

Hyperbranched Redox-Active Polymers for Redox Flow Battery Applications



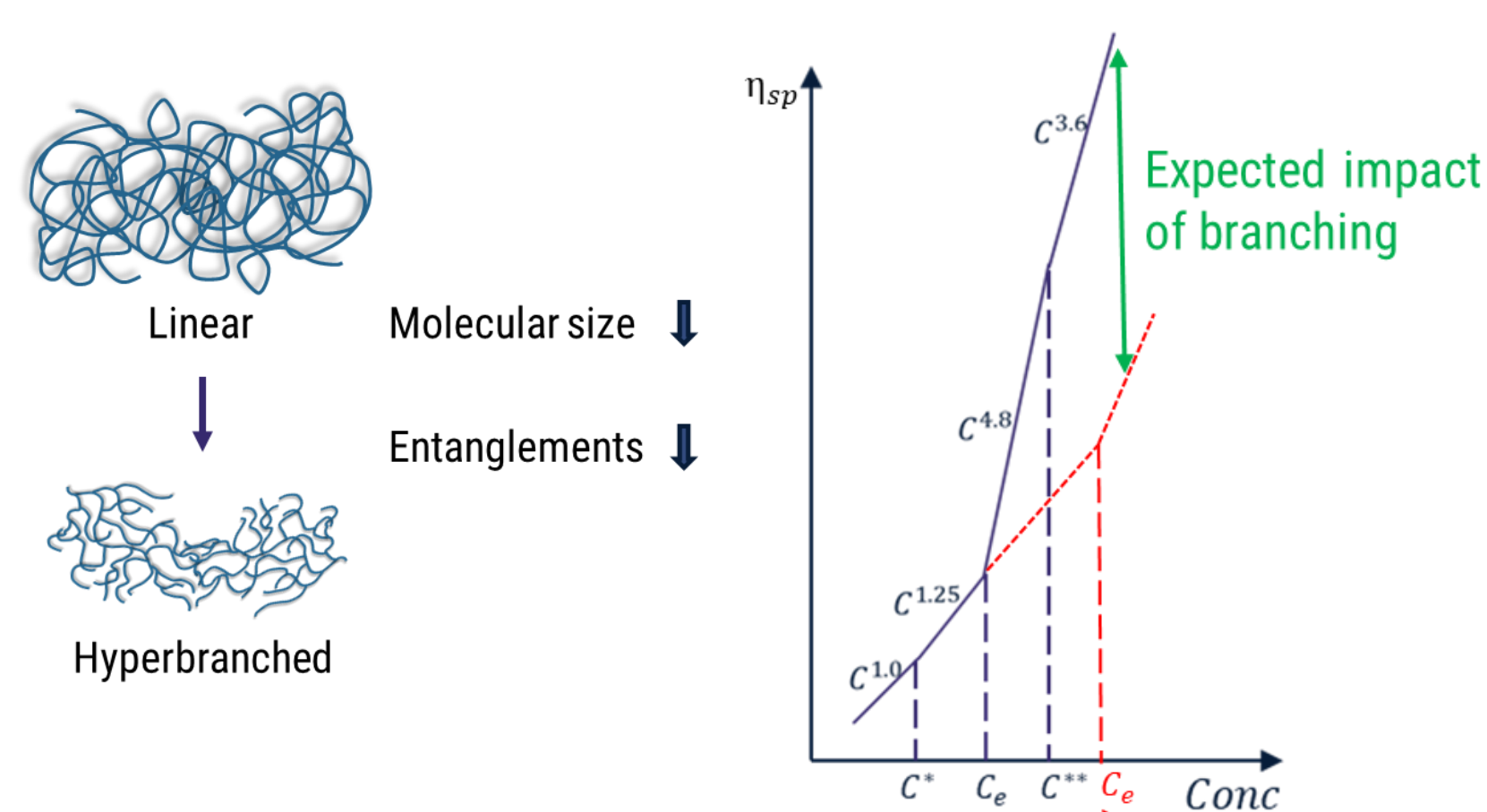
Koosha Ehtiati,^{1,2} Ilya Anufriev,^{1,3} Christian Friebe,⁴ Ivan A. Volodin,^{1,2} Christian Stolze,^{1,2} Simon Muench,^{1,2} Grit Festag,^{1,3} Ivo Nischang,^{1,2,4,5} Martin D. Hager,^{1,2,3,4} and Ulrich S. Schubert*^{1,2,3,4}

- Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstrasse 10, Jena 07743, Germany.
- Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7a, Jena 07743, Germany.
- Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, Jena 07743, Germany.
- Helmholtz Institute for Polymers in Energy Applications Jena (HIPOLE Jena), Lessingstr. 12 – 14, 07743 Jena, Germany.
- Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), Hahn-Meitner-Platz 1, 14109 Berlin, Germany.

Email: koosha.ehtiati@uni-jena.de

Introduction

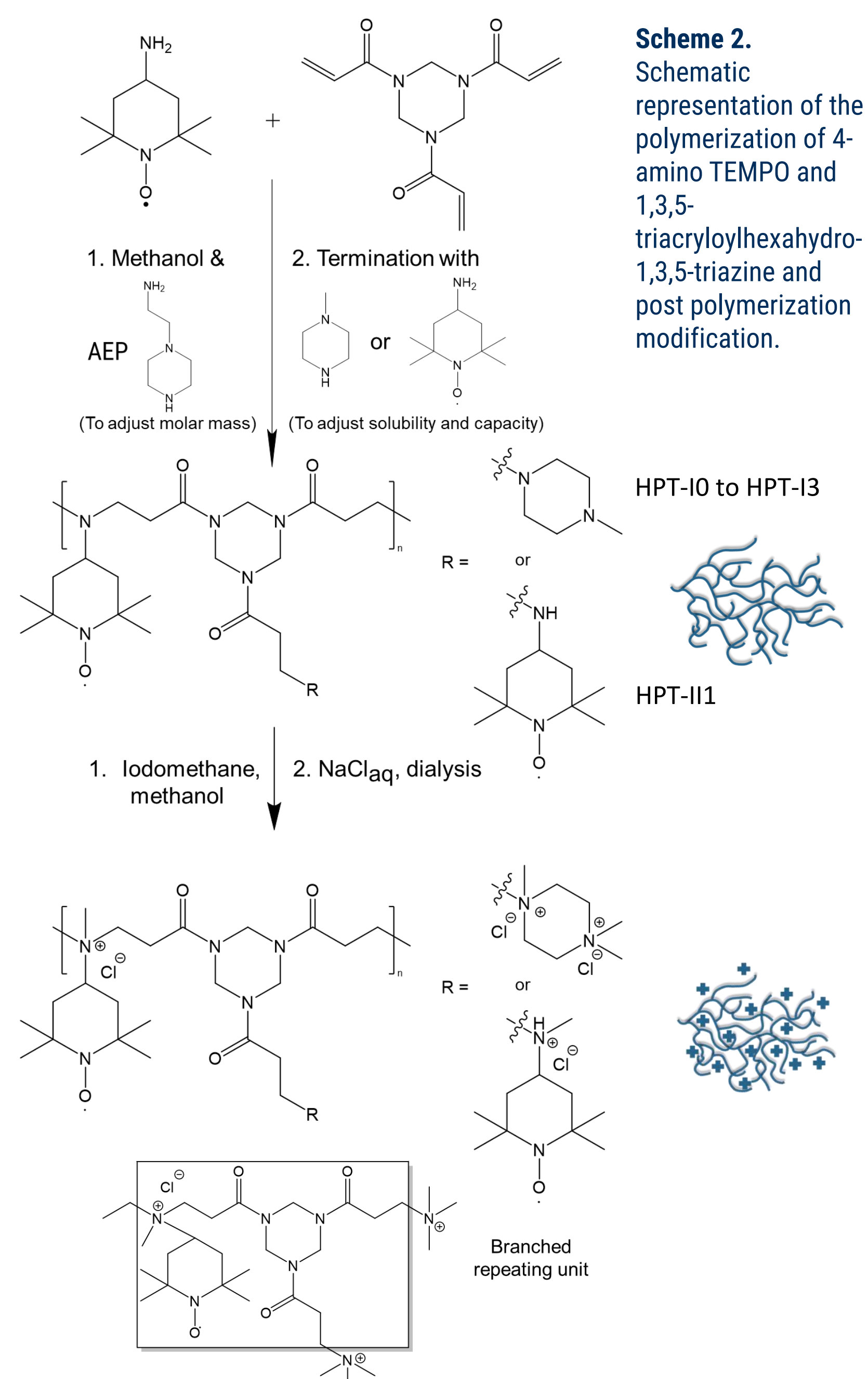
- The high cost of the cell stacks in redox flow batteries (RFB) calls for a cost reduction strategy.¹
- Polymer-based RFBs enable substitution of expensive ion exchange membranes with cheap size exclusion membranes.²
- One major challenge with polymer-based RFBs is the high solution viscosity.



