

Electronic Supplementary Information for
**Aliovalent Titanium Substitution on Layered Mixed Ni-Mn-Co Oxides
for Lithium-ion Battery Applications**

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Methods & Characterizations

Titanium oxy-nitrate was added to a mixture consisting of stoichiometric amounts of manganese (II) nitrate solution (45-50 wt% in nitric acid, Aldrich), cobalt (II) nitrate hexahydrate (98+%, Aldrich), and nickel (II) nitrate hexahydrate (98%, Aldrich) in the desired proportions. Titanium oxy-nitrate was prepared by hydrolysis of TiCl_4 (Aldrich) with ammonia (cooled to $\sim 4\text{ }^\circ\text{C}$ in a salted ice bath) followed by reaction with concentrated nitric acid (both EMD Chemicals Inc). After stirring for 10 minutes, an approximately 5 wt.% excess of anhydrous lithium nitrate was added to the solution. Glycine (98.5+%, Aldrich) was then added to the solution so that the glycine to nitrate ratio was 0.55 with enough distilled water to ensure solubilization. After stirring for 30 minutes, the mixture was heated on a hot plate until combustion occurred. The powders obtained were planetary ball-milled in acetone for 1 h, dried under nitrogen, and subsequently heat-treated at $800\text{ }^\circ\text{C}$ ($4\text{ }^\circ\text{C}/\text{min}$ ramp rate) for 4 h in air to obtain the desired product.

Powder X-ray diffraction was performed on a Phillips X'Pert diffractometer with an X'celerator detector using Cu K_α radiation. The powder diffraction patterns were typically scanned over an angular range of $10\text{--}90^\circ$ (2θ) with a step size of 0.0167° . Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-7500F field-emission microscope to examine particle size and morphology. Elemental analyses for all NMCs were obtained at Columbia Analytical Services (Tucson, AZ).

Electrochemical Cell Assemblies

Cathode composites consisting of 84:8:4:4 wt% ratios of active material, polyvinylidene fluoride (Kureha Chemical Ind. Co. Ltd.), acetylene black (Denka, 50%

compressed), and SFG-6 synthetic graphite (Timcal Ltd., Graphites and Technologies) in 1-methyl-2pyrrolidinone (99.5+%, Aldrich)) were cast onto a carbon-coated Al-foil current collector (Exopack Advanced Coatings), and dried *in vacuo* at 120 °C for 12 h before punching out electrodes for cell assembly. These were assembled inside a He-filled glovebox, into 2032 coin cells with 3401 Celgard separators soaked in electrolyte and Li foils as anodes. The electrolyte solution consisted of 1M LiPF₆ in 1:2 ethylene carbonate: dimethyl carbonate (Ferro Corp.). Potentiostatic or galvanostatic experiments were carried out on a Macpile II (Bio-logic, S.A., Claix, France) and Bio-logic VMP3 at room temperature. All cells were cycled at a current density of 0.1 mA/cm² unless otherwise stated. At least two cells of each type were tested.

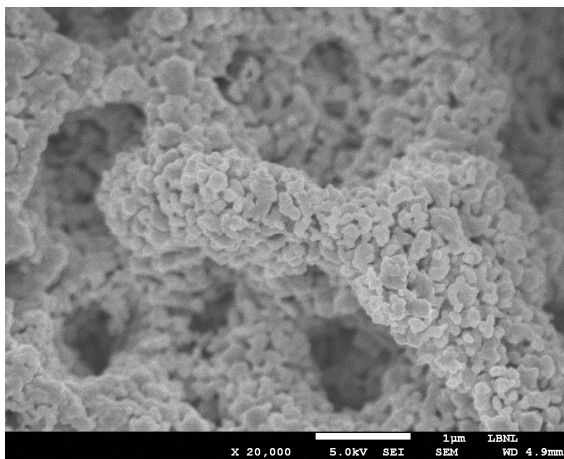


Fig. S1 SEM image of the Ti-00 powder. The morphology is typical of the NMCs used in this study.