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Pristine Surface Investigation of $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ towards Improving Capacity and Rate-capability for Lithium-ion Batteries

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ABSTRACT

Understanding the nature of pristine surface associated with lithium- and manganese-rich cathodes is the key to optimizing the electrochemical performance for Li-ion batteries. In this work, $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ cathodes with phase and element homogeneity were synthesized by a facile hydroxide co-precipitation strategy. Two routes of adjusting lithium content and post-treatment were applied to tune the surface structure of pristine samples. It is found that the sample with 5 wt%-excess lithium and after post-treatment exhibits excellent capacity and rate-capability: delivering initial discharge capacities of 254 mAh/g at current densities of 100 mA/g, 200 mAh/g at 1000 mA/g, and 142 mAh/g at 4000 mA/g. The capacity of this cathode at 4 A/g thereby remains 55 percentage of the discharge capacity at 100 mA/g. The reason for the better performance of this cathode was attributed to the removal of surficial amorphous Li_2CO_3 layer, as revealed by the detailed analyses of transition electron micrograph and X-ray photoelectron spectrum. The amorphous layer was demonstrated by electrochemical impedance to show a block effect on increasing the interfacial resistance. This work may shed light on the importance of pristine surface and provide a hint for searching cathodes of high-energy Li-ions batteries with excellent capacity and rate properties.

1. Introduction

Ubiquitous uses of lithium-ion batteries (LIBs) in modern society greatly push the research for cathode materials, which is however restricted by the capacity and safety of battery systems [1]. Available cathode materials, like $LiCoO_2$, $LiFePO_4$ and $LiMn_2O_4$ used in portable devices for decades have been criticized for their low capacity especially when applied to electric vehicles (EVs) and electrical energy storage (EES) [2,3]. Among alternative cathodes for EVs and EES, lithium- and manganese-rich oxides (LMROs) have drawn intense attention recently [4–8]. Incorporation of more lithium and manganese ions into cathode material could decrease the cost of batteries and improve thermal stability, but also contribute to generating Li_2MnO_3-like phase (space group of $C/2m$) with transition metal layer that contains parts of lithium ions [9–12]. Thus, in LMROs, partial extraction of lithium ions from transition metal layer and oxygen ions provides extra capacity when electrode is activated over 4.5 V (vs. lithium metal) [13–17]. Even so, commercialization of LMROs has been stumbled by critical issues like detrimental rate-capability [7,18,19].

Various synthetic methods, including co-precipitation, have been applied to overcome rate-capability drawback of LMROs [20]. Due to the structural complexity of LMROs, the immediate relationship between synthetic methods and rate performance is somewhat problematical and worth further understanding [21]. High-temperature annealing above 800 °C is essential for the formation of layered LMRO structure, since the formation reaction undergoes multi-process of oxidation and migration of transition metal ions, lithium evaporation and so on. These processes could produce particles of various pristine surface that would subsequently comprise the interface between electrode and electrolyte and strongly affect the electrochemical behavior [22]. Far excess of lithium salt used in annealing process should be paid attention in this regard, though excess lithium need to be compensated for evaporation. Luo et al. reported that the overmuch enrichment of

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lithium on the particle surface will hinder the diffusion of Li-ions. [23] Thermodynamically driven elemental segregation phenomenon on particle surface could be another important issue for tuning pristine surface [24–26]. For instance, Yan et al. found that Ni and Co elements show surface segregation and distinctive plane selectivity, leading to surficial spinel-like and rock-salt-like structure, respectively [27,28]. Zheng et al. demonstrated that the samples with uniform element distribution exhibit electrochemical performances much better than those with significant nonuniform Ni distribution [29]. Therefore, unfavorable surface components and elemental segregation should be examined and further eliminated.

Herein, $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ materials were synthesized by a facile hydroxide co-precipitation method in combination with high-temperature calcination. Slightly tuning lithium content is conducive to produce samples with different surface features, and further two-step post-treatment (i.e. water-washing and re-calcination) over the samples is designed to remove surface amorphous layer formed when adding excess of lithium in the preparation courses. The electrochemical performances of pristine materials with different lithium amounts and corresponding post-treated samples are first comparatively studied. Through a careful characterization using X-ray diffraction, transition electron microscopy, Raman spectrum, and X-ray photoelectron spectroscopy, and electrochemical test as well, we identified the difference of surface features for the pristine samples, discussed the influence the excess lithium on the electrochemical performance, and presented the effect of two-step treatment on surface structure.

