

Interfacial Stabilization Enhances the Cycling Ability of Tin-Based Battery Anodes

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The control of interfacial reaction between tin-based anodes and electrolyte, and the solid electrolyte interphase (SEI) composition is a promising approach for enhancing cycling performance. Our earlier studies showed that in the conventional electrolyte tin is unstable due to the attack by electrolyte components.^{1,2} Inevitable large volume change of tin during alloying/dealloying with lithium is accompanied by dynamic change in active interfacial area,³ then, the interfacial instability of tin deteriorates with during cycling. As a result, formation of a stable SEI layer seems to be hardly obtainable. Interfacial stabilization of tin by finding interfacially compatible electrolyte component, in addition to accommodation of volume change, is necessary for enhanced cycling ability. Studies of carbon- and binder-free film model electrode can give a clearer insight into the electrode-electrolyte interfacial reaction.^{1,2,4} We report here the impacts of interfacial stabilization of tin-nickel film model electrode, prepared by pulsed laser deposition (PLD), on the SEI stability and cycling ability. Applying our strategy of interfacial stabilization to bulk tin-nickel anode, enhancement of cycling ability is demonstrated.

The ~500 nm thick films of tin-nickel on stainless steel substrate were prepared using PLD at 40 °C in ~1 mtorr of Ar, using KrF excimer laser with an energy density of ~3-4 mJ/cm² at 10 Hz impinging on the targets that possessed 35 mol% of nickel. Lithium cells containing tin-nickel film electrode as a working electrode, and lithium reference and counter electrodes are examined for their cycling ability at 90 μ A/cm² between 0.05 and 1.5 V vs. Li/Li⁺ in the electrolyte of 1M LiPF₆/EC:EMC (3:7) without or with inorganic additive as an interfacial stabilizing agent. The composition of the SEI layer is determined *ex situ* using attenuated total reflectance FTIR spectroscopy.

Fig. 1 compares differential capacity plots of the lithium cells with tin-nickel electrodes in the electrolyte without and with additive at different cycle number. Cathodic peak below 0.4 V and anodic peaks ranged from 0.6 to 0.8 V are attributed to alloying/dealloying of tin with lithium. The redox peaks tend to diminish in the electrolyte only (Fig. 1a), whereas with additive higher capacity and greater capacity retention are obtained, maintaining the structural resolution of lithiation and delithiation till the 50th cycle (Fig. 1b). This demonstrates the role of additive in stabilizing the interface and enhancing the cycling ability of tin-nickel electrode.

After cycling in electrolyte only in Fig. 2a, no clear spectral feature is observed. This reveals no formation of the SEI. With additive (Fig. 2b), electrode shows the signatures from the SEI; mainly lithium carbonate and low concentration of alkyl carbonate salt and organic phosphorous fluorides. The data indicate that electrode surface is significantly better passivated by the SEI, which is correlated to enhanced cycling ability. Further

interfacial chemistry-performance relation would be discussed in the meeting.

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References

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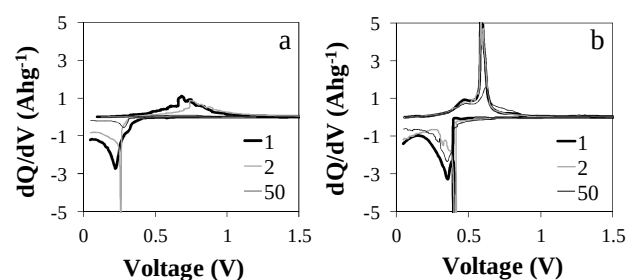


Fig. 1. Differential capacity plots of the lithium cells with tin-nickel electrodes in the electrolyte of (a) 1M LiPF₆/EC:EMC and (b) with additive at different cycle number.

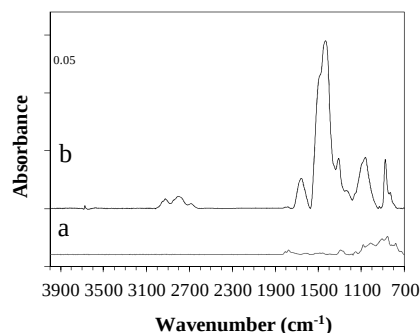


Fig. 2. IR spectral comparison for tin-nickel electrodes after cycling in the electrolyte of (a) 1M LiPF₆/EC:EMC and (b) with additive.