Scheme 1. Schematic illustration of the impact of branching on the molecular interactions and the corresponding viscosity of the polymer solutions.

- The impact of the microstructure and the molecular size on the polymer-based RFBs is underinvestigated.

Synthesis



Characterisation

- Increasing molar mass and the corresponding growth in the intrinsic viscosity with addition of AEP.
- Verification of the compact structure of the synthesized hyperbranched polymers with:
 - Mark-Houwink-Sakurada ($[\eta] = K M_i^{\alpha_{MHS}}$): linear: $\alpha_{MHS} > 0.5$, hyperbranched: $\alpha_{MHS} < 0.5$

Polymer sample	AEP:TEMPO	M_w (g mol ⁻¹)	$[\eta]$ (cm ³ g ⁻¹)	α_{MHS}
HPT-10	0	3,100±700	3.2±0.1	0.24±0.05
HPT-11	0.1: 1	4,100±300	3.7±0.1	0.19±0.04
HPT-12	0.2: 1	7,600±900	3.9±0.3	0.23±0.05
HPT-13	0.3: 1	18,300±2,400	4.4±0.2	0.28±0.04

Table 1. Structural and hydrodynamic properties of the synthesized hyperbranched polymers obtained using SEC with viscometric detection.

Viscosity - crossover trade off

- The optimal molar mass: TEMPO:AEP = 1:0.1
- Further addition of AEP increased viscosity but did not decline crossover.

