Comprehensive Interpretation of Operating States for Performance Management in Li-ion Batteries with Tailored Electrodes

Abstract: Among all the rechargeable batteries, lithium ion batteries (LIB) are the most commercially produced ones. Tin (Sn) operates in a suitable potential window and attains a higher specific capacity compared to other materials commercially established as anode for LIB. In this thesis work, Sn is electrodeposited on polymer template assisted porous current collector to alleviate the volumetric stress induced material and capacity loss. The anode consisting of Sn coating over surface modified copper (Cu) current collector maintains the structural integrity after 100 charge-discharge cycles along with possessing a good rate capability (423 mAh g^{-1} at 2C). However, for a considerably known material system like Sn, it becomes utmost important to dig deep into the thermodynamics and kinetics of lithiation-delithiation process while in operation. Certain states of charge (SoC), where Sn lithiates to LiSn, Li_7Sn_3 and Li_7Sn_2, are very crucial. Major structural alterations at those points dictate the Li^+ ion diffusion kinetics in the electrode. During high voltage charging at elevated SoC, overpotential, dominated by the concentration polarization component, escalates causing a considerable voltage loss. Li-ion insertion in Sn anode takes place through a combination of diffusion controlled process and nucleation-growth driven phase transformation. Depending upon the nucleation overpotential, nucleation shifts from instantaneous to progressive mode with cycling for the formation of Li_7Sn_2 phase. Growth dimension increases at the initial stages of cycling leading to a faster phase transformation. This aging dependent nucleation-growth mechanism controls the stress release and stability of the Sn anode. As aging continues, the capacity contribution by nucleation-growth phenomenon slowly fades away compared to that from diffusion process. Driven by the need for high energy density applications like the electric vehicles (EVs), this thesis extends its focus on high voltage cathode material, lithium nickel manganese oxide (LNMO). Various structural properties along with the chemical composition in terms of Mn^{3+} content are influenced by the parameters like temperature and time during the synthesis of LNMO. Moreover, the relative extent of {100} and {111} faceted surface is optimized to regulate stable cathode-electrolyte interface (CEI) formation. The optimized LNMO with suitable electrolyte, containing the same additive used for Sn anode, delivers an excellent rate capability and retains 93% of its first cycle capacity after 200 cycles run at C/2 rate. The tailor made LNMO with controlled properties can be suitable for purposes with specific applications. Degradation assessment through electrochemical impedance spectroscopy (EIS) reveals that the solid-electrolyte interface (SEI) and its stability primarily determine the state of health (SoH) for Sn anode by affecting other impedance elements. LNMO is quite stable in terms of charge transfer and surface film resistance. However, here the concern is at ~4 V (20% SoC) featuring the Mn^{3+}/Mn^{4+} redox reaction and close to 5 V (100% SoC), where structural modification occurs. This thesis aims to fill the gap between lab scale experimentation and dynamic functioning of two promising electrodes for LIB, considering materials, electrochemical and operational aspects with equal importance.

Keywords: *Surface engineering, Tin anode, Lithium nickel manganese oxide cathode, Electrode-electrolyte interface, Battery states, Thermodynamics and kinetics.*