

## Supporting Information

# Suppressing Hydrogen Evolution at Catalytic Surfaces in the Aqueous Lithium Ion Batteries

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## Experimental Section

### Materials

Lithium bis(trifluoromethane sulfonyl) imide ( $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ , LiTFSI) (>98%) was purchased from Tokyo Chemical Industry. Water (HPLC grade) was purchased Sigma-Aldrich. The water-in-salt aqueous electrolyte is prepared by dissolving LiTFSI in water according to molality (21 mol salt in 1 kg water). The  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{LiMn}_2\text{O}_4$  materials were purchased from MTI Corporation.

### Materials Characterizations

The morphology of the sample was investigated by transmission electron microscopy (TEM, JEM 2100 FEG, 200 keV). Raman measurements were performed on a Horiba Jobin Yvon Labram Aramis using a 532 nm diode-pumped solid-state laser, attenuated to give 900 mW power at the sample surface. X-ray photoelectron spectroscopy (XPS) was conducted on a high sensitivity Kratos AXIS 165 X-ray photoelectron spectrometer with Mg  $K\alpha$  radiation.

### Electrochemical Measurements

The  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anode electrodes were prepared by mixing 80% active material, 10% carbon black, and 10% polyvinylidene fluoride (PVDF) in *N*-methylpyrrolidinone (NMP) and the slurry mixture was then coated on Al foil. After coating, the electrodes were dried at 80 °C for 10 min to remove the solvent before pressing. The electrodes were cut into 1 cm<sup>2</sup> sheets, vacuum-dried at 100°C for 24 h, and weighed before assembly. The  $\text{LiMn}_2\text{O}_4$  electrodes were fabricated by compressing active materials, carbon black, and polytetrafluoroethylene (PTFE) at weight ratio of 8:1:1 onto the stainless steel mesh. The three-electrode devices use activated carbon as counter and Ag/AgCl as reference electrodes, respectively. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) was carried out using CHI 600E electrochemical work station. The potentials vs. Ag/AgCl were converted to those vs. standard  $\text{Li}^+/\text{Li}$ , supposing that the potential of Ag/AgCl electrode was 3.239 V vs  $\text{Li}^+/\text{Li}$ . The full ALIB cell was assembled in CR2032-type coin cell using  $\text{LiMn}_2\text{O}_4$  cathode,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anode and glass fiber as separator. To minimize side reactions between the electrolyte and the coin cell components, the Al-Clad coin cell case was used at for the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anode. The charge-discharge experiments were performed on a Land BT2000 battery test system (Wuhan, China) at room-temperature.

### ALD Coating of the LTO Electrodes

ALD- $\text{Al}_2\text{O}_3$ : The ALD  $\text{Al}_2\text{O}_3$  process was developed in BENEQ TFS 500 reactor with a 2 mbar base pressure. Precursors used for the ALD process were trimethyl-aluminum (TMA, Aldrich,

97%) and deionized water (H<sub>2</sub>O), and the reactor temperature was 150 °C. The ALD process used a 0.1 s/5 s/0.1 s/5 s TMA pulse/N<sub>2</sub>purge/ H<sub>2</sub>O pulse/N<sub>2</sub>purge sequence with a growth rate of 1.2 Å/cycle.

ALD-ZnO: The ALD ZnO process was developed in BENEQ TFS 500 reactor with a 2 mbr base pressure. Pure nitrogen was used as carrier gas and preheated to 150 °C for the whole process. Each cycle included alternating flows of diethyl zinc (DEZ, 1.5 s Zn precursor) and water (1.5 s, oxidant) separated by flows of pure nitrogen gas (4 and 10 s, respectively) with the growth rate of 2.0 Å/cycle.

ALD-TiO<sub>2</sub>: The ALD Al<sub>2</sub>O<sub>3</sub> process was developed in BENEQ TFS 500 reactor with a 2 mbr base pressure. Precursors used for the ALD process were tetrakis(dimethylamino)titanium (TDMAT, Aldrich, 99%) and deionized water (H<sub>2</sub>O), and the reactor temperature was 150 °C. The ALD process used a 0.5 s/10 s/0.1 s/10 s TDMAT pulse/N<sub>2</sub>purge/ H<sub>2</sub>O pulse/N<sub>2</sub>purge sequence with a growth rate of 0.5 Å/cycle.