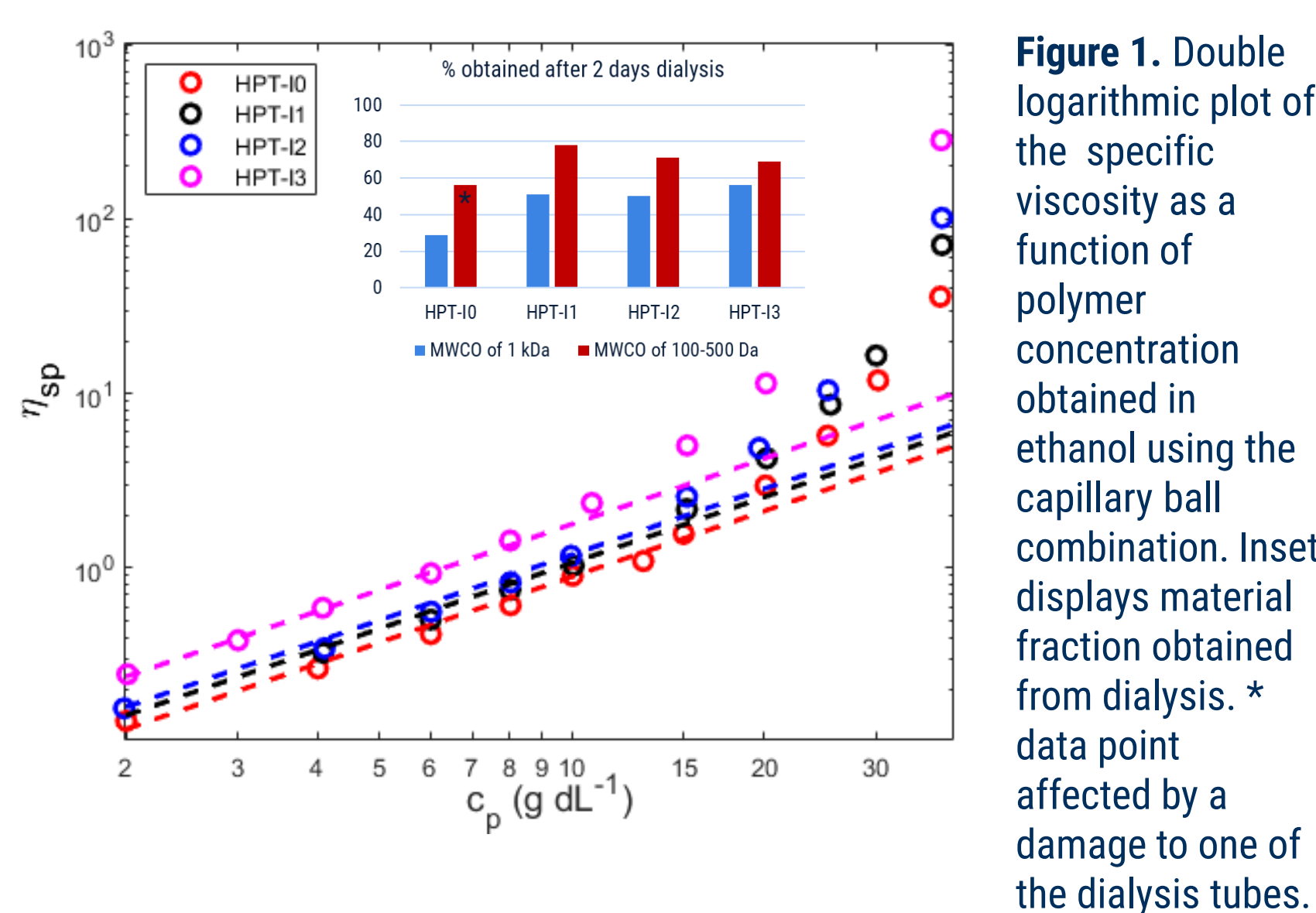


Figure 1. Double logarithmic plot of the specific viscosity as a function of polymer concentration obtained in ethanol using the capillary ball combination. Inset displays material fraction obtained from dialysis. * data point affected by a damage to one of the dialysis tubes.

- Hyperbranched structure showed low viscosity but deactivation of TEMPO moieties reduced the active TEMPO concentration.

