Supplementary.

INVESTIGATION OF MORPHOLOGICAL FEATURES OF CATHODE MATERIALS FOR LITHIUM-ION BATTERIES BASED ON LITHIUM-RICH LAYERED OXIDES

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Synthesis of cathode materials by co-precipitation and solvothermal methods.

As precursors for synthesis were used: Ni(NO3)2 6 H2O (99. 9%, ABCR), Co(NO3)2 6 H2O (99%, Acros Organics) and Mn(NO3)2 4 H2O (98%, Alfa Aesar), Ni(CH3COO)2 xH2O (99+%, Alfa Aesar), Co(CH3COO)2 4H2O (98%, Alfa Aesar), Mn(CH3COO)2 4H2O (98%, Alfa Aesar), LiOH H2O (99+%, Sigma-Aldrich puriss.), CH3COOLi (99%, Alfa Aesar), Na2CO3 (reagent grade, Chimmed), NaOH (reagent grade, Chimmed), KOH (analytical grade, Chimmed), (NH4)2C2O4 (high-purity grade, Chimmed), NH4OH (special purity grade, Chimmed), (CH3)2CHOH (special purity grade, Chimmed), C2H5OH (special purity grade, Chimmed).

In the synthesis by precipitation method, the effect of the nature of precipitant and pH of precipitation were investigated.

The precipitation process was carried out in a glass reactor with a volume of 1000 cm–3 using a specially developed program (based on LabView), controlling the synthesis parameters. Solutions of metal salts and precipitant were injected simultaneously using peristaltic pumps at a rate of ≈ 1 ml/min. The total concentration of metals in the aqueous solution of nickel, cobalt, and manganese nitrates with the metal ratio Ni:Mn:Co = 0.167:0.667:0.167 was 2 mol/L. The concentration of Na2CO3 or KOH precipitant solution was also 2 mol/L; ammonia solution was added to the latter to a concentration of 0.36 mol/L. The synthesis parameters were automatically maintained throughout the process (pH of the medium was 7.5 for carbonate precursor or 11 for hydroxide precursor, T – 60 °C, stirring speed 1000 rpm). The synthesis was carried out in CO2 atmosphere for precipitation of carbonate precursor and in argon atmosphere for synthesis of hydroxide precursor. The formed precipitates were incubated for 16 h. The precipitates were washed on a filter with a large amount (up to 8 L) of deionized water and then with acetone and diethyl ether. The powders thus obtained were transferred to a quartz tube and dried in a tube furnace in an argon stream at 105°C for 20 h. The precursors obtained by the above methods were homogenized multiple times in a solid-phase reaction with lithium hydroxide. The reaction was carried out at temperatures of 480 °C (6 h) and 900 °C (12 h).

In the process of solvothermal synthesis, the influence of the nature of the reaction medium (isopropyl alcohol (IPA), deionized water) and precipitant (potassium hydroxide, ammonium oxalate) were investigated.

For the synthesis of the precursor denoted as PR-S1 (KOH precipitant, IPA medium), a solution of transition metal nitrates with metal ratio Ni:Mn:Co = 0.167:0.667:0.167 with a total metal concentration of 0.5M in isopropyl alcohol (dark crimson color) was prepared. A 1M solution of potassium hydroxide in isopropyl alcohol was used as precipitant. KOH solution was added dropwise to the beaker with metal nitrates under constant stirring (injection rate ≈ 4 mL/min). The resulting brown-colored mixture was transferred to an autoclave. The mixture was incubated at 180 °C for 20 h. Then the precipitate was filtered, washed on an IPS filter, dried in a tube furnace in argon atmosphere (105 °C, 20 h).

For the synthesis of the precursor in aqueous medium PR-S2 (KOH/DW), an aqueous solution of transition metal nitrates (1.87 M) with the ratio Ni:Mn:Co = 0.167:0.667:0.167 (red-pink color) and an aqueous solution of precipitant – potassium hydroxide (4.6 M) were simultaneously poured into the aqueous medium at 60 °C under argon atmosphere (pH 11 was maintained by adding KOH solution) while constant stirring. The resulting dark gray colored mixture was transferred to an autoclave after 5 minutes. In the autoclave the mixture was kept at 180 °C for 18 h. The precipitate was filtered, washed on the filter with deionized water and dried in a tube furnace under argon atmosphere (105 °C, 20 h).

PR-S3 precursor (ammonium oxalate precipitant in aqueous medium, (NH4)2C2O4/DW). An aqueous transition metal nitrate solution (1.94 M) with a Ni:Mn:Co ratio = 0.167:0.667:0.167 (red-pink color) was added dropwise (≈ 4 mL/min) to the ammonium oxalate solution (0.38 M). The resulting light pink colored mixture was transferred to an autoclave. It was incubated at 180 °C for 18 h. Then the precipitate was filtered, washed on the filter with deionized water and dried in a tube furnace in argon atmosphere (105 °C, 20 h).

The prepared precursors were mixed with lithium hydroxide and thoroughly homogenized by grinding in an agate mortar in ethanol medium. The resulting mixture was multistep annealed at temperatures of 480 °C (6h) and 900 °C (12h), during the annealing process the mixtures were repeatedly homogenized.



**Fig. S1.** SEM images of primary particles of the hydroxide precursors PR-CH (a), PR-S1 (b) and PR-S2 (c) and the lithiated oxides LR-CH (d), LR-S1 (e) and LR-S2 (f)



**Fig. S2.** SEM images of primary particles of carbonate precursor PR-CC (a), transition metal oxalate precursor PR-S3 (b) and lithiated oxides LR-CC (c) and LR-S3 (d)

**Fig. S3.** Charge-discharge curves of samples at 0.1 C