Supporting Information

Deliberate modification of the solid electrolyte interphase (SEI) during lithiation of magnetite, Fe_3O_4: Impact on Electrochemistry

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Experimental Section

Synthesis and Characterization

The synthesis of ca. 35 nm Fe_3O_4 nanoparticles was adapted from a previous report.[1] Briefly, iron (II) chloride hexahydrate was slowly dropped into an aqueous ammonium hydroxide solution. After the addition was complete, the solution was allowed to stir under air. Precipitated Fe_3O_4 was isolated by centrifugation and dried.

X-ray diffraction data was collected using a Rigaku Miniflex lab diffractometer with Cu Kα radiation and D/teX area detector. Materials were characterized by XRD and compared with the reported Fe_3O_4 reference pattern (PDF #01-088-0315). Multipoint BET (Brunauer, Emmett, Teller) surface area data were collected using a Quantachrome Nova 4200e instrument on both Fe_3O_4 nanoparticles and carbon black using $N_2(g)$ as adsorbent.

Electrochemical Methods

Electrodes were prepared on copper foil substrates with a ratio of 70:20:10 Fe_3O_4:carbon black:PVDF binder. The Fe_3O_4 mass loading for the electrodes were 1.50 +/- 0.05 mg/cm^2. Coin-type half cells were used for electrochemical tests with lithium metal counter electrodes and polypropylene separators. The electrolytes used in the study consisted 1 M lithium hexafluoroborate ($LiPF_6$) in mixtures of EC, FEC and DMC in ratios (v:v:v) of 30:0:70, 27:3:70, 20:10:70, and 10:20:70, corresponding to FEC molar concentrations of 0 M, 0.4 M, 1.33 M, and 2.66 M FEC, respectively. The coin cells were assembled inside under Ar atmosphere with H_2O and O_2 content < 1ppm to avoid moisture and oxygen contamination. Cyclic voltammograms were collected at a scan rate of 0.1 mV/s between 0.01 and 3.0 V vs. Li/Li^+ Galvanostatic cycling tests were performed using a rate of C/2 (calculated based on the active mass Fe_3O_4 in the electrode) between 0.1 and 3.0 V vs. Li/Li^+. Rate capability tests were

performed using the same voltage window and rates of C/5, C/2, 1C, 2C, and 5C. C-rates were calculated based on the mass of Fe_3O_4 only in the electrode (excluding carbon black and PVDF) and theoretical capacity of 924 mAh/g).

Isothermal microcalorimetry

Isothermal microcalorimetry measurements were performed using a TA Instruments TAM III calorimeter. Coin cells were attached to a Biologic VSP potentiostat via wire leads. The cells were then placed in microcalorimetry ampuoles which were subsequently submerged in an oil bath programmed to keep a constant temperature of 30 °C. The cells were allowed to rest for 12 hours to allow for temperature equilibration before being cycled at a rate of C/10 to between 3.0 and 0.1 V for 5 cycles. Between discharge and charging steps, the cells were allowed to rest for 6 hours to allow for heat dissipation before the subsequent step. Heat flow from the sample ampuoles was measured relative to heat flow from empty reference ampuoles.