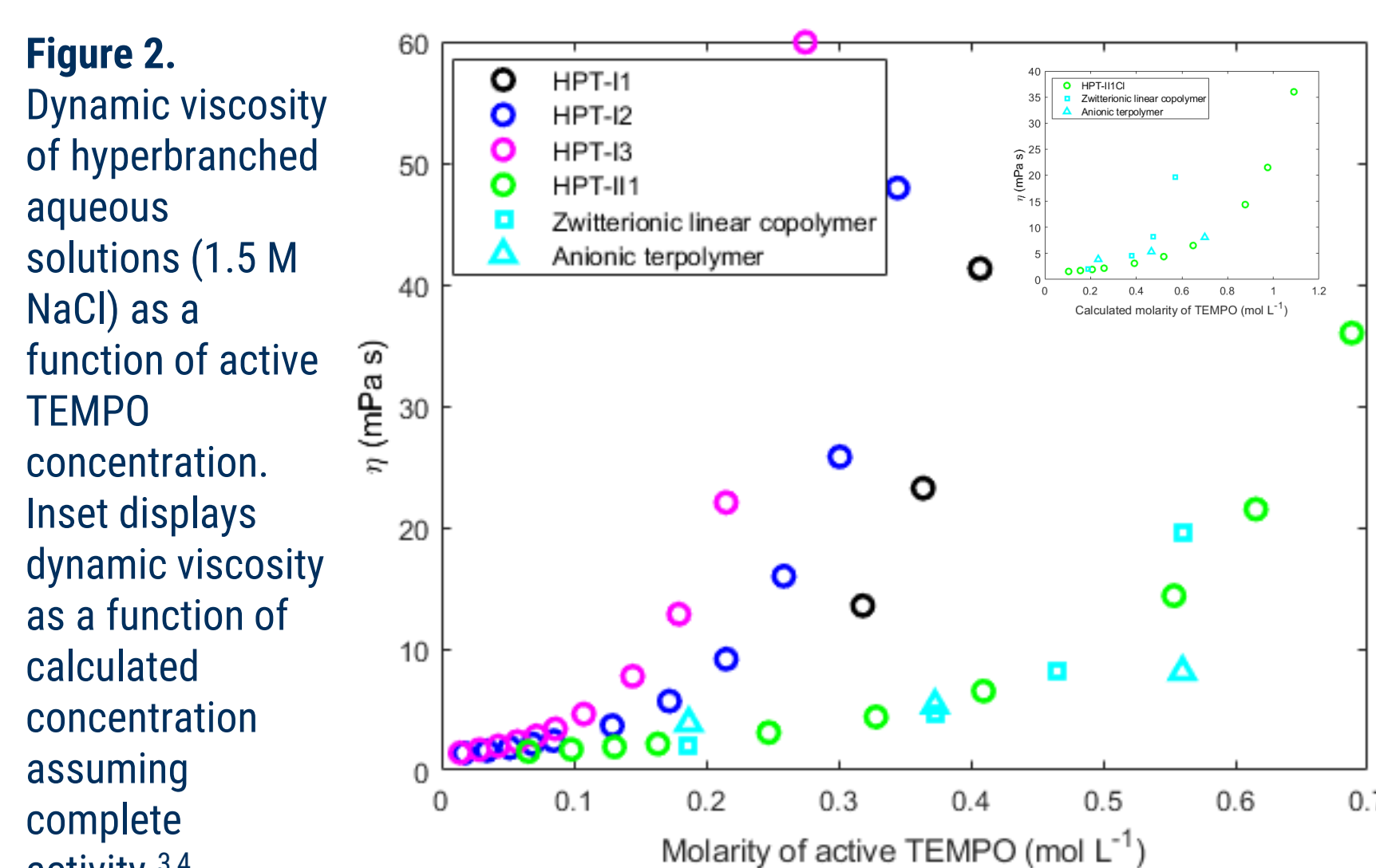


Figure 2. Dynamic viscosity of hyperbranched aqueous solutions (1.5 M NaCl) as a function of active TEMPO concentration. Inset displays dynamic viscosity as a function of calculated concentration assuming complete activity.^{3,4}

Electrochemical properties

- Electrochemically quasi-reversible with:
 - $E^0 = 0.72 \text{ V vs Ag/AgCl}$
 - $D = 1.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

