

## Experimental methods

### Cathode material synthesis

$\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  and  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.18}\text{Ti}_{0.02}\text{O}_2$  were synthesized according to a co-precipitation technique explained in a previous study.<sup>1</sup> 200 mL of a solution of transition metal nitrates in de-ionized (DI) water (0.2 M  $\text{Ni}(\text{NO}_3)_2$ , 0.2 M  $\text{Mn}(\text{NO}_3)_2$ , and 0.1 M  $\text{Co}(\text{NO}_3)_2$ ) was combined with 200 mL of 0.5 M  $\text{LiOH}\cdot\text{H}_2\text{O}$  solution by simultaneously dripping both solutions into a beaker using a Masterflex C/L peristaltic pump and stirring continuously. In the case of Ti substitution, the transition metal solution contained 0.01 M  $\text{TiO}(\text{SO}_4)$  and 0.09 M  $\text{Co}(\text{NO}_3)_2$ . The precipitate was filtered and washed with DI water, then dried overnight at 100 °C. The dried precipitate was ball milled with  $\text{LiOH}\cdot\text{H}_2\text{O}$  using a 5 at% excess, and then heated in air at 900 °C for 12 h with a 3 h temperature ramp.

### Electrode preparation

Composite electrodes had a composition of 84 wt% active material, 8 wt% polyvinylidene fluoride (PVDF) (Kureha Chemical), and 8 wt% acetylene carbon black (Denka, 50% compressed). For these, PVDF was dissolved in N-methyl-2-pyrrolidinone (NMP) and the carbon black and active material were then added and stirred to form a slurry. The slurry was then cast onto carbon-coated aluminum current collectors (Exopack Advanced Coatings) using a doctor blade set to 75  $\mu\text{m}$  height. These electrodes were dried under an IR lamp and transferred to an Ar filled glovebox after 12 h under vacuum at 120 °C. Typical loadings were 4.3 mg per  $\text{cm}^2$ .

### Coin cell assembly and electrochemical measurements

CR2032 coin cells were assembled in an Ar-filled glovebox using the composite electrode as the cathode and Li metal as the anode. A 3/8" diameter cathode was covered with a Celgard 2400 separator, and 1 M  $\text{LiPF}_6$  electrolyte solution in 1:2 w/w ethylene carbonate/dimethyl carbonate (Ferro Corporation) was added. A 1/2" diameter Li metal anode was placed on the other side of the separator and a stainless steel disk and spring were added to the stack to complete the cell. Battery testing was performed using a computer controlled VMP3 potentiostat/galvanostat (BioLogic). Cells were cycled galvanostatically at C/20, where 1C was defined as the current required to fully charge a cell in 1 h, corresponding to a specific capacity of 280  $\text{mA g}^{-1}$ . Upon completion of electrochemical cycling, positive electrodes were transferred back to an Ar atmosphere, removed from disassembled coin cells, rinsed in dimethyl carbonate and stored for further study.

### Materials characterization

Scanning electron microscopy was carried out on as-synthesized NMC cathode powders using a JEOL JSM-7000F equipped with a Thermo Scientific EDS (energy dispersive X-ray spectroscopy) detector. Annular dark-field scanning transmission electron microscopy (ADF-STEM) was performed on a Hitachi HD-2700, which is a combined SEM and STEM operating at an accelerating voltage of 200 kV. Specific surface area measurements using nitrogen physical adsorption based on Brunauer-Emmett-Teller (BET) theory were carried out on a Micromeritics Tristar surface area and porosity analyzer. XAS measurements were performed on the 31-pole wiggler beam line 10-1 at the Stanford Synchrotron Radiation Lightsource using a ring current of 350 mA and a 1,000  $\text{mm}^{-1}$  spherical grating monochromator with 20  $\mu\text{m}$  entrance and exit slits, providing  $\sim 10^{11}$   $\text{ph s}^{-1}$  at 0.2 eV resolution in a 1  $\text{mm}^2$  beam spot. All battery electrode samples were attached to an aluminum sample holder using conductive carbon tape. Data presented were acquired under ultrahigh vacuum ( $10^{-9}$  Torr) in a single load at room temperature using total electron yield (TEY) and Auger electron yield (AEY) measurements. The sample drain current was collected for TEY. AEY was collected with a cylindrical mirror analyzer using pass energy of 200 eV and a kinetic energy window of 2eV near the main Auger for oxygen and nitrogen, respectively. Contributions from visible light were carefully minimized before the acquisition, and all spectra were normalized by the current from freshly evaporated gold on a fine grid positioned upstream of the main chamber, followed by processing according to,

$$I_{\text{norm}} = \frac{I - I_{\text{min}}}{I_{\text{max}} - I_{\text{min}}}. \quad (1)$$

## References

- [1] F. Lin, I. M. Markus, D. Nordlund, T.-C. Weng, M. D. Asta, H. L. Xin and M. M. Doeff, *Nat Commun*, 2014, 5, 3529.