Electrochemistry of calcium electrode in organic solvents

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Multivalent battery technologies based on alkali-earth metals anodes have arisen as a promising alternative for replacing lithium-ion batteries, alleviating some inherent problems connected with resources, value chains and also performance. Metallic magnesium and calcium anodes possess high energy densities, much higher than the graphite used in current lithium-ion batteries and are comparable to lithium metal anodes. Additionally, these metals are not as prone to dendrite formation as lithium metal, reducing the risks of fires or explosions. However, the inhibiting layers, which form on these metals in organic solvents, are very stable and do not allow fast migration and/or diffusion of calcium cations through them, quite unlike the SEI layers enabling the operation of lithium-ion batteries. To develop calcium batteries with reversible redox reactions it is therefore necessary to carefully optimize the electrolyte and tailor the surface layers formed on the metal anode.

In this work we have tested a series of different electrolyte solvents (ethylene carbonate, propylene carbonate, dimethylformamide, acetonitrile, THF, DME *etc.*) with either $Ca(BF_4)_2$ or $Ca(TFSI)_2$ salts to understand the mechanisms and kinetics of calcium plating/stripping. We used Ca metal disc electrodes or inert Pt electrodes in three-electrode cells with Pt-pseudo reference electrodes, and activated carbon as counter-electrodes. A range of different electrochemical methods were used: cyclic voltammetry, electrochemical impedance spectroscopy, EQCM, potential step methods, *etc*. Detailed characterization of the composition and the structure of the obtained surface layers was done by FTIR spectroscopy and X-ray diffraction.

We correlate the influence of the solvents and salts with the electrochemical behaviour of the calcium metal anode, which advances the field of calcium metal layers and opens ways to improved stability and efficacy in calcium battery-based energy storage solutions.

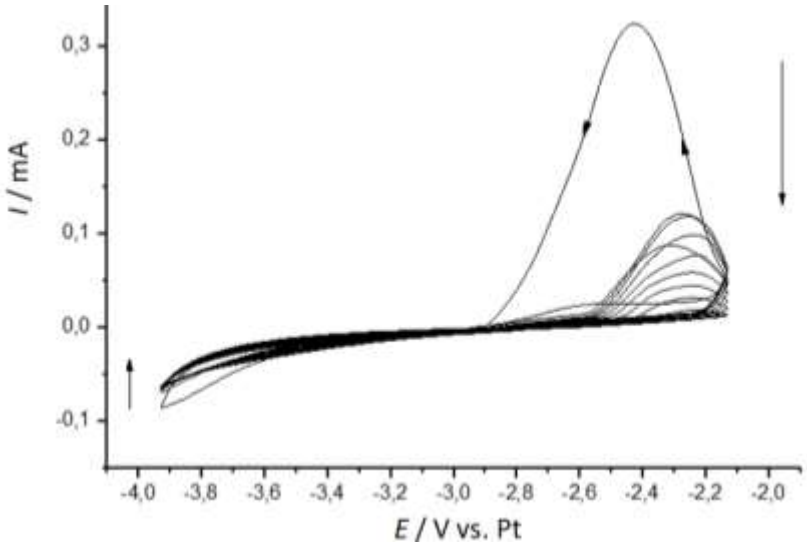

Figure 1. Plating and stripping of calcium electrode in $Ca(BF_4)_2$ / ethylene carbonate. Scane rate 10 mV /s

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References

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