Ionic Charge Transfer Kinetics between Solid State and Liquid Lithium Electrolytes

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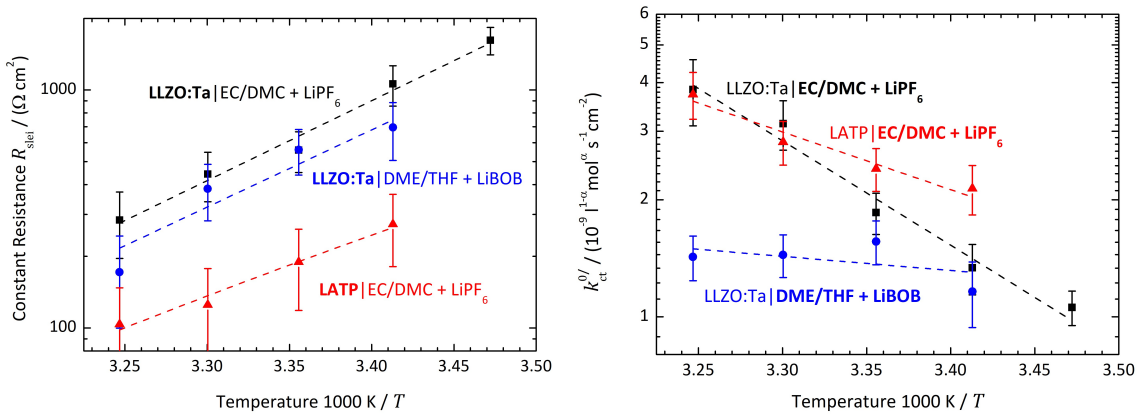
Solid Li^+ electrolytes are not only discussed for applications in all-solid-state batteries (ASSB) but also as ceramic membranes in Li-S and Li-O_2 cells with liquid Li^+ electrolytes to separate the anode from cathode space. This allows the use of different (*e.g.* non-aqueous, aprotic and aqueous, protic) anolytes and catholytes and may also avoid short circuits by metal dendrite growth when using metallic Li anodes. [1] Despite the possible relevance for future applications only few studies on Li^+ transfer between solid/liquid electrolytes can be found in literature. It is discussed whether a Butler-Volmer-like transfer process in the electric double layer between solid and liquid electrolyte or a low conducting degradation layer formed on the solid electrolyte is responsible for the observed interface resistance. [2,3]

In this contribution the kinetics of the ionic transfer between combinations of solid and liquid electrolytes with different tendency to form degradation layers and solvation energy are investigated. A garnet-type ($Li_7La_3Zr_{1.6}Ta_{0.4}O_{12}$, LLZO:Ta) and a NASICON-type ($Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$, LATP) solid Li^+ electrolyte is combined with an alkyl carbonate-based ($LiPF_6$ + EC/DMC) and an alkyl ether-based (LiBOB + DME/THF) liquid Li^+ electrolyte. Temperature dependent measurements in a wide range of electrolyte concentrations c_{LiPF_6} were performed using a liquid/solid/liquid DC polarisation cell. [4,5]



Symmetric S-shaped polarization curves can be found, *i.e.* current density *vs.* interfacial potential drop. At Li^+ concentrations below 0.1 mol/l, the polarisation resistance R_P depends on c_{Li^+} and obeys a power law. At higher concentrations above 0.1 mol/l, R_P reaches a constant value. This behaviour indicates a simultaneous presence of a Butler-Volmer-like transfer process and a constant ohmic resistance due to a low conducting surface layer (solid-liquid electrolyte interphase, SLEI). [4] The SLEI formed on LLZO:Ta has a higher areal resistance (600 Ω cm²) as formed on LATP (200 Ω cm², 25 °C). The activation energy for Li^+ transport in the SLEI formed on LLZO:Ta is significantly higher (70 kJ/mol) as formed on LATP (50 kJ/mol). The rate constant $k_{ct}^{0\prime}$ of the Butler-Volmer-like transfer process for alkyl carbonate-based liquid electrolytes is significantly higher compared to the alkyl ethers-based electrolyte. Remarkably, the activation energy for alkyl carbonate-based electrolytes is much higher (30–50 kJ/mol) compared to the alkyl-ether based electrolyte (about 10 kJ/mol). [5] This does not resemble an only dependence on the solvation energy as suggested in literature. [3] Focusing only on this feature may be an oversimplification and disregards entropic effects present in the pre-exponential factor.

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