2. Experimental

2.1. Synthesis of samples

2.1.1. Pristine materials

All lithium-rich materials were prepared using a hydroxide co-precipitation method followed a heat treatment process. The hydroxide co-precipitation route could be briefly described as follows: 2.253 g manganese sulfate, 0.876 g nickel sulfate, 0.937 g cobalt sulfate and 1 g Polyvinylpyrrolidone K30 (PVP-K30) were dissolved into 200 mL de-ionized water in a flask; Then, the aqueous solution was speedily stirred under N_2 gas flow, into which 90 mL NaOH (0.4 M) and 10 mL ammonia mixed solution were slowly added (at a rate of about 1 drop per second to finish this adding process in about 1 hour). 15 minutes later, pH value of the solution increased to 10 ~ 11; Four hours later, the hydroxide precipitates produced in the flask were filtrated, washed with de-ionized water and dried at 80 °C for 5 h. The previous precursors were respectively mixed with 5 wt%, 3 wt% and 0 wt% excess of lithium hydroxide, noted as sample L5, L3 and L0. The mixtures were calcined at 900 °C for 12 h and quenched to room temperature to give the final lithium-rich oxides.

2.1.2. Treated material

0.5 g powders of sample L5 was washed with 100 mL de-ionized water and re-calcined at 300 °C for 3 h, and this treated material was named as WL5.

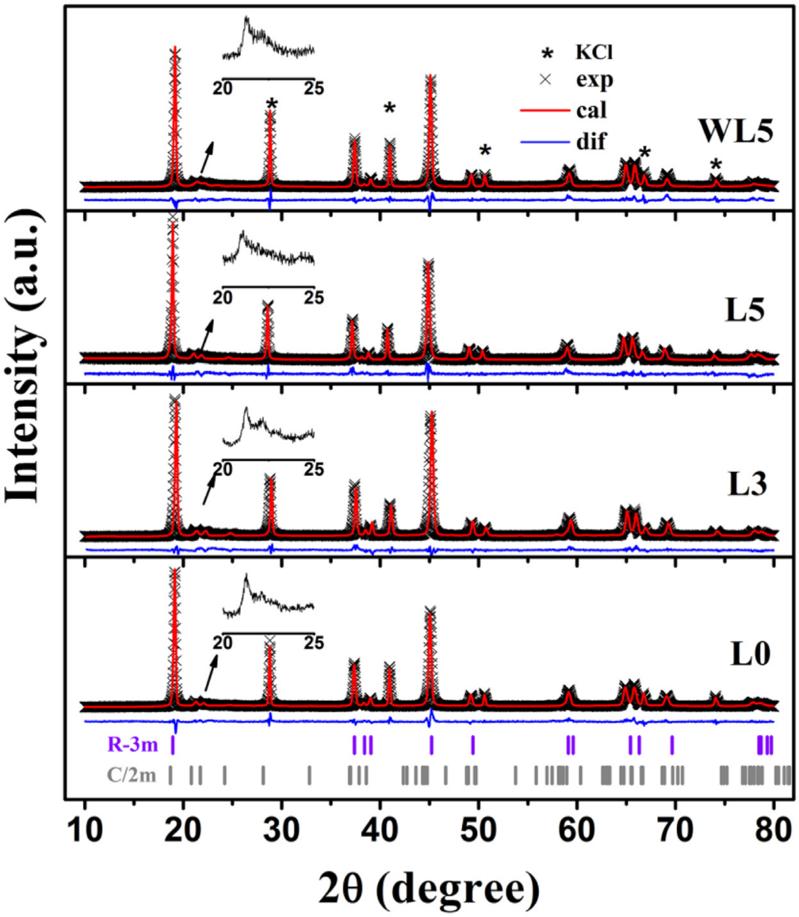

Fig. 1. Calculated XRD patterns of sample L0, L3, L5 and WL5, and the insets showing the regions of experimental data between 20 and 25 degree. The symbol "*" refers to KCl as an internal standard.