Aqueous processed thick-film $Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$ electrodes with 3D architectures

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Abstract

The development of high areal energy density electrodes with layered metal oxide cathode materials is currently worldwide a main topic in research and industry. Water-based binders were applied in the presented work for the manufacturing of NMC 622 ($Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$) cathodes in order to achieve environmental friendly and cost-reduced production, replacing the conventional organic PVDF binder and the toxic and volatile NMP solvent. However, the pH value of aqueous processed cathode slurries increases to over 12 due to the reaction between NMC 622 particles and water, which decreases the specific discharge capacity of the cells and on the other side results in the chemical corrosion of the current collector during casting. In order to avoid the damage of the current collector and protect the cathode material, different acids could be applied during mixing process to adjust the slurry pH value. In addition, the energy density at battery level can be increased with increasing electrode film thickness which corresponds to an enhanced areal capacity. However, capacity fading of thick-film electrodes at C-rates above C/2 is mainly due to a limited lithium-ion diffusion kinetics and crack formation in cathode particles. 3D electrode architectures produced by ultrafast laser ablation are proven to improve the capacity retention at high discharge rates and the electrolyte wettability of electrodes as reported in our previous works.

In this work, NMC 622 electrodes with a film thickness of 150 µm (5.8 mAh/cm^2) were manufactured with aqueous binders TRD 202A and CMC, and were subsequently laser structured. With increasing film thickness from 70 µm to 150 µm, the mass loading of cathodes increased from 17 mg/cm^2 to 36 mg/cm^2. The slurry pH values were adjusted between 9 - 10 with citric acid (CA), phosphoric acid (PA), and acetic acid (AC). The dried electrodes were characterized using XPS and SEM. The unstructured and structured electrodes with different thicknesses were afterwards assembled versus lithium in coin cells. Rate capability test and cyclic voltammetry (CV) were performed in order to investigate the electrochemical performance of the electrodes. Cells containing 70 µm cathodes with PA and CA+PA showed about 10 mAh/g higher capacity at C/20 to C/5 compared to cells with PA, while at 1C to 3C cells with CA showed the lowest capacities With increasing electrode film thickness, cells with PA and PA+CA retained 5-10 mAh/g more capacity than cells with CA at C/20 to C/5. The cells with PA maintained about 120 mAh/g discharge capacity at C/2, while cells with PA+CA and CA showed about 80 mAh/g and 45 mAh/g, respectively. In comparison to cells with unstructured electrodes, laser structuring increased the discharge capacity of cells with 70 µm electrodes from 1C to 3C, regardless of the type of added acid. As for cells with thick-film electrodes, the discharge capacity of cells containing structured electrodes with CA+PA increased to 120 mAh/g, which is about 40 mAh/g higher compared to cells with unstructured electrodes. Finally, CV proved that the addition of acids had no effect on the redox reaction of NMC 622.