Post-mortem XRD of cycled electrodes

For post-mortem XRD investigations of the Fe_3O_4 electrodes, cells were disassembled after cycling 100x under Ar atmosphere (H_2O and O_2 content < 1ppm) and washed with dimethyl carbonate. XRD measurements were collected under dry room atmosphere (H_2O < 0.5%) in transmission geometry with Cu K_α radiation. Rietveld analysis was performed using GSAS-II software assuming isotropic crystallite size and structural models of bcc Fe^0, Li_2O, and LiF.
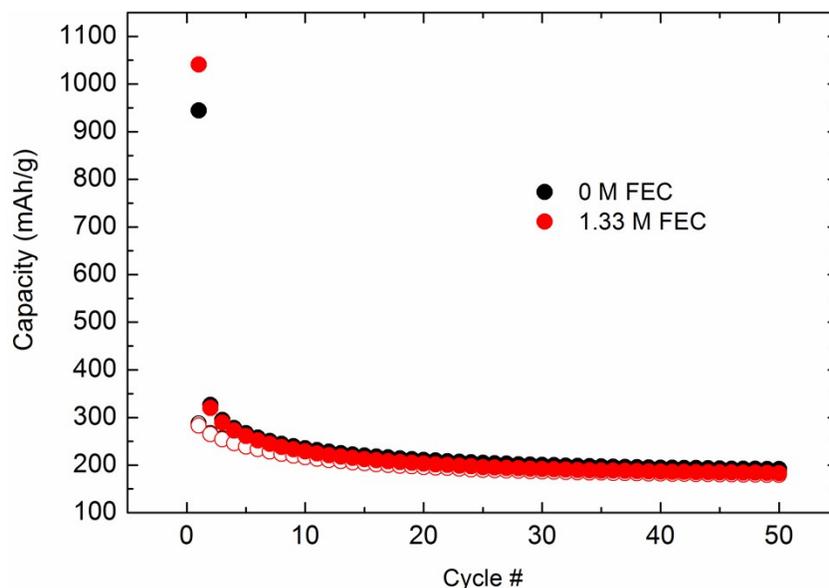

Figure S1: Charge/discharge capacities of 80% carbon black, 20% PVDF electrodes for 50 cycles at a current rate of C/2 obtained in the voltage range 0.1 to 3.0 V, with discharge and charge capacities indicated by filled and open icons, respectively. Capacity is calculated based on the mass of carbon black in the electrode.
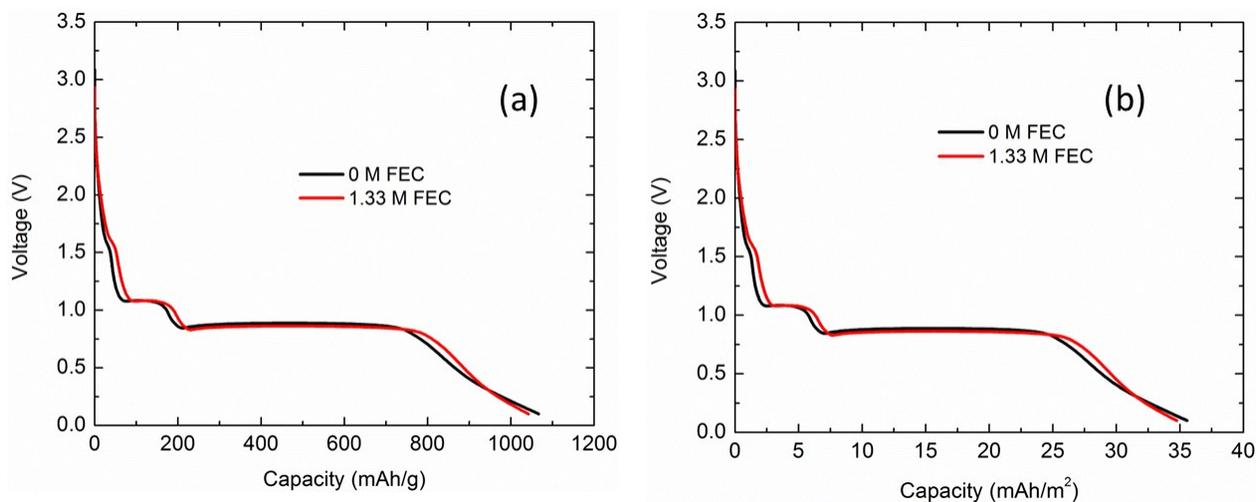
Figure S2: First discharge capacities of 80% Fe_3O_4 , 20% PVDF electrodes at a current rate of 50 mA/g to a cutoff voltage of 0.1 V Capacity is normalized by (a) grams of Fe_3O_4 and (b) surface area of Fe_3O_4.
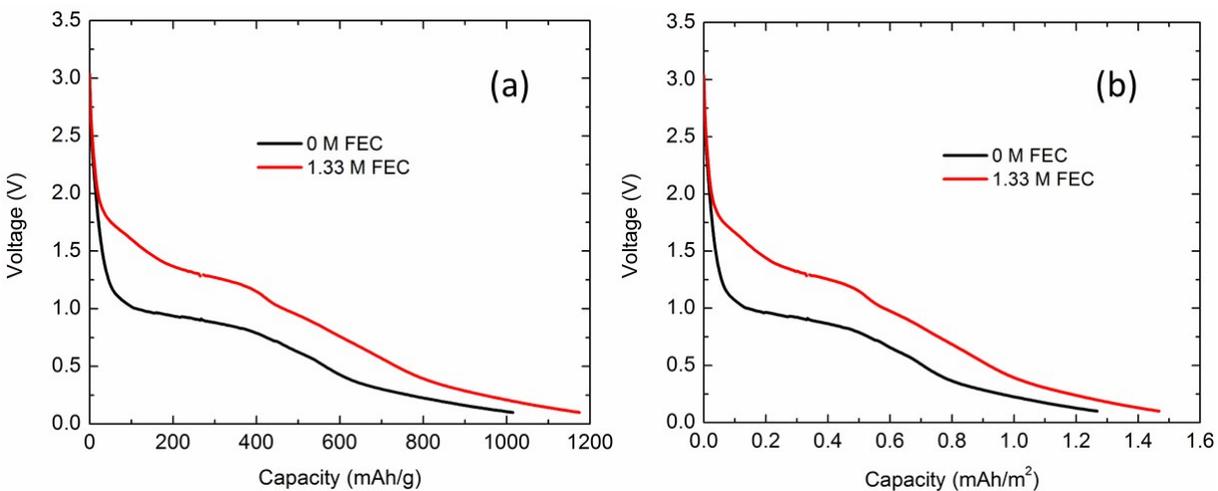

