Fabrication of $LiNi_{0.5}Mn_{0.4}Ti_{0.03}Mg_{0.03}Nb_{0.01}Mo_{0.03}O_2$ Cathode for low-cost long-life Lithium-ion Battery

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1. Materials synthesis.

NCM504 is synthesized using a typical co-precipitation method in water solution. Carbonate precursor with stoichiometric ratio $Ni_{0.5}Mn_{0.4}Ti_{0.03}Mg_{0.03}Nb_{0.01}Mo_{0.03}CO_3$ is synthesized. First, $NiSO_4·6H_2O$ (99.8%, Fisher), $MnSO_4·4H_2O$ (99%, Fisher), $MgSO_4·7H_2O$ (98%ACROS), $TiOSO_4$ solution (Sigma-Aldrich), $Nb(HC_2O_4)_5$ (Alfa-Aesar), and $(NH_4)_6Mo_7O_{24}$ (99.98%, Sigma-Aldrich) is dissolved in pure water with a total TM concentration of 1M. The TM solution is mixed uniformly using magnetic stirring for 12h and stored in an Ar-filled bottle. Then, the base solution with 2M Na_2CO_3 and 0.2M NH_4OH is mixed and prepared before the reaction. 30mL of the as-prepared base solution is used as starting solution. Then, the pH of the starting solution is adjusted to 8.0 by diluted sulfuric acid, and then the reaction is started by injecting both the TM solution and base solution simultaneously with a flow of around 4mL/min. The product is synthesized by stirring the solution at pH = 8.0±0.2, 60°C under Ar protection. The light-green precipitate is collected via vacuum filtration and washed with pure water to remove the residual ions, and then dried in a vacuum oven at 100 °C. Second, the dried TM carbonate precursor powder is pre-heated in a box furnace at 500 °C for 3 hours and then mixed thoroughly with Li_2CO_3 powder with 5% excess Li as compensation at high temperatures. The NCM504 precursor is calcined in a tube furnace at 850°C for 15h under an airflow of 0.5L/min. The NCM523 cathode material used in this work is a commercial material (Targray, Product: SNMC03004, Lot#12846).

2. Cost evaluation.

The cathode materials cost is calculated based on the transition metal price and lithium source price which is used for typical synthesis of NCM materials. The calculation method can be obtained from the technique report from Argonne National Lab[29]. Specifically, the total cathode price depends on the baseline cost, C_0, and the contributions of the lithium and transition metal raw materials, C_i. Here we assign C_0 as 7$/kg and C_i is calculated by the transition metal price which can be accessed at www.metalary.com and https://tradingeconomics.com/. It should be noted that the cost evaluation model in our work is merely based on the raw materials price, which only reflect the cost difference from the raw materials side rather than the real manufacturing/production cost.

3. Electrochemical tests.

The half-cell electrochemical performances are tested in the CR-2032 coin cell. First, the cathode slurry is prepared by uniformly mixing the active material, super P carbon, and 5% (polyvinylidene fluoride) PVDF in N-methyl-1,2-pyrrolidone (NMP) solvent at a mass ratio of 8:1:1. Second, the well-mixed slurry is coated on Al foil and dried in a vacuum oven overnight at 105°C. The electrode is cut into disks with a diameter of 12mm, and the mass loading of active material is 3 mg/cm^2 for the half-cell test and ~8.5 mg/cm2 for the pouch-cell test. Finally, the coin cell is assembled in the Ar glovebox using a Li chip (D=16.7 mm) as a counter electrode and Celgard-2025 as the separator. The electrolyte is 1M $LiPF_6$ dissolved in EC: EMC=3:7 solvent with 2 wt% vinylene carbonate (VC) as an additive. In the single-layer pouch cell test, the cathode areal capacity is around 2 mAh/cm^2, and the cathode size is slightly smaller than the anode size. The electrochemical performance is conducted on a NEWARE BTS-4000 battery test system at room temperature (25°C). The cells are rested for 24 hrs before two formation cycles. The formation cycles use 0.1C charge/discharge rate current. Rate test is tested in half cell with symmetric rate current—the charge current is the same to the discharge current. For the long-term cycling, the charge rate is the same to the discharge rate. The voltage window is 2.7V-4.5V for half-cell tests and 2.8V-4.3V for pouch-cell tests.

4. Characterizations

X-ray diffraction (XRD) spectrum was performed on a Bruker D8 Advance diffractometer with Cu Kα radiation. The (S)TEM experiments are performed on a JEM-ARM300F electron microscope with a field emission source operated at 300 KeV. The atomic-resolution imaging is performed in high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) mode. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed with Super-X EDS detectors integrated into the STEM. The hard X-ray absorption spectroscopy of transition metal ions is performed on 7-BM at National Synchrotron Light Source II (NSLS II), Brookhaven National Laboratory, and 20-BM-B at the Advanced Photon Source (APS).

