Promoting Transport Kinetics in Li-Ion Battery with Aligned Porous Electrode Architectures

Xiao Zhang,¹ Zhengyu Ju,¹ Lisa M. Housel,² Lei Wang,³ Yue Zhu,¹ Gurpreet Singh,² Nahian Sadique,² Kenneth J. Takeuchi,^{2,4} Esther S. Takeuchi,^{2,3,4} Amy C. Marschilok,^{2,3,4} Guihua Yu¹

- Materials Science and Engineering Program and Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX 78712, United States
- Department of Chemistry, Stony Brook University, Stony Brook, NY 11794, United States
- Energy Sciences Directorate, Brookhaven National Laboratory, Upton NY 11973, United States
- Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11794, United States
- *E-mail: ghyu@austin.utexas.edu

Experimental section

Materials synthesis GO/Fe_3O_4 was synthesized through a modified co-precipitation method. 0.5 mmol $FeCl_2·4H_2O$ and 1.0 mmol $FeCl_3·6H_2O$ were dissolved and then slowly added to aqueous GO solution containing 8 mg GO. The resulting mixture was then slowly added to 10 mL 1 M TEA solution under vigorous stirring. The resulting precipitates was collected and washed after 30 min of stirring.

Electrode fabrication GO/Fe₃O₄, super P and Nafion aqueous solution were prepared into slurry with mass ratio of 18:1:1. For AGF electrodes, the slurry was dropped onto Cu foil and subjected to a cold finger, where the bottom of the cold finger was immersed into liquid nitrogen, followed by a freeze-dry process. For GF electrodes, the slurry was directly casted onto Cu foil and dried. For F electrodes, Fe₃O₄ nanoparticles, super P and Nafion aqueous solution were mixed at ratio of 14:3:3. The resulting slurry was casted onto Cu foil and dried in oven. Unless specified, all electrochemical characterization is based on electrodes with 5 mg·cm⁻² mass loading.

Cell assembly. All electrochemical measurements were performed in a half-cell configuration. CR2032 coin cell assembly was carried out in an argon-filled glovebox with lithium metal as anode and reference electrode. Celgard 2320 was used as separator between cathode and anode. The electrolyte was 1.0 M LiPF₆ dissolved in a mixture of ethylene carbonate and dimethylene carbonate with 1:1 ratio. All electrochemical tests were conducted at room temperature (25 °C) with a voltage range 0.1~3.1 V.

Phase identification and morphology characterization. Powder XRD patterns were collected on a Philips Vertical Scanning diffractometer to identify the phase of the assynthesized samples. Scanning electron microscope, STEM (Hitachi S5500) and TEM (JEOL 1400) were used to characterize the morphology of the samples. X-ray fluorescence (XRF) mapping was conducted at the 5-ID beamline of the National Synchrotron Light Source-II (NSLS-II) at Brookhaven National Laboratory. The energy was calibrated using a Fe reference foil at 7112 eV. The XRF maps were collected at 7200 eV over a 70 μ m x 70 μ m area in 2 μ m increments using an acquisition time of 0.1 s. PyXRF software was used to the Fe contribution of the fluorescence spectra.¹ XPS was performed using Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer equipped with a monochromatic Al K α X-ray source (1,486.7 eV) for excitation.

Electrochemical measurements. Rate performance, cycling tests and GITT of asassembled coin cells were tested using a LAND battery test system (CT2001A). GITT was performed under 0.2 A/g constant current discharge/charge for 30 min, with rest of 2 h. CV and EIS data were collected using a BioLogic potentiostat (VMP3). For all EIS measurements, the a. c. amplitude was set to 10 mV, and frequency range from 1000 kHz to 10 mHz. All electrochemical testing were conducted under room temperature (25 °C).

CV analysis. b-values are calculated through $i = av^b$, where i is the measured peak current in each CV curve, v is scan rate, and a is adjustable parameters.



Figure S1. Active material (Fe_3O_4) is estimated to be 81% in the as-synthesized nanocomposite through thermogravimetric analysis (TGA).



Figure S2. FTIR results reveal strong chemical interaction between Fe₃O₄ and GO.



Figure S3. XPS results of (a) C 1s of GO and Fe_3O_4/GO , (b) O 1s and (c) Fe 2p of Fe_3O_4/GO .



Figure S4. SEM images of aligned channel walls in AGF under different magnifications.



Figure S5. SEM images of GF from (a) top and (b) side views.



Figure S6. SEM images of F from (a) top and (b) side views.



Figure S7. Fe X-ray fluorescence maps of (a) AGF-1, (b) GF-1, and (c) F-1 electrodes.



Figure S8. TEM microtome of (a-c) F, (d-f) GF, (g-i) AGF under different magnifications.



Figure S9. STEM, as well as Fe and C elemental mapping images of (a-c) F, (d-f) GF, and (g-i) AGF electrodes, scale bar= $2 \mu m$.



Figure S10. Cycling stability of AGF electrode (a) under $0.2 \text{ A} \cdot \text{g}^{-1}$ for 200 cycles and (b) 2.0 A $\cdot \text{g}^{-1}$ for 500 cycles.



Figure S11. SEM images of AGF after cycling.



Figure S12. (a) GITT profiles of AGF and GF. V_{relax} - V_I comparison during (b) discharge and (c) charge.



Figure S13. CV profiles of (a) GF and (b) F electrodes under various scan rates. (c) b values of cathodic II peak.



Figure S14. N_2 adsorption-desorption isotherms of the as-prepared (a) AGF and (b) GF electrodes.



Figure S15. Nyquist plots of (a) AGF, (b) GF and (c) F electrodes. (d) Modified Randle's circuit used for simulation and the estimated impedance values.

Reference:

1. Li, L., Yan, H., Xu, W., Yu, D., Heroux, A., Lee, W.K., Campbell, S.I. and Chu, Y.S. "PyXRF: Python-based X-ray fluorescence analysis package." *X-Ray Nanoimaging: Instruments and Methods III*, **2017.** 10389, p. 103890U.