Insights into surficial processes of pristine and coated magnesium anodes in magnesium-sulfur batteries

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The electrochemical couple of magnesium and sulfur represents a promising high-energy battery system with improved sustainability due to higher abundance and better recyclability of the raw materials. Furthermore, the Mg-S battery offers improved safety as magnesium exhibits a lower tendency to form dendrites compared to lithium metal. However, in contrast to Li, magnesium metal is prone to be passivated by surface layers, e.g. a solid electrolyte interphase (SEI), comprising electrolyte decomposition products like MgF_2 and MgO, but also sulfur compounds like $MgSO_4$ and MgS [1]. Latter originates in sulfur species (S_8 and S_x^{2-}) being dissolute at the sulfur composite cathode and diffuse to the Mg anode surface. The passivation character of the SEI is due to the sluggish diffusion of Mg^{2+} ions in most solid materials caused by its large charge density. A promising approach to overcome this issue is the implication of an *ex situ* prepared surface layer with sufficient Mg ion conductivity, a so-called artificial SEI [2,3].

To gain insights into the surficial processes of pristine and artificial-SEI-coated Mg anodes, electrochemical impedance spectroscopy (EIS) was applied. To distinguish between stripping and plating in symmetrical Mg-Mg cells and to exclude the impedance response of the sulfur cathode in full Mg-S cells, half-cell EIS measurements are performed by the use of a magnesium metal reference ring electrode. By analyzing the distribution of relaxation times (DRT), Nyquist, Bode and f-Im plots, the number of present processes was determined and suitable equivalent circuits (EC) were defined. Comparing EIS spectra at open-cell voltage (OCV), different current densities and states of charge (SOC), the processes are assigned to the Mg/Mg^{2+} charge transfer and the SEI diffusion. Furthermore, the porous nature of the artificial SEI is identified and a high-ohmic adsorption layer was found to be present during extended non-current conditions.

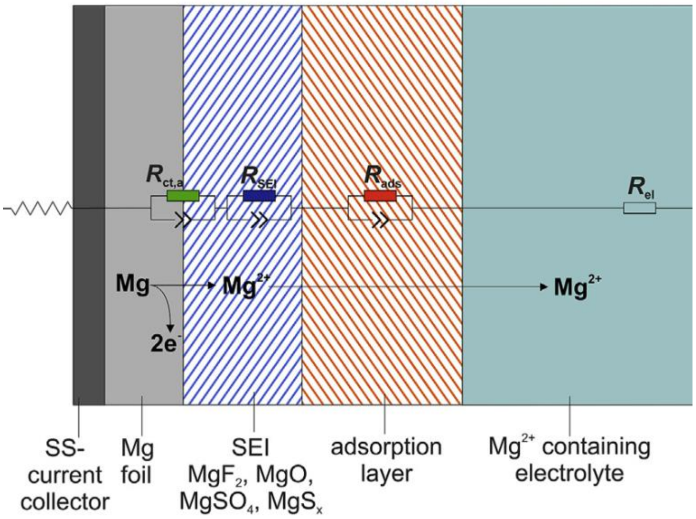

Fig.1: Scheme of the Mg anode surface with the proposed equivalent circuit elements.

References

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