

Understanding the Initial Interfacial Reaction Behavior of Tin-Nickel Battery Anode

S. Hong,¹ M.-H. Choo,¹ Y. H. Kwon,³
S.-W. Woo,³ J. Y. Kim,³ S.-W. Song^{1,2}

¹Graduate School of Green Energy Technology, ²Department of Fine Chemical Engineering & Applied Chemistry, Chungnam National University, Daejeon 305-764, ³LG Chem. Ltd., Battery R&D Center, Daejeon, 305-380, Korea

Tin-based materials are potential alternative anode materials because of about three times larger theoretical specific capacity (990 mAh/g) of tin than conventional graphite and high electronic conductivity.^{1,2} However, major drawback is a short cycle life caused by volume change during alloying/dealloying with lithium and by consequent particle cracking, disintegration and isolation.¹⁻⁴ Interfacial control by screening and selecting interfacially compatible electrolyte components is one of the most effective methods to improve cycling performance. Reductive decomposition of interfacially compatible electrolyte can form a stable passivation film at the surface of tin, which prevents from further irreversible electrolyte decomposition and thereby improves cycling ability. In that aspect, it is important to understand basically how interfacial reaction affects cycling behavior of tin-based anodes. In this presentation, we report initial interfacial reaction behavior, formation and composition of solid electrolyte interphase (SEI) of tin-nickel film model electrode. Correlation of those initial changes to cycling performance would be discussed.

The ~500 nm thick films of tin-nickel composite on stainless steel substrate were prepared by pulsed laser deposition (PLD) at 40 °C in 6 mTorr of Ar, using KrF excimer laser with an energy density of ~3-4 mJ/cm² at 10 Hz impinging on a tin-nickel target. Lithium cells, which consists of tin-nickel film electrode as a working electrode and lithium as counter and reference electrodes, and the electrolyte of 1M LiPF₆/EC:EMC (3:7) with additive, were examined for their cycling ability at 90 μA (~2.4C) between 0.05 and 1.5 V vs. Li/Li⁺. In order to examine how interfacial reaction behavior changes during the initial cycling, several identical cells were cut-offed at different state of charge (SOC). Electrodes obtained at each SOC were subjected to ex situ infrared spectroscopic and scanning electron microscopic analyses.

Fig. 1 shows initial voltage profile and differential capacity plots of the lithium cell with tin-nickel film electrode. In the voltage range from open circuit voltage to 0.5 V, no cathodic peak due to electrolyte reduction is observed, in contrast to severe electrolyte decomposition usually observed on tin.^{3,4} Tin-nickel electrode seems to be interfacially stabilized by the use of appropriate electrolyte additive. Cathodic peaks ranged from 0.4 to 0.2 V and anodic peaks at 0.55 - 0.65 V are attributed to lithiation of tin and delithiation, respectively.³ The first charge (lithiation) and discharge (delithiation) capacities are 547 and 411 mAh/g, respectively, with initial coulombic efficiency of 75 %.

Fig. 2. shows IR spectral evolution of tin-nickel composite electrode upon initial charging and discharging to various SOC (cut-off voltages). The appearance of new but low absorbance peaks after charging to 0.45 V indicates that initial reductive electrolyte decomposition

occurs but just a little. After charging to 0.18 V, the peaks near 1525 cm⁻¹ and 882 cm⁻¹ due to lithium carbonate is observed as the main surface species, together with alkyl functionality. The evolution of spectral feature with charging and discharging reflects the change in the SEI species. Further discussion of initial interfacial reaction behavior and its correlation to cycling performance would be presented in the meeting.

Acknowledgements

This work was supported by the Converging Research Center Program (2012K001255) through the Ministry of Science, ICT & Future Planning of Korea.

References

1. M. Winter and J. O. Besenhard, *Electrochim. Acta*, **45**, 31 (1999).
2. M. Wachtler, J. O. Besenhard and M. Winter, *J. Power Sources*, **94**, 189 (2001).
3. S.-W. Song and S. W. Baek, *Electrochim. Acta*, **54**, 1312 (2009).
4. S. W. Baek, S. J. Hong, D. W. Kim and S.-W. Song, *J. Power Sources*, **189**, 660 (2009).

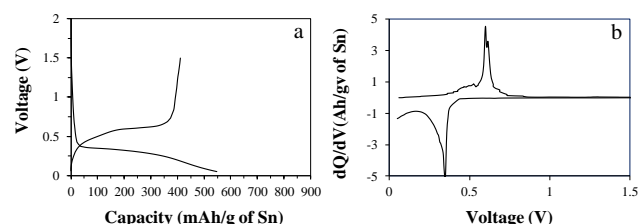


Fig. 1. Initial voltage profile (a) and differential capacity plot (b) of the lithium cell with tin-nickel film model electrode.

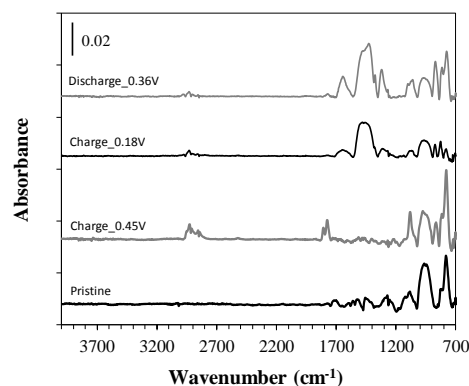


Fig. 2. IR spectral evolution upon charging and discharging to different state of charge.