

Operando Electron Magnetic Measurements in Li-ion Batteries

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Supporting Information

Electrode preparation:

FeSb₂ was synthesized according to a published procedure.¹ The orthorhombic FeSb₂ phase was obtained by placing stoichiometric amount of iron metal and antimony powders in a silica tube sealed under vacuum. The silica tube was placed in a furnace and heated to 730 °C during 4 days using a ramp of 2 °C/min. The tube was then air quenched and the product characterized by XRD.

Electrode formulation was made using a 1/1 mixture of carbon black and vapor ground carbon fibers (VGCF-S) as the conductive additive and carboxymethyl cellulose (CMC) (DS = 0.7, Mw = 250 000 Aldrich) as the binder. An aqueous slurry containing 70 wt% active material, 12 wt% binder and 18 wt% conductive additive was homogeneously mixed by a planetary ball-milling for 1 h, tape casted on a 20 µm thick copper foil, and dried at room temperature for 12 h and finally at 100 °C under vacuum for another 2 h. The final mass loading of active material on the electrode was 1.66 mg/cm².

The electrochemical tests were performed versus Li metal (Chemetall Foote Corporation, USA), in LiPF₆ 1 mol L⁻¹ electrolyte in EC/DMC (1:1) (Aldrich) and a separator (Cellgard, PE monolayer), using either coin cells (2523, NRC, Canada) or a designed polypropylene cell. The cells were assembled in an argon-filled glove box, with a purifying system (MBraun GmbH, Germany),

¹ Villevieille, C.; Fraisse, B.; Womes, M.; Jumas, J.-C.; Monconduit, L. *J. Power Sources* **2009**, *189*, 324–330.

oxygen and water contents below 1 ppm. The electrochemical measurements were controlled by a Bio-Logic VMP3 multi-channel potentiostat (for ex situ experiments) or a Bio-Logic SP-50 single channel potentiostat (for in situ experiments).

The magnetic measurements were performed on a Quantum Design MPMS SQUID using a modified magneto-transport sample rod for the in situ measurements.

Control experiment

In a control experiment, the magnetic measurements are also performed on a polypropylene cell assembled without FeSb₂. The working electrode is replaced with a Cu foil while the cell, electrolyte and counter electrode are kept identical. The control cell displays a constant value during cycling (Figure S1).

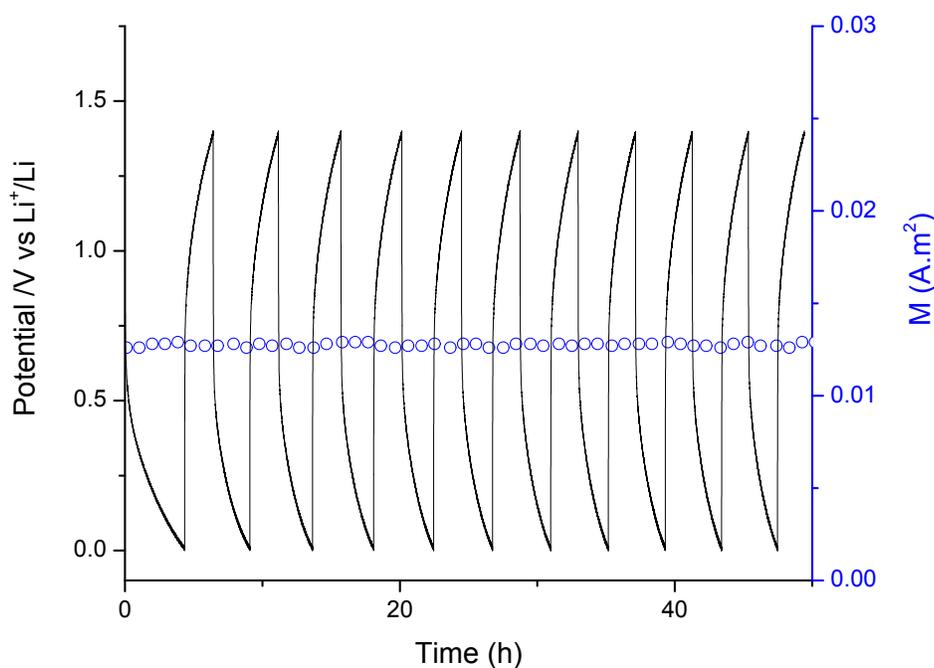


Figure S1: Control experiment with a Cu electrode showing the electrode potential vs lithium during galvanostatic cycling (plain line) and magnetic moments at 300 K (blue dots) (C)

The ex situ measurements are performed on the working electrode after stopping the galvanostatic cycling of the coin cell, opening in Ar filled glovebox and extracting the working electrode. The electrode is then washed, dried and inserted in an Ar filled cap for SQUID measurements.

We have performed several low temperature hysteresis during the first lithiation (Figure S2A) and ZFC/FC at $\mu_0 H = 5.0$ mT on the fully lithiated sample after n cycles.

