Enhanced rate performance and cyclic stability of Fe₃O₄-graphene nanocomposites for Li ion battery anodes

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Electronic Supplementary Information

Experimental

Materials Processing

Fe³⁺ and Fe²⁺ chlorides (Alfa Aesar) were mixed at the molar ratio of 2:1 in deionized water. The solution was destabilized with the addition of 1M NaOH solution while being irradiated with an ultrasonic horn (20 kHz). The resulting black suspension was centrifuged and washed in deionized water several times to harvest the magnetite nanoparticles. Graphene oxide was supplied by PDC Energy, LLC (Louisville, CO, USA) and was used without further processing. The Fe₃O₄ nanoparticles and graphene oxide (GO) were mixed in the ratio of 3:1 and baked in a furnace (Thermolyne, IA) at 450 °C for 1 hour in flowing Ar. The resulting magnetite-graphene nanocomposites were used as active materials in the anode.

Materials Characterization

Transmission electron microscopy (TEM, 2000FX JEOL, Japan), at an accelerating voltage of 200 kV, was performed to study the size and morphology of the calcined magnetite nanoparticles. Selected area diffraction (SAD) in the TEM was performed on the powders to check the crystallinity. Crystallography of the nanoparticles was determined by an X-ray diffractometer (Philips PW1730, Philips, Eindoven, Netherlands) with Cu-Kα radiation (λ=1.54056
Å) operated at a scan rate of 2°.min$^{-1}$ between 20°–80° of 2θ. N$_2$ adsorption–desorption isotherms of the magnetite nanoparticles were collected at 77 K with relative pressure $p/p_0$ between 0.05 to 0.99 (Micromeritics ASAP 2010, Norcross, GA, USA). Samples were degassed for 220 °C overnight before analysis. Specific surface area was computed by the Brunauer-Emmet-Teller (BET) model. Barrett-Joyner-Halenda (BJH) model was applied for calculating the pore size, pore volume distribution and average pore diameter. Raman spectroscopy at a laser wavelength of 632 nm was performed on the reduced graphene oxide powders (Jobin Yvon). The carbon content in the magnetite-graphene powders was determined by a LECO carbon analyzer.

**Electrochemical Characterization**

The electrochemical response was measured with CR-2032 type coin cell assembly in half cell configuration with Li as counter electrode. Anode composition was formulated with Fe$_3$O$_4$ powders, acetylene black (AB), and polyvinylidene difluoride (PVdF) in the ratio of 80:10:10. In other words, the anode composition constituted of 60% magnetite nanoparticles, 20% graphene, and 10% each of AB and PVdF. The composition was mixed with 1-methyl-2-pyrroldinone and was cast onto a Cu foil (Goodfellow) by doctorblading, dried in an oven, and circular electrodes were cut. LiPF$_6$ (1 M) dissolved in a solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) in 1:1 ratio (Novolyte, USA) was used as the battery electrolyte. Polymeric microporous membranes (Celgard, USA) soaked in the electrolyte were used as the separator between the working electrode and Li foil. The half cells were layer-assembled, punched and crimped inside a glove box with <1 ppm of moisture and oxygen levels. Galvanostatic charge-discharge cycles were recorded between the 0.01V to 3V window in a battery tester (BT–2000, Arbin Instruments) with current densities varying between 100–20,000 mAgm$^{-1}$, following symmetric cycling.
Supplementary Figures

Figure 1: BET adsorption-desorption isotherm of the Fe₃O₄, mesoporosity (pore size between 2 and 50 nm) is indicated by the hysteresis in the sorption branches. The average pore diameter of ~12 nm is in agreement with the results from electron microscopy.
Figure 2: (top) X-ray diffractogram of Fe$_3$O$_4$-graphene nanocomposites; while the peaks clearly confirm to ICDD files card no. 85–1436 for magnetite, no peaks are observed for graphene/graphite except for a diffused peak at 25°; (bottom) Raman spectrograph of the composites indicating the D-band at 1311 cm$^{-1}$, and G-band at 1586 cm$^{-1}$ for graphene, indicating thermal reduction of graphene oxide to graphene.
Figure 3: Voltage profiles of the cell cycled at different C-rates; the rate and the cycle numbers are indicated.

Figure 4: Galvanostatic charge-discharge capacities of nanomagnetite powder anodes; The charge-discharge C-rates in Hr$^{-1}$ are indicated.
Figure 5: Galvanostatic charge-discharge capacities of graphene powders; Numbers in square brackets are current density in mA.g\(^{-1}\).