

Calcium Metal Anodes – Similarities and Differences to their Mg and Li Counterparts

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Since decades, the realization of a lithium metal anode is targeted due to its appealing high capacity (3860 mAh g⁻¹ and 2060 mAh cm⁻³) and low redox potential (-3.04 V vs. SHE). However, its tendency to dendrite formation and oxidation still hinders an application. Abundant multivalent metals like magnesium or calcium not only offer cost advantages, but also a potentially safer operation. Specifically, calcium metal is promising due to its redox potential being competitive to lithium (-2.87 V vs. SHE). Indeed, the research on Ca batteries is still in its infancy, but might benefit from the gained knowledge on other metal anode systems. Hence being neighbors in the periodic table and the diagonal relationship, Ca²⁺ features similarities to either Mg²⁺ or Li⁺ ions in terms of carried charge and charge density, respectively.

To examine the transport properties and interfacial processes, polarization measurements in Mg/Mg, Ca/Ca and Li/Li symmetrical cells applying different separator materials were performed. An electrolyte comprising B(hfp)₄⁻ anions in monoglyme (G1) was applied in either case to ensure comparability. It was found, that the cation charge density plays a crucial role in terms of solvent shell size and rigidity to further cause a cation-dependent separator tortuosity and different desolvation characteristics at the anode/electrolyte interface. Furthermore, utilizing operando electrochemical impedance spectroscopy (EIS) insights into the charge transfer characteristics as well as the adsorption and SEI layer formation were gained.

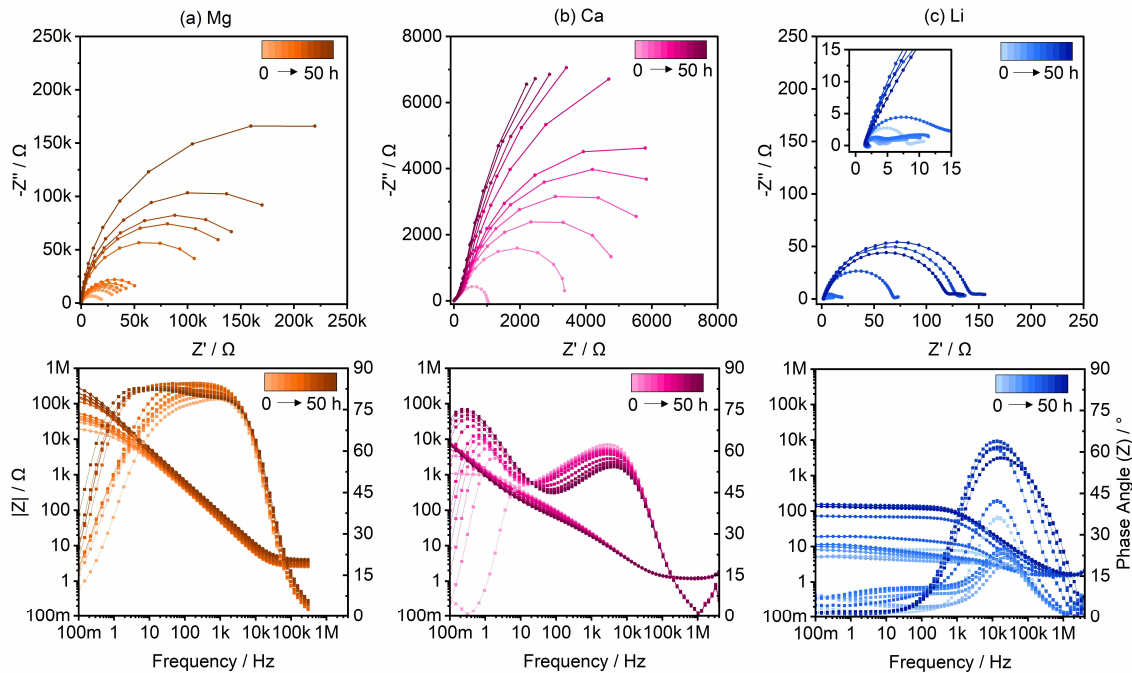


Fig. 1: Impedance evolution in Mg/Mg, Ca/Ca and Li/Li cells during 50 h OCV indicating differences in the charge transfer resistance as well as the formation of a SEI and high-ohmic adsorption layer.