Figure S3: First discharge capacities of 80% carbon black , 20% PVDF electrodes at a current rate of 50 mA/g to a cutoff voltage of 0.1 V. Capacity is normalized by (a) grams of carbon black and (b) surface area of carbon black.
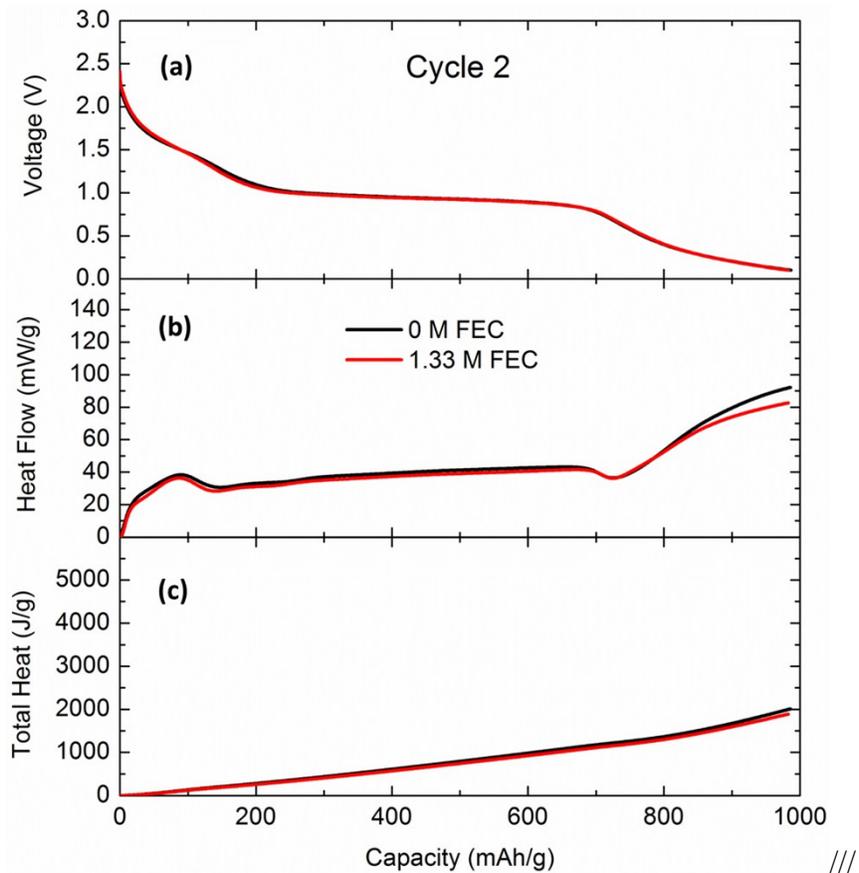
Figure S4. (a) Voltage profiles of Li / Fe_3O_4 coin cells with either 0 M or 1.33 M FEC in the electrolyte during 2nd cycle discharge at a rate of C/10 with voltage cutoff of 0.1 V vs. Li/Li$^+$. (b) Corresponding heat flow of cells as a function of capacity as determined via isothermal calorimetry at 30 °C. (c) Corresponding total heat output of cells as a function of capacity.
