Ion mobility and plating in Mg and Ca based electrolytes

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Various metals have been used as battery anodes in electrochemical cells ever since the birth of batteries with Volta's pile and also in the first commercialized primary (Zn/MnO_2, Leclanché 1866) and secondary (Pb/acid, Planté 1859) batteries. The first Li-MoS_2 cells, employing Li metal anodes, with specific energies two to three times higher than both Ni/Cd and Pb/acid cells were withdrawn from the market after safety issues related to dendrites growth were observed. In contrast to Li and Na metal anodes, however, electrodeposition of Mg and Ca does not seem to be plagued with dendrite formation.[1,2] Pioneering work by Aurbach *et al.* in the early 1990's showed a surface-film controlled electrochemical behavior of Ca and Mg metal anodes in conventional organic solvent based electrolytes.[3,4] The lack of metal plating was attributed to the poor divalent cation migration through the passivation layer. Conversely, the recent demonstration of Ca and Mg plating and stripping in the presence of a passivation layer or an artificial interphase [1,5,6] has paved the way for evaluation of new electrolyte formulations with high resilience towards oxidation. However, several challenges remain to be tackled for the development of Ca and Mg based batteries.[7] Among these a need for reliable electrochemical test protocols and, as stronger cation-solvent and cation–anion interactions are present in divalent cation based electrolytes as compared to Li and Na systems, mass transport limitations are implied.[8] Here the reliability of electrochemical set-ups is discussed, alternative reference electrodes are proposed, and a systematic investigation on the impact of the electrolyte formulation on the cation transport is presented.

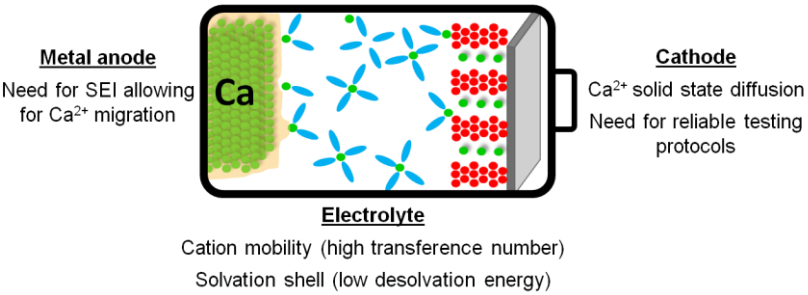

Figure 1: Scheme of a Ca metal anode-based battery with the main problems/ requirements outlined.[7]

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