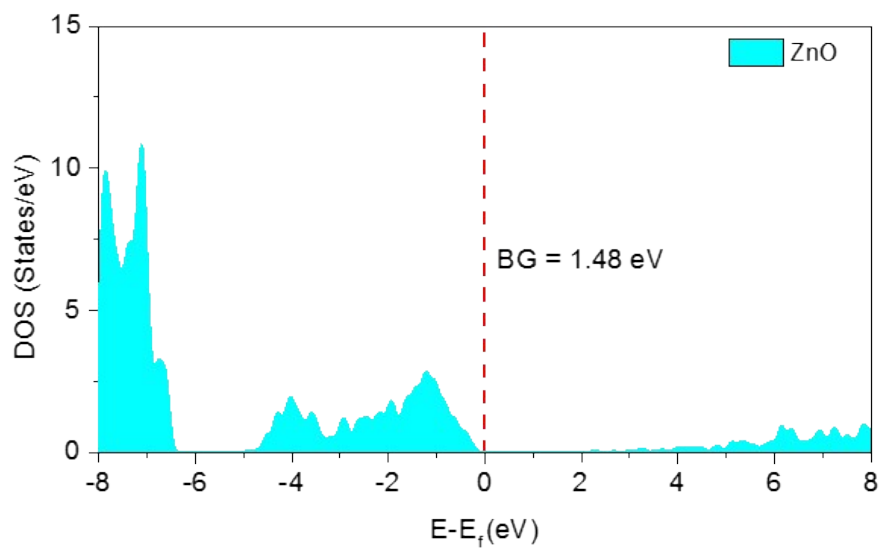
Thickness of the deposited layer was determined by ellipsometric measurements of a blank Si wafer from the same ALD batch using a Cauchy optical model.

### **Simulations of $\Delta G_H$**

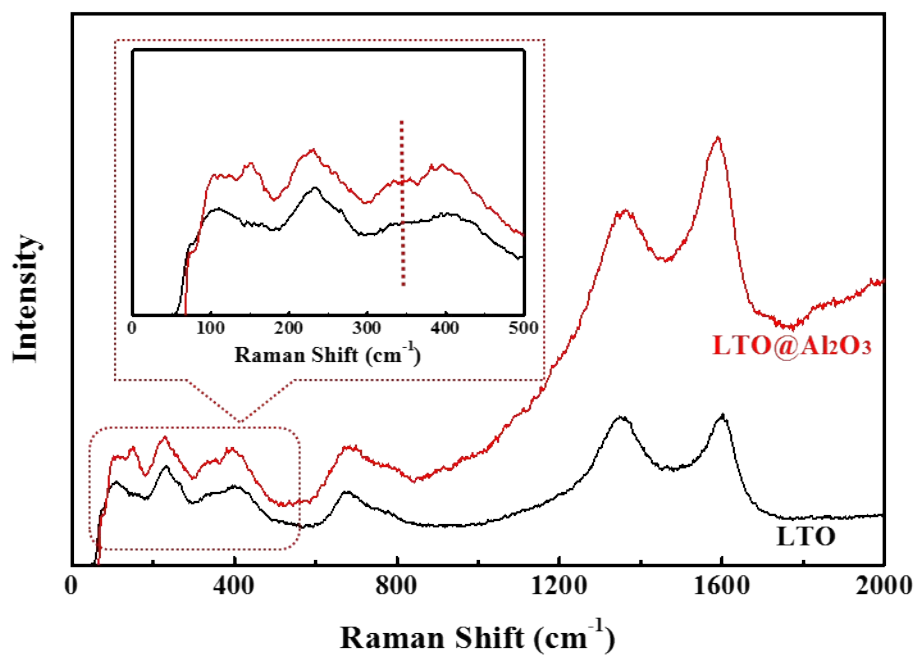
The  $\Delta G_H$  is defined as  $\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H$ , where  $\Delta E_{ZPE}$  and  $T\Delta S_H$  are the zero point energy and entropic corrections, respectively. In this work, the value of  $\Delta E_{ZPE} - T\Delta S_H$  is set to be 0.24 eV based on previous report.<sup>36</sup> And  $\Delta E_H$  is the hydrogen absorption energy, which is defined as:  $\Delta E_H = E_{nH} - E_{(n-1)H} - 1/2E_{H_2}$ , where  $E_{nH}$  and  $E_{(n-1)H}$ , are the total energy of the subtract with  $n$  and  $n-1$  hydrogen atoms, respectively. And  $E_{H_2}$  is the total energy of of H<sub>2</sub> gas molecule. All of the density functional theory (DFT) calculations<sup>37, 38</sup> are performed using Vienna Ab Initio Simulation Package (VASP)<sup>39</sup> with projector augmented wave (PAW) method.<sup>40</sup> The exchange-correlation energy is described by the functional of Perdew, Burke, and Ernzerhof (PBE) version of the generalized gradient approximation (GGA).<sup>41</sup> And the energy cut-off for the plane wave basis is 520 eV. A vacuum layer of 12 Å is used for all calculated models. Visualization of the structures are made by VESTA.<sup>42</sup>

