

## Supporting Information

### Suppression of O<sub>2</sub> evolution from oxide cathode for lithium-ion batteries:

#### VO<sub>x</sub>-impregnated 0.5Li<sub>2</sub>MnO<sub>3</sub>-0.5LiNi<sub>0.4</sub>Co<sub>0.2</sub>Mn<sub>0.4</sub>O<sub>2</sub> cathode

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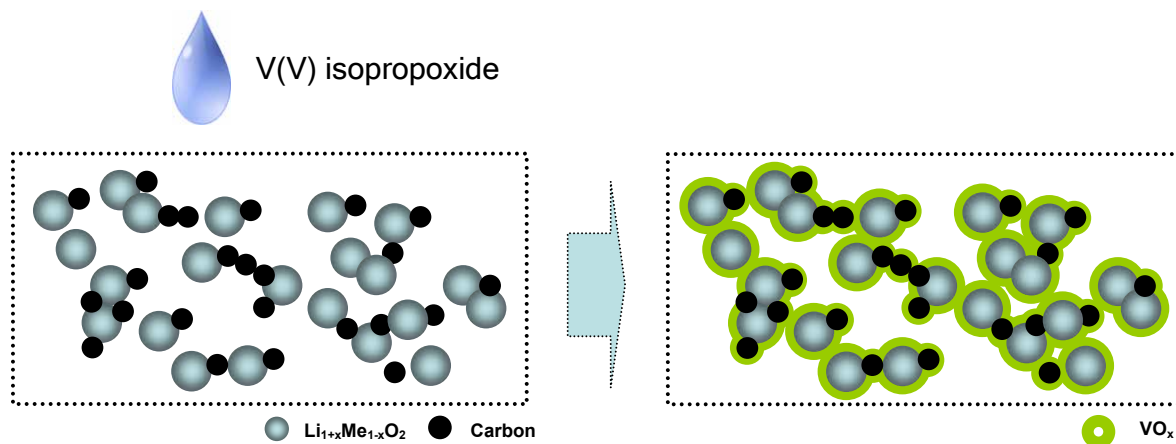
## Experimental

### *Powder synthesis:*

To make a composition,  $0.5\text{Li}_2\text{MnO}_3\text{-}0.5\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ , stoichiometric amount of lithium acetate, nickel acetate, cobalt acetate, and manganese acetate was dissolved in the deionized water. Under adjusted temperature of  $40\text{ }^\circ\text{C}$ , the solution was stirred until the acetate precursors were completely dissolved. Oxalic acid solution was poured into the acetate solution, and the precipitates appeared in a few seconds. After evaporating the water on the hotplate overnight, the precipitates were decomposed at  $500\text{ }^\circ\text{C}$  for 3 hours and calcined at  $900\text{ }^\circ\text{C}$  for 12 hours in air.

### *Electrode preparation and $\text{VO}_x$ impregnation:*

The electrode was deposited on the Al foil by slurry coating method and the composition of the electrode composite was active material/Super P/PVdF = 95/3/2 in weight. The electrode modification with  $\text{VO}_x$  was done by painting the electrode with the vanadium isopropoxide oxide solution (in hexane) in Ar-filled glove box. After aging the wet-coated electrode for a few days in air, it was vacuum dried at  $120\text{ }^\circ\text{C}$  for 2 hours to complete the vanadium oxide coating.



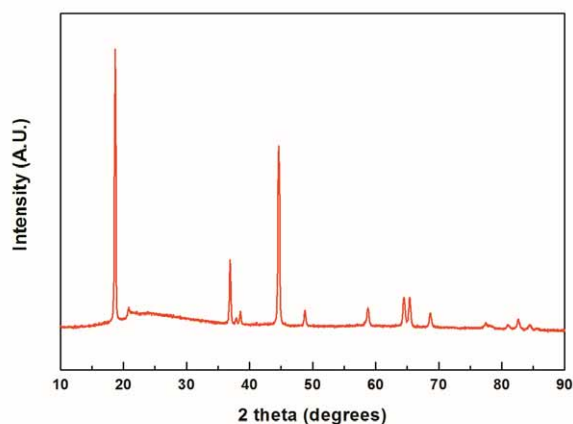
### *Internal cell pressure analysis during electrochemical test:*

