Electronic Supplementary Information

Lithium-ion Batteries Based on Vertically-Aligned Carbon Nanotubes and Ionic Liquid Electrolytes

Wen Lu,* Adam Goering, Liangti Qu, and Liming Dai*

1. Synthesis of Li salt-doped ionic liquid electrolytes

The Li salt-doped ionic liquid electrolyte consists of three major components, namely an ionic liquid (as solvent), a Li salt, and a SEI film-forming additive. LiTFSI is a frequently used salt in ionic liquid electrolytes^{s1-s3}. EC is the most commonly used SEI film-forming additive in conventional organic electrolytes^{s4} and has been employed in ionic liquid electrolytes^{s1-s3}. Referring to the frequently used Li salt and EC concentrations of Li salt-doped ionic liquid electrolytes reported previously, we obtained our ionic liquid electrolyte by doping [EDMMEA][TFSI] (from MERCK) with 1 M LiTFSI and 20% EC (by volume). Structure of [EDMMEA][TFSI] is shown below:



A PGSTAT30 potentiostat (Eco Chemie B.V) was used to measure ionic conductivity (by AC impedance spectroscopy) and electrochemical window (by linear sweep voltammetry) of the

resultant electrolyte, 1 M LiTFSI/20% EC/[EDMMEA][TFSI], in a cell consisting of two identical Pt plate electrodes (size S of each electrode: 0.5 cm², distance d between two electrodes: 0.038 cm). All measurements were carried out at room temperature (20 °C). Conditions for ionic conductivity measurement: AC voltage amplitude, 0.005 V, frequency range, 1M Hz ~ 1K Hz. According to $\sigma = d/(SZ')$ (where Z' is the real resistance at the imaginary resistance Z'' = 0 Ω), ionic conductivity of the electrolyte was calculated to be 3.0 mS/cm. Electrochemical window of the electrolyte was determined to be 5.8 V (Figure S1).



Figure S1. Linear sweep voltammogram of a 1 M LiTFSI/20% EC/[EDMMEA][TFSI] electrolyte. Scan rate: 50 mV/s.

2. Preparation and characterization of VA-CNT electrodes

A 10-nm thick Al layer was sputter coated on the Ni foil prior to the deposition of a 3-nm thick Fe film as the catalyst for VA-CNT growth by chemical vapor deposition. The pre-coated Al layer prevented Fe catalytic particles from aggregation during the high temperature CNT growth^{s5}, and enhanced interfacial adhesion between the Ni substrate and the CNTs, ensuring a

high electrical conductivity for the electrodes and thus a low interface resistance for the batteries. The catalyst-coated substrate was then inserted into a quartz tube furnace with a temperature of 750°C, followed by flowing a gas mixture of 48% Ar, 28% H₂, 24% C₂H₂ for 10-20 minutes. Subsequently, the resultant VA-CNTs were subject to water plasma etching to remove the surface contamination and amorphous carbon. This was performed in a custom-built reactor powered by a commercial radio frequency plasma generator operating at 250 kHz, 30 W, and 0.62 Torr for 20 minutes. Under these conditions, the amorphous carbon layer covering on the CNT can top surface was properly removed without damaging the nanotubes^{s6}. Morphology of the VA-CNTs was investigated by scanning electron microscopy (SEM) with a Hitachi S-4800 high-resolution scanning electron microscope.

In a dry glove box (KEMEX GB1000), using a half-cell configuration, the VA-CNT electrodes (size: 1 cm²) were fabricated into CR2032 coin cells with a Li foil reference/auxiliary electrode (thickness: 1 mm, size: 1.23 cm²), a 23-µm thick PTFE membrane separator (from W. L. Gore & Associates), and the 1 M LiTFSI/20% EC/[EDMMEA][TFSI] electrolyte. Electrochemical testing (cyclic voltammetry and galvanostatic charge/discharge) of the cells was performed with a PGSTAT30 potentiostat at room temperature. The effect of plasma etching on the electrochemical behavior of VA-CNT electrodes is shown in Figure S2.



Figure S2. CVs obtained in 1 M LiTFSI/20% EC/[EDMMEA][TFSI] electrolyte for VA-CNT electrodes with (a) and without (b) plasma etching. CVs shown are the 10th cycles. Scan rate: 1 mV/s.