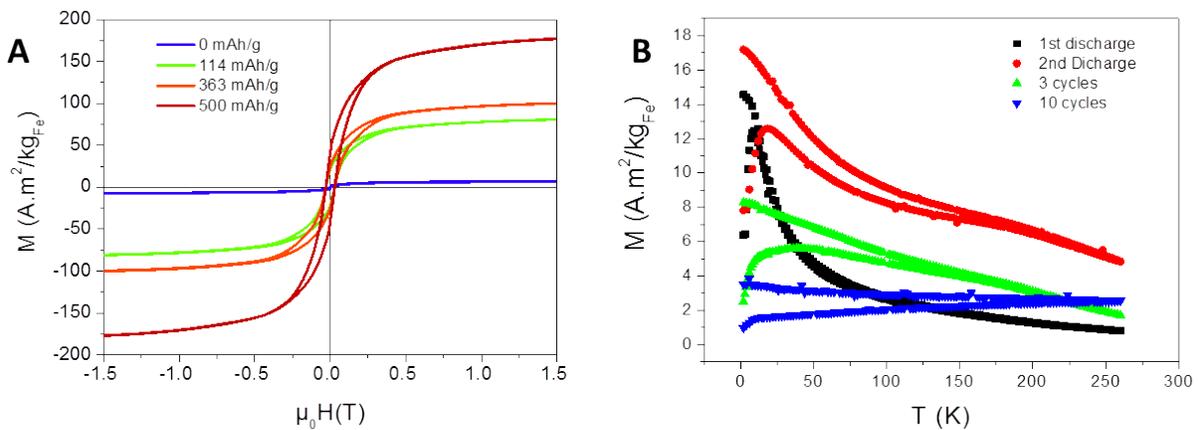


Figure S2: Ex-situ magnetic measurements during the first lithiation: hysteresis at 2 K (A); ZFC/FC at $\mu_0 H = 5.0$ mT on the fully lithiated sample after n cycles (B)

Even though Fe does not directly participate in the electrochemical process, the presence of Fe nanoparticles improves the cycling performances of Fe/Sb compared to a Sb electrode (500 mA h/g¹ capacity after 50 cycles at C/10 rate on Fig. S3).

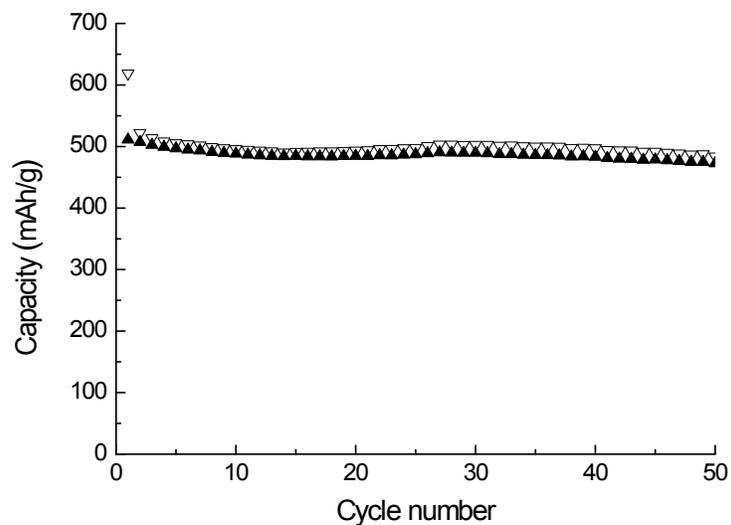


Figure S3: Charge/discharge capacity of FeSb₂ in coin cell

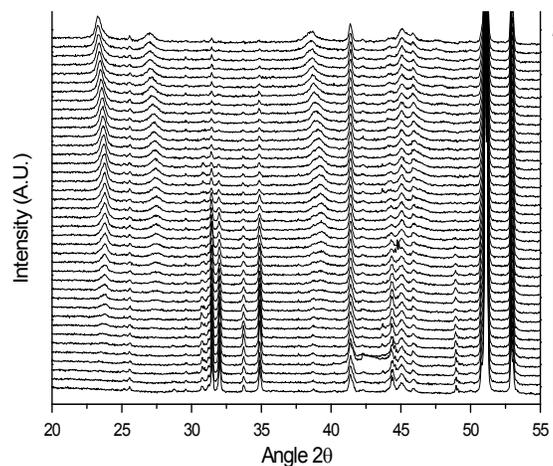


Figure S4: In situ XRD for the first cycle (adapted from ref. 2)²

² C. Villevieille, C. M. Ionica-Bousquet, B. Fraisse, D. Zitoun, M. Womes, J. C. Jumas, and L. Monconduit, *Sol. State Ionics*, 2011, **192**, 351–355.

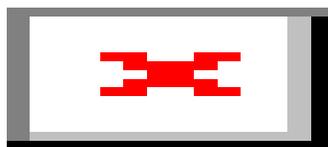


Figure S5: ^{57}Fe Mössbauer Spectrum recorded at 300 K at the end of lithiation showing that the intermediate ternary phase (phase X) is not magnetic (adapted from Ref. 2)