### **Reference**

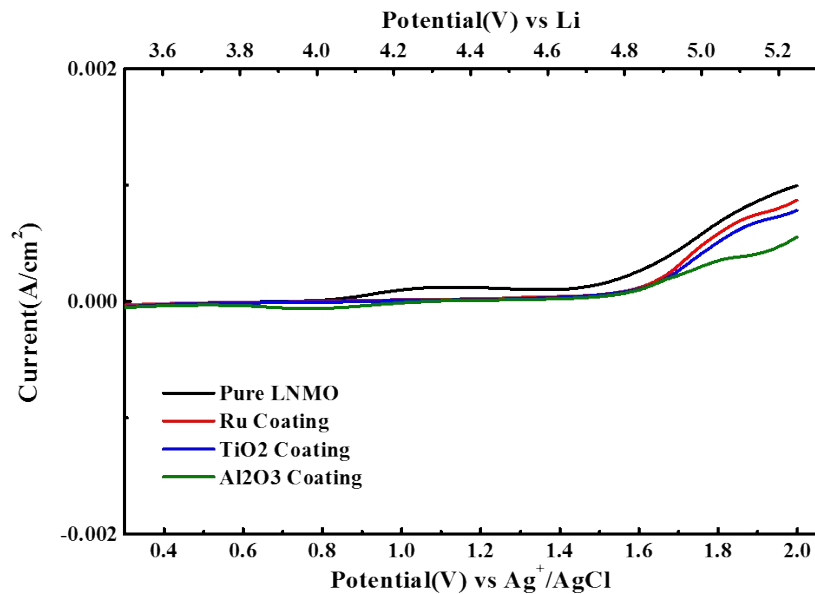
36. J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *Journal of The Electrochemical Society*, 2005, **152**, J23.
37. P. Hohenberg and W. Kohn, *Physical review*, 1964, **136**, B864.
38. W. Kohn and L. J. Sham, *Physical review*, 1965, **140**, A1133.
39. G. Kresse and J. Hafner, *Physical Review B*, 1994, **49**, 14251-14269.
40. P. E. Blöchl, *Physical review B*, 1994, **50**, 17953.
41. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical review letters*, 1996, **77**, 3865.
42. K. Momma and F. Izumi, *Journal of Applied Crystallography*, 2011, **44**, 1272-1276.