3. Preparation and characterization of V₂O₅-VA-CNT composite electrodes

During potential cycling on a plasma-etched VA-CNT electrode (size: 1 cm^2) (Figure S3), the electrodeposition of V₂O₅ occurred following the reaction^{s7}: $2\text{VO}^{2+} + 3\text{H}_2\text{O} \rightarrow \text{V}_2\text{O}_5\downarrow + 6\text{H}^+$ + 2e⁻. The increased current indicates the growth of V₂O₅ on the VA-CNT electrode. The resultant V₂O₅-VA-CNT composites were rinsed with DI water and then annealed at 200° C for 10 hours to ensure a crystalline structure for the V₂O₅ thin film^{s8}.



Figure S3. CVs of a plasma-etched VA-CNT electrode recorded in $0.1 \text{ M VOSO}_4/\text{H}_2\text{SO}_4$ (pH = 1.8). Reference electrode: Ag/AgCl (3M NaCl). Auxiliary electrode: Pt wire (diameter = 1.5 mm). Scan rate: 50 mV/s. Arrow indicates the increase of currents upon potential cycling. Total cycles: 80.

Using the fabrication and testing procedure as described for VA-CNT anode, the V_2O_5 -VA-CNT composite electrodes were fabricated into CR2032 coin cells and tested with a PGSTAT30 potentiostat at room temperature. V_2O_5 loading of the V_2O_5 -VA-CNT composites was measured with the microbalance of a Thermogravimetric Analyzer (TGA, Q500, TA Instruments) and optimized by varying the number of potential cycling during the electrodeposition of V_2O_5 (Figure S4).



Figure S4. Effect of electrodeposition cycles of V_2O_5 at a plasma-etched VA-CNT electrode on the capacity of the resultant V_2O_5 -VA-CNT composite defined by V_2O_5 mass (a) and by V_2O_5 -VA-CNT mass (b). The composite electrodes were prepared by potential cycling (as described in Figure S3) with different cycle numbers. Capacity of the electrode was measured at the discharge rate of 0.25C as described in Figure 4.

4. Fabrication and testing of battery cells

In a dry glove box, a CR2032 battery full cell was fabricated by sandwiching an ionic liquid electrolyte (1 M LiTFSI/20% EC/[EDMMEA][TFSI])-soaked PTFE membrane separator between a VA-CNT anode and a V₂O₅-VA-CNT composite cathode. The V₂O₅-VA-CNT composite cathode was prepared as described in Figure S3 with the potential cycling for 80 cycles. The VA-CNT anode was electrochemically pre-lithiated prior to its use for full cell assembly. This was done by potential cycling the VA-CNT electrode (between 0 ~ 2.5 V against a Li foil reference/auxiliary electrode) in a 1 M LiTFSI/20% EC/[EDMMEA][TFSI] electrolyte. Potential cycling was performed at 1 mV/s for five cycles (to achieve a high columbic

efficiency) and then terminated at 0 V vs. Li/Li^+ (to ensure a charged state) for the resultant lithiated VA-CNT electrode. The battery cell was tested using a PGSTAT30 potentiostat at room temperature. The resultant Ragone plot is shown in Figure 5b.

References

- S1. M. Holzapfel, C. Jost and P. Novak, *Chem Commun*, 2004, 4, 2098.
- B. Garcia, S. Lavallee, G. Perron, C. Michot and M. Armand, *Electrochim Acta*, 2004, 49, 4583.
- H. H. Zheng, H. C. Zhang, Y. B. Fu, T. Abe and Z. Ogumi, J. Phys. Chem. B, 2005, 109, 13676.
- S4. W. A. van Schalkwijk and B. Scrosati (Eds.), *Advances in Lithium-ion Batteries* (Kluwer Academic/Plenum Publishers, 2002), pp 7-77.
- S5. L. Qu and L. Dai, J. Mater. Chem., 2007, 17, 3401.
- S6. S. Huang and L. Dai, J. Phys. Chem. B, 2002, 106, 3543.
- E. Potiron, A. Le Gal La Salle, A. Verbaere, Y. Piffard and D. Guyomard, *Electrochim. Acta*, 1999, 45, 197.
- S8. I-H. Kim, J-H. Kim, B-W. Cho and K-B. Kim, J. Electrochem. Soc., 2006, 153, A989.