To check the internal cell pressure change during charging, we made 18650-type cylindrical half cell with hole that was connected with pressure sensor. The internal volume surrounding electrode jelly-roll was fully filled with PTFE filler and the electrolyte to remove any dead volume. The cathodes were charged to  $4.6\text{ V}$  at the rate of  $\text{C}/20$  with a rest time of 12 hours.

*Materials characterization:*

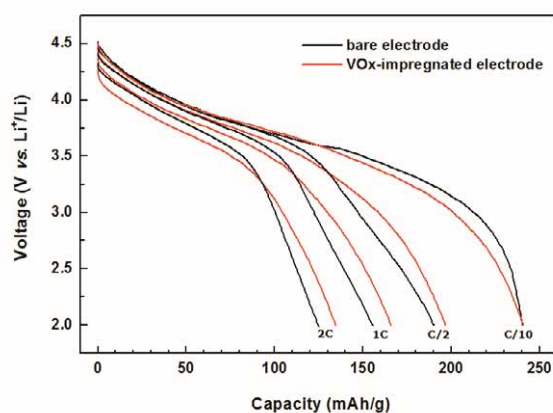
The powder morphology was examined by scanning electron microscopy (SEM; Hitachi, S-4700) and the energy dispersive spectroscopy (EDAX, GENESIS4000) elements line scanning was adopted to check the vanadium distribution in the electrode. FT-IR spectra (FTS 6000 spectrometer) were also taken to check the bonding structure between vanadium and oxygen. The X-ray photoelectron spectroscopy (XPS) analyses were performed with  $\Phi$  PHYSICAL ELECTRONICS (QUANTUM 2000 SCANNING ESCA MICROPROBE) spectrometer using a focused monochromatized Al K $\alpha$  radiation (1486.6 eV). The XPS spectra were fitted by using Multipak V6.1A software in which a Shirley background is assumed and the fitting peaks of the experimental spectra are defined by a combination of Gaussian (80%) and Lorentzian (20%) distributions. To avoid any external contamination, all samples were transferred under inert gas from the glove box to the spectrometer using a transfer chamber. To investigate the particle microstructure in charged state, we used Transmission Electron Microscope (TEM) (tecnaï F20, FEI) operating at 200 kV and equipped with a field-emission gun. Elemental composition was measured with energy dispersive spectrometry (R-TEM, EDX) equipped on the TEM.

**Figure S1.** X-ray diffraction pattern of  $0.5\text{Li}_2\text{MnO}_3\text{-}0.5\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  powder prepared by the oxalate co-precipitation method. (Rigaku, RINT2200HF+) Rietveld analysis with RIETAN-2000 was conducted to calculate the lattice information.

