

Disclosing the Electronic Properties of the Native Solid Electrolyte Interface in Mg-ion batteries by means of Scanning Electrochemical Microscopy

Carla Santana Santos,^[a] Martina Romio,^[b] Yuri Surace,^[b] Edgar Ventosa,^[c] Wolfgang Schuhmann,^[a]

[a] Analytical Chemistry - Center for Electrochemical Sciences (CES), Faculty of Chemistry and Biochemistry, Ruhr University Bochum; Universitätsstr. 150, D-44780, Bochum, Germany

[b] Battery Technologies, Centre for Low-Emission Transport, AIT Austrian Institute of Technology GmbH, Giefinggasse 2, 1210, Vienna, Austria

[c] Department of Chemistry; University of Burgos; Pza. Misael Bañuelos s/n, 09001, Burgos Spain

carla.santanasantos@rub.de

In the last years, lithium-ion batteries (LIBs) have had a considerable impact on our society due to their long-lasting lifetime and energy density, thus becoming a widely used battery system. However, since LIBs contain flammable solvents and toxic or scarce raw materials, the development of more environmentally friendly and safer battery systems is pivotal.^[1] Amongst the most promising beyond-Li technologies are the Na-ion (NIB) and multivalent-ion batteries (e.g. Mg²⁺, Al³⁺).^[2] Among those, magnesium-ion batteries (MIBs) are of high interest due to their higher volumetric energy density of 3833 mAh cm⁻³ in contrast to 2046 mAh cm⁻³ for Li and 800 mAh cm⁻³ for graphite^[3]. One of the challenges in developing MIBs is the spontaneous formation of a native solid electrolyte interphase (n-SEI), which might prevent the reversible Mg²⁺ plating and Mg⁰ stripping.

The SEI plays a key role in the stability of the batteries as it prevents the continuous degradation of the electrolyte at the anode. Ideally, the SEI needs to be an insulating layer for electron transfer reactions (low electronic conductivity), and in parallel still allowing ion flux (high ionic conductivity). Hence, studying the electrochemical properties of the n-SEI is required^[2,3]. The ionic properties of the SEI can be investigated using electrochemical impedance spectroscopy (EIS). However, only few techniques are employed to quantify the protecting characteristic of the SEI. Advanced techniques such as scanning electrochemical microscopy (SECM) are capable methods of uncovering interfacial electrochemical properties of active materials for LIB^[4], NIB^[5] and potassium-ion (KIB)^[6] battery systems. Specifically, the feedback mode (FB-SECM) is able to interrogate the SEI properties due to its capability to electrochemically convert a redox mediator present in the electrolyte.^[4] The working principle of the FB-SECM is illustrated in Figure 1. As the SECM methodology was not explored before in the framework of MIBs, potential experimental parameters are unknown and we had to find a suitable reference electrode system as well as free-diffusing redox mediator for the used solvents. Mg discs were soaked in a variety of electrolytes to form the n-SEIs, and the samples were transferred to the SECM setup inside an Ar-filled glovebox for the feedback mode experiments. We then quantified the electronic properties of the formed n-SEI in MIBs. The SECM results suggest substantial protecting properties of the formed n-SEIs.

Acknowledgements: This project has received funding from the European Union's Horizon 2020 research and innovation programme under the grant agreement No 861962 (NanoBat). C.S.S., E.V. and W.S. acknowledge funding from the European Union's Horizon Europe research and innovation programme – European Innovation Council (EIC) under the grant agreement No 101046742 (MeBattery).

References:

- [1] J. B. Goodenough, Y. Kim, *Chem. Mater.* **2010**, *22*, 587.
- [2] J. W. Choi, D. Aurbach, *Nat Rev Mater* **2016**, *1*, 16013.
- [3] D. Aurbach, Z. Lu, A. Schechter, Y. Gofar, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature* **2000**, *407*, 724.
- [4] a) C. S. Santos, A. Botz, A. S. Bandarenka, E. Ventosa, W. Schuhmann, *Angew. Chem., Int. Ed. Engl.* **2022**, *61*, e202202744; b) Z. J. Barton, J. Rodríguez-López, *Anal Bioanal Chem* **2016**, *408*, 2707; c) L. Danis, S. M. Gateman, C. Kuss, S. B. Schougaard, J. Mauzeroll, *ChemElectroChem* **2017**, *4*, 6; d) S. Daboss, F. Rahmanian, H. S. Stein, C. Kranz, *Electrochem. Sci. Adv.* **2021**, *2*, e2100122; e) E. Ventosa, W. Schuhmann, *Phys. Chem. Chem. Phys.* **2015**, *17*, 28441.
- [5] D. Sarbapalli, Y.-H. Lin, S. Stafford, J. Son, A. Mishra, J. Hui, A. Nijamudheen, A. I. B. Romo, Z. T. Gossage, A. M. van der Zande et al., *J. Electrochem. Soc.* **2022**, *169*, 106522.
- [6] Z. J. Barton, J. Hui, N. B. Schorr, J. Rodríguez-López, *Electrochim. Acta* **2017**, *241*, 98.

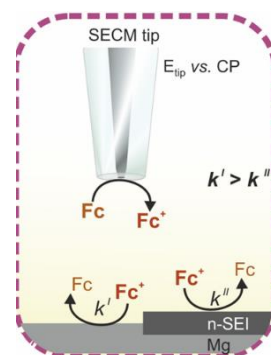


Figure 1. Illustration of FB-SECM working principle, where the redox mediator ferrocene (Fc) is dissolved in the Mg-chemistry electrolyte.