Supporting Information

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

Fei Wang, *1+ Chuan-Fu Lin,2,3+ Xiao Ji,4+ Gary W. Rubloff,2 and Chunsheng Wang*4,5

1. Department of Materials Science, Fudan University, Shanghai, 200433, China
2. Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA
3. Department of Mechanical Engineering, The Cathode University of America, Washington, DC 20064, USA
4. Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, USA
5. Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

Corresponding Author
Fei Wang, E-mail: feiw@fudan.edu.cn
Chunsheng Wang, E-mail: cswang@umd.edu
Experimental Section

Materials

Lithium bis(trifluoromethane sulfonyle) imide (LiN(SO₂CF₃)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 Li₄Ti₅O₁₂ and LiMn₂O₄ 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 Kα radiation.

Electrochemical Measurements

The Li₄Ti₅O₁₂ 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 cm² sheets, vacuum-dried at 100°C for 24 h, and weighed before assembly. The LiMn₂O₄ 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 Li⁺/Li, supposing that the potential of Ag/AgCl electrode was 3.239 V vs Li+/Li. The full ALIB cell was assembled in CR2032-type coin cell using LiMn₂O₄ cathode, Li₄Ti₅O₁₂ 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 Li₄Ti₅O₁₂ 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-Al₂O₃: The ALD Al₂O₃ process was developed in BENEQ TFS 500 reactor with a 2 mbr base pressure. Precursors used for the ALD process were trimethyl-aluminum (TMA, Aldrich,
97%) and deionized water (H₂O), and the reactor temperature was 150 °C. The ALD process used a 0.1 s/5 s/0.1 s/5 s TMA pulse/N₂purge/ H₂Opulse/N₂purge 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-TiO₂: The ALD Al₂O₃ 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 (H₂O), and the reactor temperature was 150 °C. The ALD process used a 0.5 s/10 s/0.1 s/10 s TDMAT pulse/N₂purge/ H₂Opulse/N₂purge 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 ΔGₜₜ

The ΔGₜₜ is defined as ΔGₜₜ = ΔEₜₜ + ΔEₚ - TΔSₜₜ, where ΔEₚ and TΔSₜₜ are the zero point energy and entropic corrections, respectively. In this work, the value of ΔEₚ - TΔSₜₜ is set to be 0.24 eV based on previous report. And ΔEₜₜ is the hydrogen absorption energy, which is defined as: ΔEₜₜ = Eₜₜ - Eₜₜ₋₁ - 1/2Eₜₜ, where Eₜₜ and Eₜₜ₋₁ are the total energy of the substrate with n and n-1 hydrogen atoms, respectively. And Eₜₜ is the total energy of of H₂ gas molecule. All of the density functional theory (DFT) calculations are performed using Vienna Ab Initio Simulation Package (VASP) with projector augmented wave (PAW) method. The exchange-correlation energy is described by the functional of Perderw, Burke, and Ernzerhof (PBE) version of the generalized gradient approximation (GGA). 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.

Reference
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 Al$_2$O$_3$ coated LTO electrode and pristine LTO electrode.
**Figure S3.** Anodic limits evaluated by linear sweep on different surface coated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ electrodes (inset the enlarged view). Counter electrode: activated carbon; Reference electrode: Ag/AgCl; Scan rate: 1 mV/s.

**Figure S4.** The CV scan of uncoated Li$_4$Ti$_5$O$_{12}$ anodes in water-in-salt electrolytes at the scanning rate of 5 mV/S using a activated carbon counter electrode and an Ag/AgCl reference.
**Figure S5.** The typical voltage profile of LiMn$_2$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.