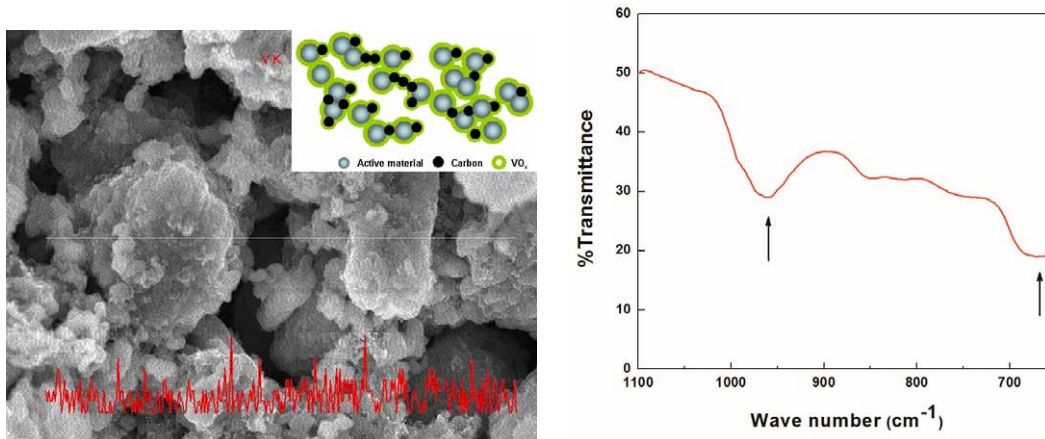


Composition	a (Å)	c (Å)	c/a	V (Å <sup>3</sup> )	R <sub>wp</sub> (%)
$\text{Li}_{1.2}\text{Ni}_{0.16}\text{Co}_{0.08}\text{Mn}_{0.56}\text{O}_2$	2.86428	14.29615	4.99118	101.5738	1.50

**Figure S2.** Discharge voltage profiles of bare- and  $\text{VO}_x$ -impregnated  $0.5\text{Li}_2\text{MnO}_3\text{-}0.5\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$  at different current densities.



**Figure S3.** Vanadium EDAX line scan image (inset image represents an ideal VO<sub>x</sub>-impregnated electrode) and FT-IR transmittance spectrum of VO<sub>x</sub>-impregnated 0.5Li<sub>2</sub>MnO<sub>3</sub>-0.5LiNi<sub>0.4</sub>Co<sub>0.2</sub>Mn<sub>0.4</sub>O<sub>2</sub> cathode.



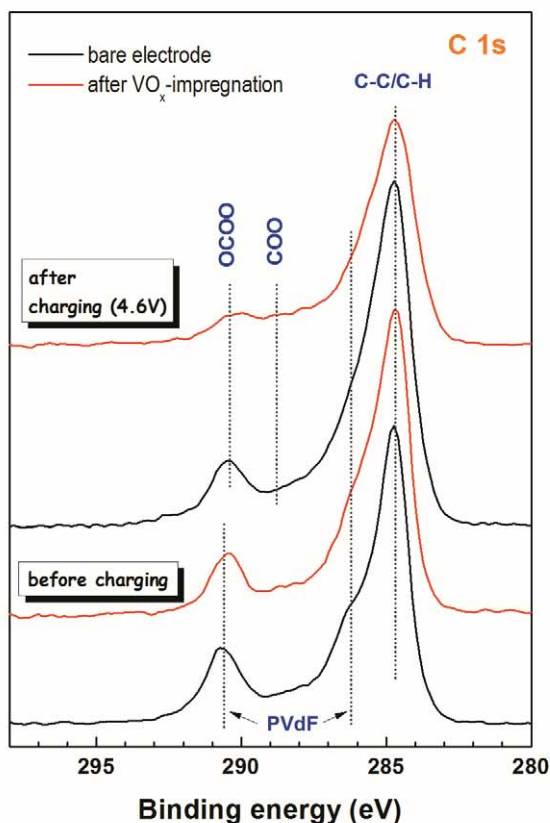
The surface and the pores are fully covered by the vanadium oxide surface layer (5 wt.% in the electrode composite). The EDS line scan spectrum of vanadium indicates that vanadium oxide is uniformly coated on the surface of the electrode particles.

To confirm the chemical bonding state of the vanadium oxide, FT-IR spectrum revealed that the relative transmittance peaks are assigned to V<sub>2</sub>O<sub>5</sub> xerogel. The band intensities located at 962 and 750 cm<sup>-1</sup> are the clear signature of V=O stretch and V-O-V asymmetric stretch vibration, respectively.