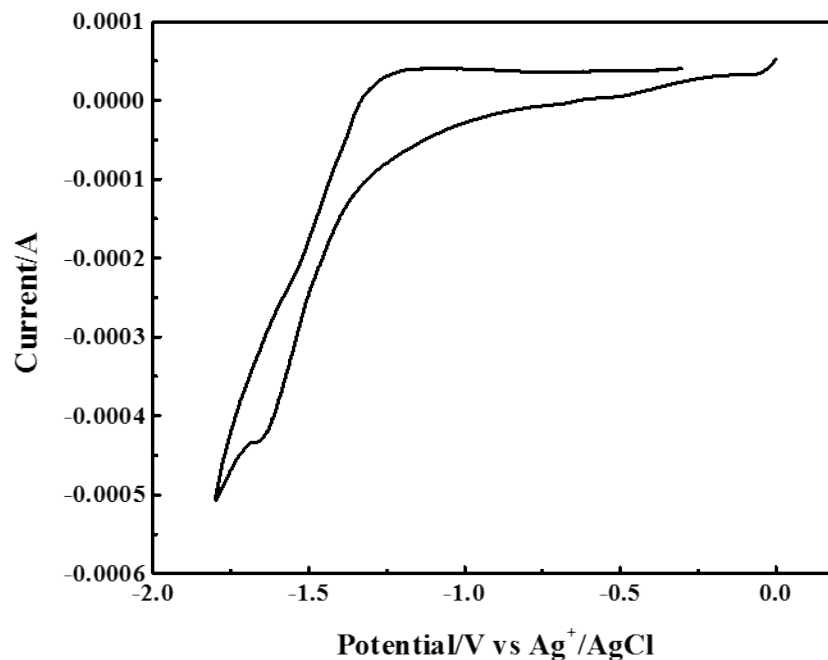
**Figure S1.** The density of state for ZnO. The red dash lines indicate the Fermi energies, and the band gaps (BG) are listed.



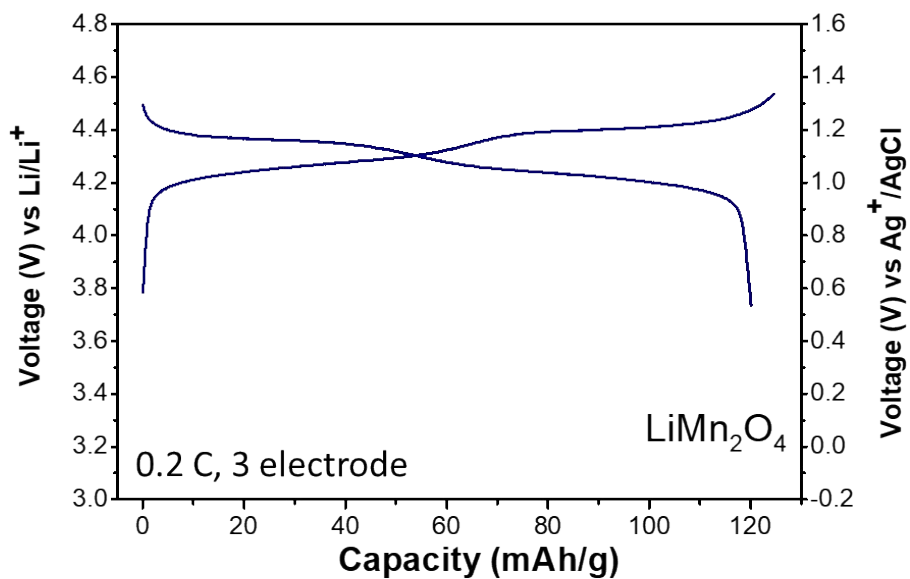
**Figure S2.** The Raman spectra comparison of the  $\text{Al}_2\text{O}_3$  coated LTO electrode and pristine LTO electrode.



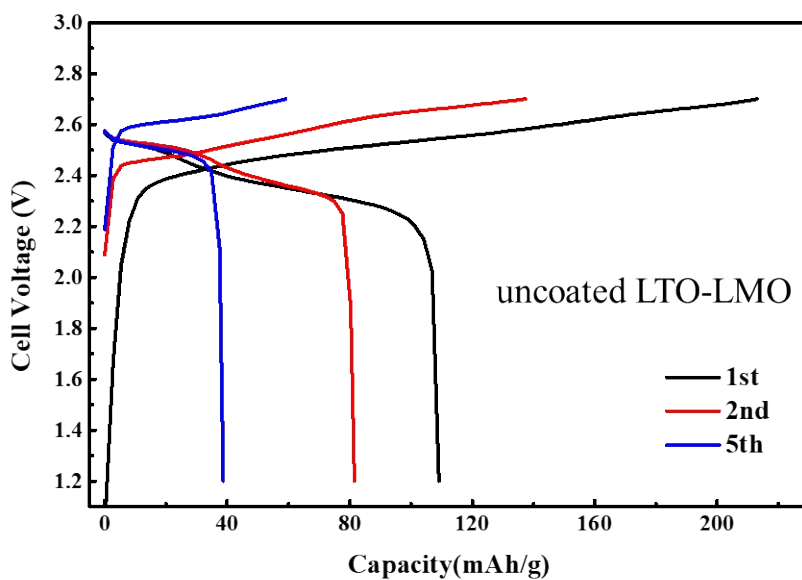
**Figure S3.** Anodic limits evaluated by linear sweep on different surface coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes (inset the enlarged view). Counter electrode: activated carbon; Reference electrode:  $\text{Ag}/\text{AgCl}$ ; Scan rate: 1 mV/s.



