Ultrathin Lithium Ion Conductor Coatings on $LiNi_{1/2}Mn_{3/2}O_4$ for High Energy Li-ion Batteries

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Spinel structured oxides, such as $LiNi_{1/2}Mn_{3/2}O_4$ have attracted significant interst as the positive electrode materials for rechargeable lithium ion batteries because the potential where lithium is removed from the host structure is very high (~4.7V vs Li^+/Li^0).[1-3] One of the barriers to commercialization of $LiNi_{1/2}Mn_{3/2}O_4$ is precisely due to the high voltage of operation, which is outside the window of stability of the electrolyte solutions used in current Li-ion batteries. As a result, spurious reactions occur during cycling that lead to the electrolyte decomposition on the surface of the electrode that compromise the life of the whole device. This undesirable process is aggravated at small particle sizes because of the increase in surface area.[4-8]

To mitigate unfavorable side reactions with the electrolyte solutions, surface coating of the electrodes proved an effective ways to improving the performance of Li-ion batteries. [9-12] Among various techniques, atomic layer deposition (ALD) has been used to significantly enhance both the durability and safety of positive/negative electrodes (e.g. $LiCoO_2$ and graphite) of Li-ion batteries by ultrathin coating of Al_2O_3.[13-15] Although coating of electrochemically inactive metal oxide materials such as Al_2O_3 showed high energy and rate performances, the performances of the coated electrodes degrades as the thickness of inactive layers increases. In addition, the detailed mechanisms of lithium ion conduction paths were not clearly explained yet.

To this ends, we prepared $LiNi_{1/2}Mn_{3/2}O_4$ electrodes with both electrochemically inactive and active coatings by employing ALD. $LiNi_{1/2}Mn_{3/2}O_4$ was synthesized via coprecipitaion method, $NiSO_4 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$ and NaOH were used as starting materials. The stoichiometric $NiSO_4 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$ (cationic ratio of Mn : Ni = 3 : 1) were dissolved in deionized water to form a metal solution with a concentration of 1.5 mol/L. Ultrathin lithium ion conductor, $LiAlO_x$ layers were coated on composite electrode with different thicknesses (2cycles, 20cycles, and 100cycles). For comparison, Al_2O_3 layers were coated on the same electrodes.

In order to systematically explore the effect of coating materials and the thickness on the electrochemical properties, the resulting samples were tested in both Li half cells and full cell employing graphite as an anode using constant current and rate capability experiments. In addition to electrochemical characterizations, we employed X-ray absorption spectroscopy (XAS) to better understand local electronic structure differences in ALD coated samples at different state of charge/discharge.

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