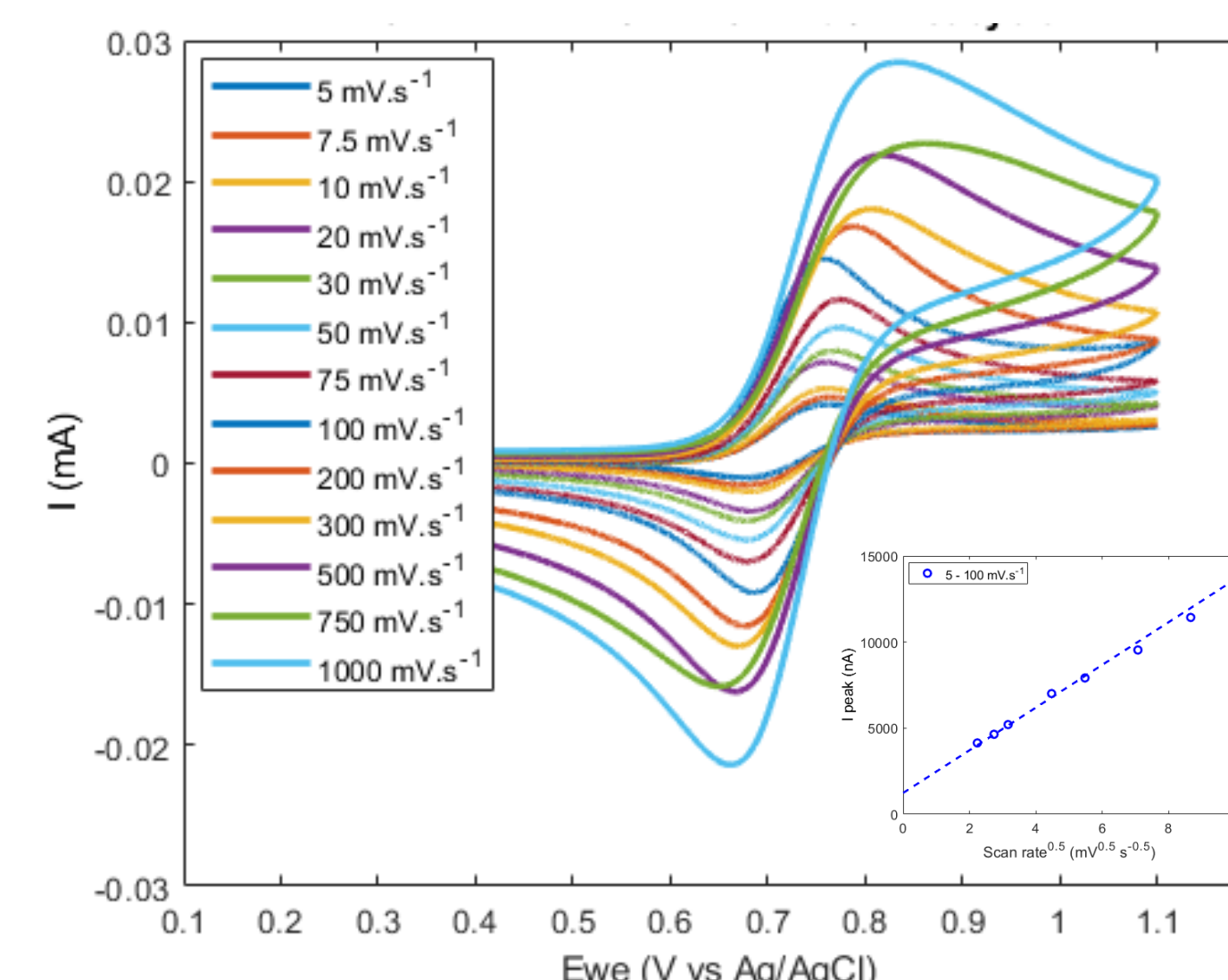


Figure 3. Cyclic voltammogram of the selected hyperbranched polymer (equivalent to 5.7 mM TEMPO) at various scan rates in 1.5 M NaCl solution pH = 2.0.

- Electrochemical properties obtained from rotating disc electrode voltammetry (RDE):

- $D = 1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$
- $k^0 = 1.9 \times 10^{-3} \text{ cm s}^{-1}$

