

New Functional Electrolyte for Improved Cycling Stability of Lithium Storage Alloy Anodes

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Driven by the fact that Lithium Storage Metals and Alloys like Sn, SnSb, Si, Al show higher specific charges and charge densities than carbonaceous materials, they have been repeatedly proposed as new anode materials for lithium ion cells [1]. However, as a result of the large volume changes during the uptake and removal of lithium, these materials show rather poor cycling stability. Strategies like the reduction of the particle size, the use of multiphase materials that undergo phase separation during cycling in combination with a proper design of composite electrodes [2] lead to an improvement, but the excellent cycling stability of carbon based anode materials has not been achieved yet.

Most of the research so far was done to improve the active materials itself while only little emphasis was put on new functional electrolytes and the Solid Electrolyte Interphase (SEI) [3]. It is widely accepted that the SEI formed between the surface of the electrode and the electrolyte is a most important prerequisite for good electrode performance. While the surface of lithiated carbon remains passivated by the SEI formed in the first few charge/discharge cycles a once built SEI on the surface of a Lithium Storage Metal will suffer from major and minor cracks due to the volume expansion of the active materials. The electrolyte is able to penetrate into this cracks and will decompose at sufficient low potentials. Obviously, this rather dynamic surface of Lithium Storage Alloys causes film formation not only in the first few cycles but all throughout the electrodes cycle life [4]. As a consequence, electrolyte additives or functional electrolyte components that work well with graphitic anodes may fail with Lithium Storage Alloys and vice versa. Although the situation with the SEI formation is quite difficult, there are chances to improve the cycling stability of Lithium Storage Alloys by using new functional electrolytes and appropriate charging procedures that may cause beneficial SEI properties.

This contribution will present the effect of new functional electrolyte components in propylene carbonate (PC) based electrolytes in combination with appropriate charging procedures. Fig 1. Shows that the use of a standard PC-based electrolyte and simple constant current charging leads to rapid failure of the electrode while a drastic improvement of the cycling stability is observed when the charging process and the electrolyte composition are chosen properly. These results are the more noteworthy, as the new electrolyte solvent is not capable to prevent graphitic anodes from solvent co-intercalation (Fig. 2). Therefore we conclude that for achieving some progress with the cycling stability of Lithium Storage Alloys completely different electrolyte components than those applied with graphite anodes seem to be necessary.

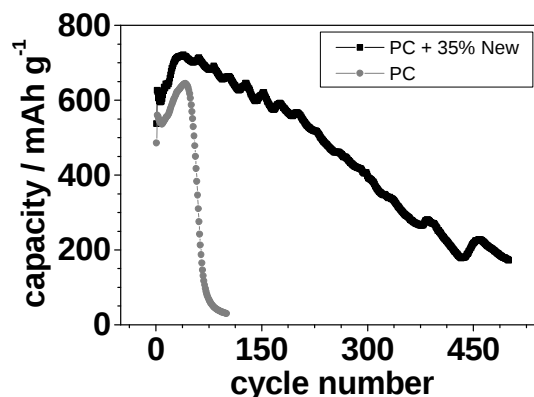


Fig. 1: Effect of a new charge procedure and a new electrolyte component on the cycling performance of an electroplated Sn_2Co anode. (●) 1 M LiClO_4 in PC and simple constant current charging (CCC) at $250 \mu\text{A cm}^{-2}$, cut-off: 20-1200 mV vs. Li/Li^+ , (■) 1 M LiClO_4 in PC + 35 Vol.-% new electrolyte component and combined charge procedure: potentiodynamic charging step ("taper charging"): 2.5 - 0.8 V vs. Li/Li^+ , followed by constant current charge/discharge cycling at $250 \mu\text{A cm}^{-2}$, cut-off: 20-1200 mV vs. Li/Li^+ .

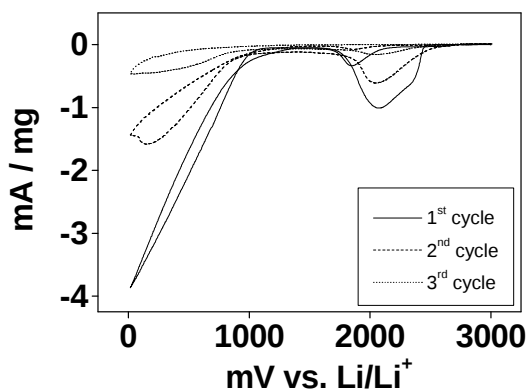


Fig. 2: Cyclovoltammogram of a KS6 (Lonza) electrode (90% KS6, 10% PVdF) in electrolyte composition: 20% new, 80% PC, 1M LiClO_4 , scan rate 0.25 mV/s

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References

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