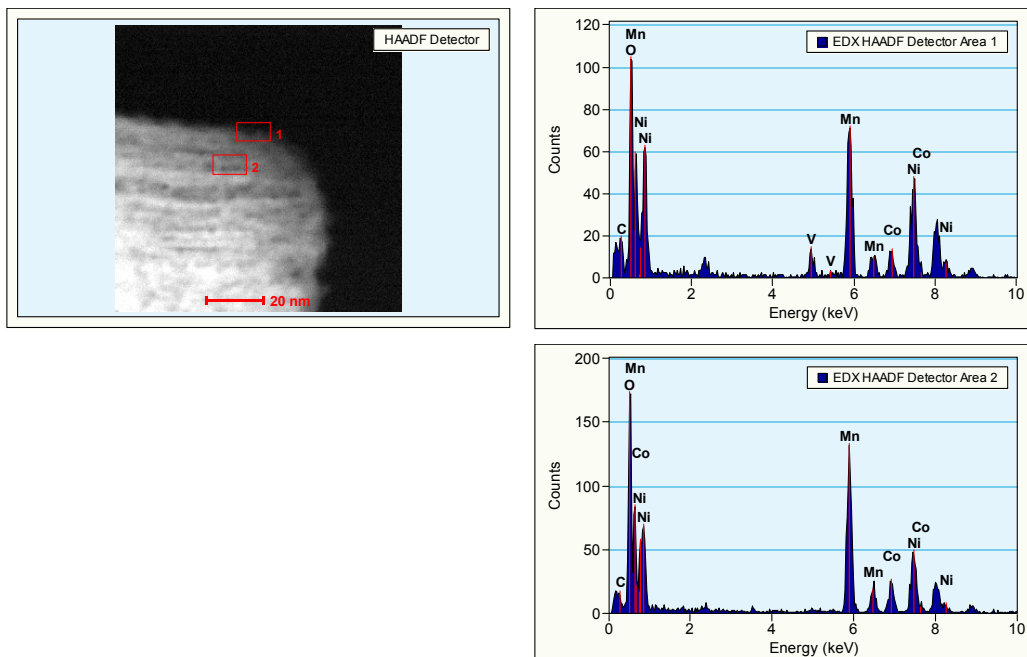
**Figure S4.** The C 1s peak registered at the surface of the pristine electrode, consists on several components indicated by dashed lines and assigned to contamination carbon and/or conductive carbon additive at  $\sim 284.8$  eV and to carbon atoms in polymeric binder PVdF at  $\sim 286.4$  and  $\sim 290.8$  eV [1]. The presence of some oxidized carbon occurring at the extreme surface cannot be excluded in this case. After  $\text{VO}_x$  impregnation, the C 1s main component shows some broadness without disappearance of binder related peaks signature, a supplementary proof of the coverage of electrode by a very thin layer of  $\text{VO}_x$ . At 4.6 V charge, the C 1s peak of bare electrode presents an asymmetry between 286.0 and 287.0 eV corresponding to CO-like bonds. Two others components located at  $\sim 289.0$  and  $\sim 290.2$  eV were observed and correspond to COO and OCOO-like carbon, respectively, which can be related to  $\text{Li}_2\text{CO}_3$  and/or lithium alkyl carbonates  $\text{ROCOOLi}$  [2]. After charging the  $\text{VO}_x$  impregnated cell to 4.6 V, the C 1s peak intensity at  $\sim 290.2$  eV decreased, and could be assigned to the presence of different proportion of  $\text{Li}_2\text{CO}_3$  and  $\text{ROCOOLi}$  as the nature of the surface electrode change.

[1] G. Beamson, and D. Briggs, *High Resolution XPS of Organic Polymers, The Scienta ESC300 Database*, JOHN WILEY & SONS, 1992.

[2] R. Dedryvère, S. Laruelle, S. Grugeon, P. Poizot, D. Gonbeau, and J.-M. Tarascon, *Chem. Mater.* 2004, **16** (6), 1056.



**Figure S5.** EDX results for bulk and surface region of the VO<sub>x</sub>-coated particle.



It confirms the presence of VO<sub>x</sub> on the cathode particle surface and, interestingly, the surface layer still exists even after TEM sampling procedure including thorough washing and sonication in methanol. The result suggests that the impregnation and the hydrolysis of vanadium isopropoxide solution make stable coated surface layer in both aspects, chemical and mechanical.