**Figure S4.** The CV scan of uncoated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anodes in water-in-salt electrolytes at the scanning rate of 5 mV/S using a activated carbon counter electrode and an  $\text{Ag}/\text{AgCl}$  reference.



**Figure S5.** The typical voltage profile of  $\text{LiMn}_2\text{O}_4$  in 21m LiTFSI electrolyte at 0.2 C measured in a three-electrode cell using Pt as counter and Ag/AgCl as reference electrodes



**Figure S6.** The voltage profile of the full cell using uncoated LTO anode and LMO cathode at 1 C current.

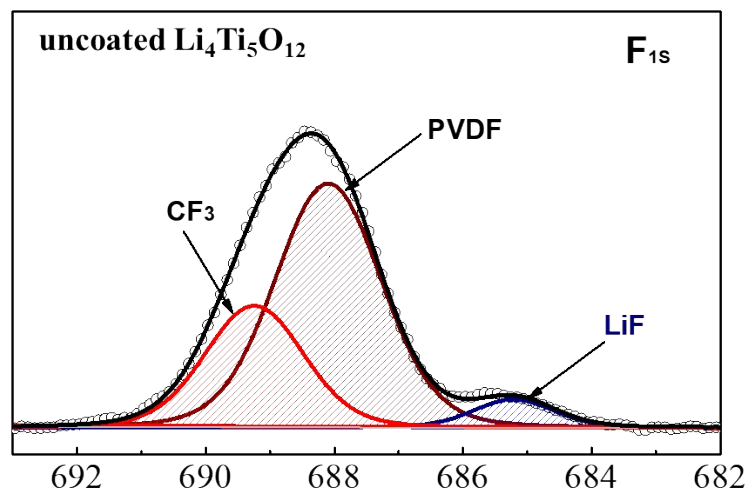


Figure S7. The  $F_{1s}$  XPS of the uncoated LTO electrode after cycling.

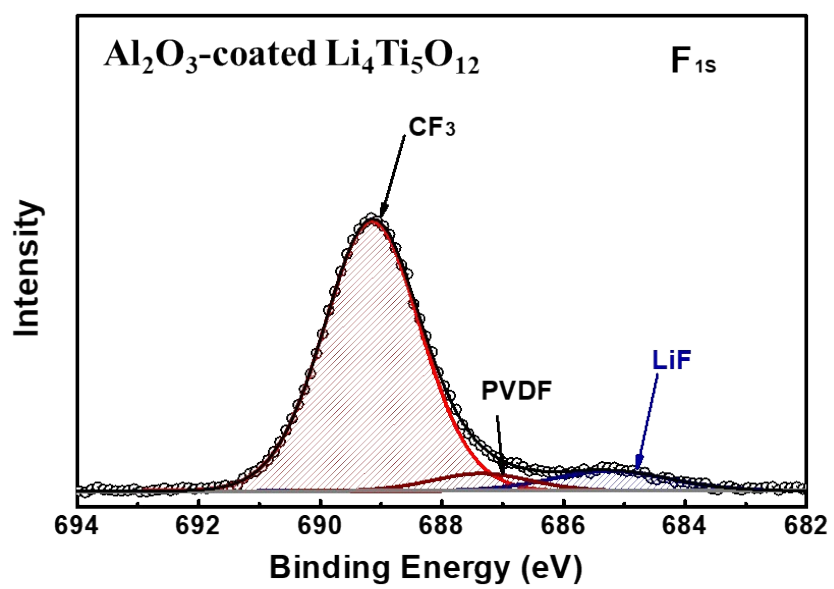


Figure S8. The  $F_{1s}$  XPS of the cycled LTO electrode.