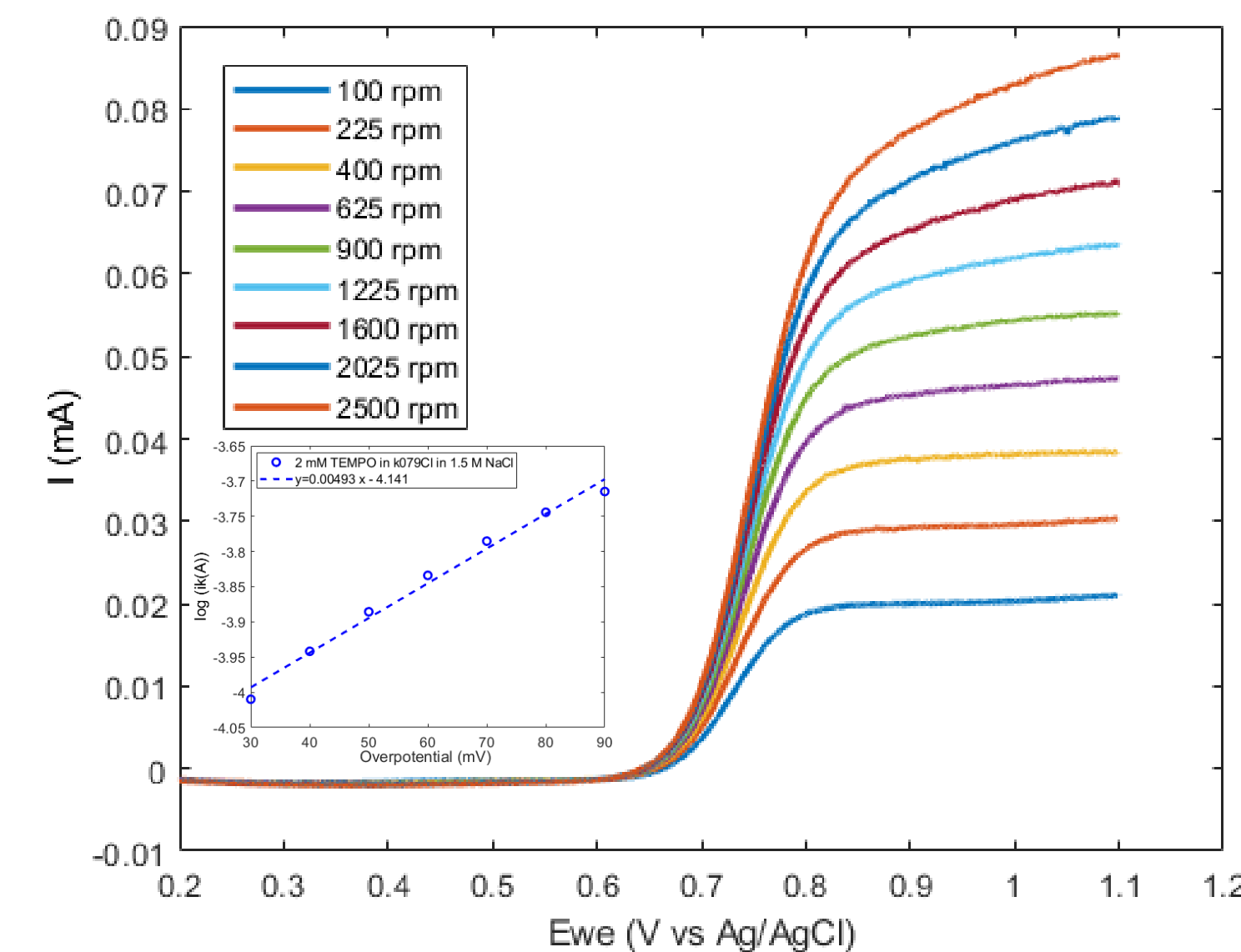


Figure 4. Background-subtracted RDE voltammograms of the selected hyperbranched polymer (equivalent to 2 mM TEMPO) at various rotation rates in 1.5 M NaCl solution pH = 2.0.

Conclusion

- Advantages of hyperbranched structure:
 - Viscosity in concentrated solution.
 - D and k^0 (higher than linear polymers^{3,4}).
- Remaining challenges:
 - Being prone to crossover.
 - Deactivation of TEMPO moieties.

¹ K. Amini, A. N. Shocron, M. E. Suss and M. J. Aziz, *ACS Energy Lett.*, **2023**, *8*, 3526-3535.
² T. Janoschka, N. Martin, U. Martin, C. Friebe, S. Morgenstern, H. Hiller, M. D. Hager and U. S. Schubert, *Nature*, **2015**, *527*, 78-81.
³ T. Hagemann, M. Strumpf, E. Schröter, C. Stolze, M. Grube, I. Nischang, M. D. Hager and U. S. Schubert, *Chem. Mater.*, **2019**, *31*, 7987-7999.
⁴ H. Fu, C. Zhang, H. Wang, B. Du, J. Nie, J. Xu and L. Chen, *J. Power Sources*, **2022**, *545*, 231905.
⁵ K. Ehtiati, I. Anufriev, C. Friebe, I. A. Volodin, C. Stolze, S. Muench, G. Festag, I. Nischang, M. D. Hager, U. S. Schubert, submitted.