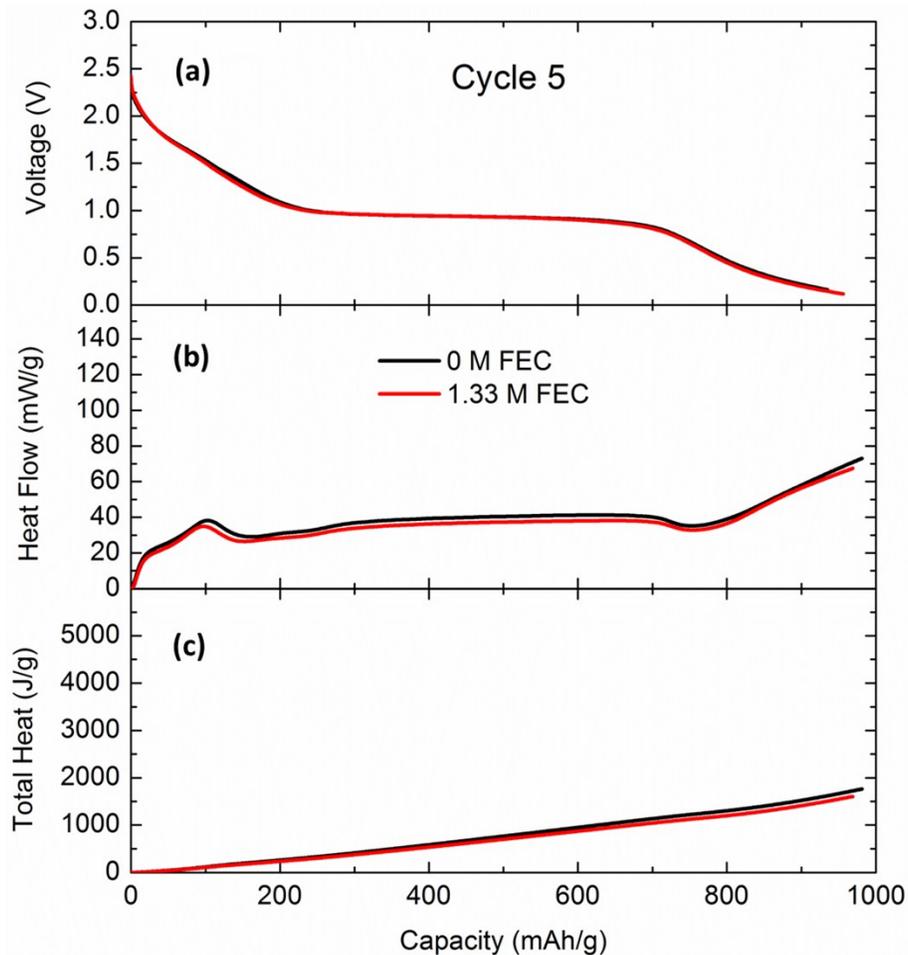
Figure S5. (a) Voltage profiles of Li / Fe_3O_4 coin cells with either 0 M or 1.33 M FEC in the electrolyte during 5th cycle discharge at a rate of C/10 with voltage cutoff of 0.1 V vs. Li/Li+. (b) Corresponding heat flow of cells as a function of capacity as determined via isothermal calorimetry at 30 °C. (c) Corresponding total heat output of cells as a function of capacity.

References

1.   Iida, H.; Takayanagi, K.; Nakanishi, T.; Osaka, T., Synthesis of Fe3O4 nanoparticles with various sizes and magnetic properties by controlled hydrolysis. *J. Colloid Interface Sci.* **2007,** *314* (1), 274-280.