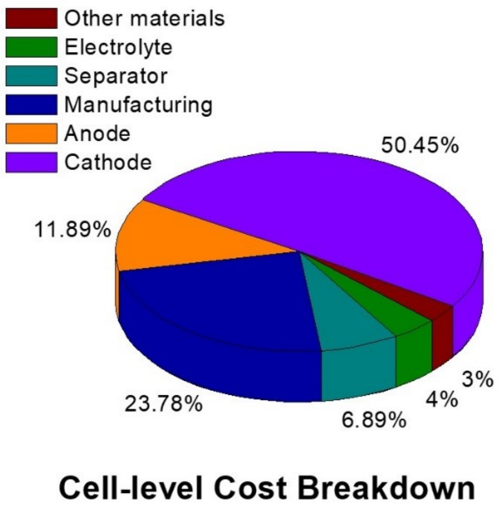


Fig.S1. Typical cost breakdown of NCM battery at cell-level.

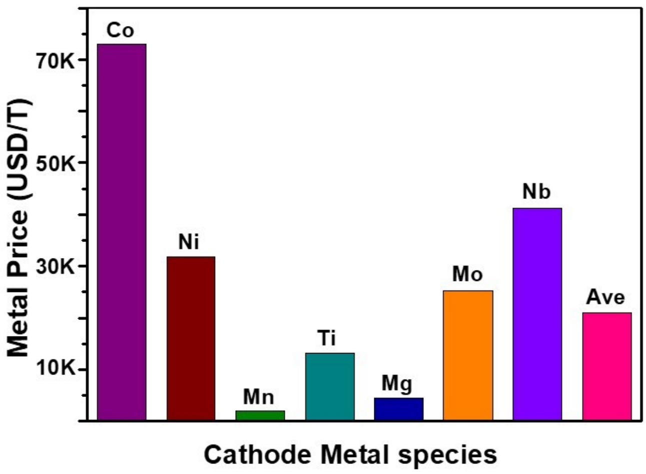
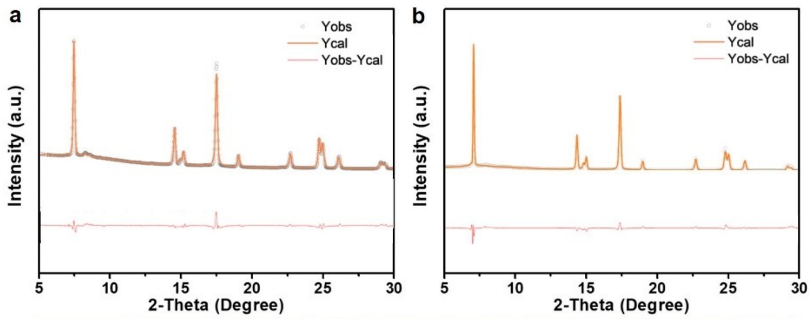


Fig. S2. Price comparison of Ni, Co, Mn and other alternative transition metal dopants.



c

	a	c	R-3m	C2m	Li in Ni site	Rwp	chi2
NCM504	2.8792	14.2741	93.92	6.08	0.0358	5.41	1.01
NCM523	2.8910	14.2873	99.12	0.88	0.0306	9.09	4.54

Fig. S3. XRD Rietveld refinement of cathodes. a, NCM504 cathode; b, NCM523 cathode; c, refinement parameters.

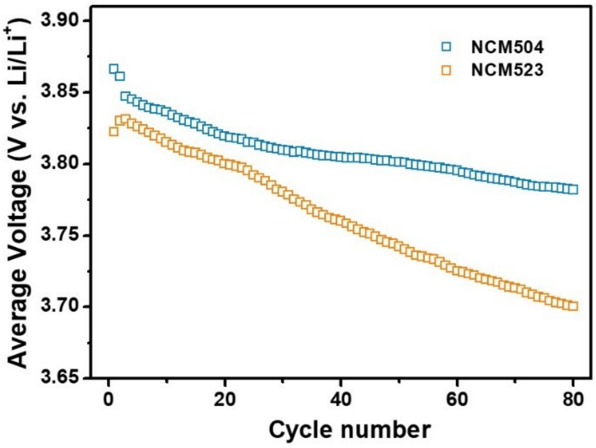


Fig. S4. Average voltage of NCM504 and NCM523 in half cell.