of-life criteria—hallmarks of careful experimental planning.

- **Triangulation by multi-modal analytics.** The research integrates N_2 isotherms/2D-NLDFT for textural change, XPS for chemical speciation, TPD-MS for volatile signatures, EQCM for mass/flux coupling, and operando GC-MS—allowing the candidate to cross-validate mechanistic claims instead of relying on a single proxy. Representative dataset lists and panels in the SI underscore this breadth.
- **Quantitative post-mortem insight.** For LIC electrodes, XPS shows marked O-content increases (e.g., C 1s drop from ~92% to ~79–81% with corresponding O 1s rise under 4.0–4.6 V), consistent with oxidation and deposition; the discussion shows the candidate's ability to connect spectroscopy to performance fade via conductivity loss and pore blockage.
- **Research leadership and accountability.** The "Paper-in-preparation" section documents the candidate's primary roles (conceptualization, methodology, operando GC-MS, TPD-MS, data curation, writing), which evidences independence and breadth.

Verdict on criterion 2: The candidate clearly demonstrates the skills to conceive, execute, and interpret high-level scientific research.

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3) Assessment of originality and potential for application

The thesis offers **original solutions and concepts** and translates them into **practical guidance** for EC/LIC engineering:

(a) A new, device-relevant view of PZC

- The work argues PZC is not a single point but a **Range of Zero Charge (RZC)**—reflecting the distributed nature of charge accommodation in porous carbons and the realities of measurement geometry—and backs this with EQCM evidence and a **SPECS-based** determination procedure executed in the same cell. This reframing corrects a long-standing oversimplification and enables more faithful modeling and optimization.

Application impact: Properly locating the RZC in the *operando* cell prevents misassignment of potential windows and reduces parasitic processes—directly informing safer voltage limits and electrolyte selection.

(b) Interfacial pH as a controllable design lever

- The operando mapping of **electrode-specific pH** shows that nominally "neutral" sulfate electrolytes develop strong, potential-dependent acidity/alkalinity at opposite electrodes (≈pH 4 vs 8.5), with implications for gas evolution, faradaic leakage, and lifetime; the thesis proposes a **"pH-maintenance"** design trade-off (e.g., electrode spacing vs resistance). This is a fresh, actionable systems-level insight rarely quantified at this resolution.

Application impact: Rational spacer design, electrolyte buffering, and geometry tweaks can now be targeted to suppress harmful local pH extremes during high-power operation.

(c) Voltage-directed aging pathways and chemical fingerprints

- In LIC positive electrodes ($LiPF_6$ in EC/DMC), the candidate **maps how increasing float voltage redirects aging chemistry**: at moderate voltages, capacitance loss plus resistance rise are associated with **surface area decrease and pore clogging**; at higher voltages, **further carbon oxidation** and **phenol/ether group formation** dominate, raising resistance to end-of-life. This causal chain is supported by porosity/XPS datasets and TPD-MS signatures.

Application impact: The community gains **voltage-specific mitigation targets** (e.g., antioxidant additives, surface passivation, or texture retention strategies) to extend LIC life while retaining power.

(d) Tailored oxygen functionalization in organic ECs (unpublished study)

- The in-review study, *The Oxygen Enigma*, shows that **which** oxygenated groups are present matters more than **how many**: acidic functionalities can promote a protective polymer-like layer and longer life, whereas fully stripping oxygen accelerates degradation; certain basic groups may foster adsorption of N-containing species and resistance growth. This nuance moves the field beyond the simplistic "less oxygen is always better" paradigm.

Application impact: A **"tailored functionalization"** strategy for activated carbons is proposed—tuning surface chemistry to balance stability with conductivity and wettability for long-life, high-voltage organic ECs.

Verdict on criterion 3: The dissertation presents original solutions to scientific and engineering problems with clear pathways to industrial relevance in EC/LIC design.

Additional scholarly merits

- **Clarity and structure.** The General Conclusion distills multi-system findings into concise design guidance (pH management, in-cell PZC/RZC determination, voltage-dependent aging) and explicitly links methods to insights—a mark of mature scientific communication.
- **Reproducibility and transparency.** Rich SI (porosity distributions, deconvoluted XPS, TPD-MS spectra lists) enhances transparency and reuse.
- **Scope and novelty.** The candidate also highlights *lithium nitrate* aqueous media probed by EQCM for the first time in this context, broadening electrolyte landscapes considered for capacitive behavior.

Minor suggestions (do not affect the positive verdict)

1. **Depth-profiling** in XPS (e.g., gentle Ar-etching or angle-resolved measurements) would help decouple surface deposits from sub-surface oxidation in aged electrodes, a limitation acknowledged by the candidate.
2. **Quantitative interphase analytics.** Where polymer-like films are implicated, complementary tools (e.g., in-situ ATR-FTIR or EQCM-D with viscoelastic modeling) could add thickness/viscoelasticity estimates to the chemical assignments.
3. **Model integration.** The RZC and local-pH insights could be embedded into physics-based lifetime models to predict optimal voltage windows vs. geometry/electrolyte—fertile ground for future work.

Final conclusion

On the basis of the evidence presented in the peer-reviewed publications, the in-review manuscript, and the dissertation's integrative conclusions, I am convinced that Ms. Sylwia Ślesińska:

- possesses the **general theoretical knowledge** required for the doctoral degree in chemical sciences, including interfacial electrochemistry, charge storage in porous carbons, and degradation chemistry;
- has demonstrated the **ability to conduct independent scientific research**, from experimental conception through multi-technique execution and mechanistic interpretation;

- and provides **original solutions** with clear **economic and societal relevance** for designing longer-lived, safer, and more efficient ECs/LICs (pH-aware cell design, RZC-aware voltage setting, and tailored carbon functionalization).

Therefore, my evaluation is clearly and unequivocally positive. I recommend awarding the doctoral degree.

Sincerely,

M. Ishikawa

Masashi Ishikawa

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