Journal Name

COMMUNICATION

In Operando Electron Magnetic Measurements in Li-ion Batteries

Gregory Gershinsky,[a] Elad Bar,[b] Laure Monconduit,[c] David Zitoun[a],*

One of the challenges in the development of batteries consists in the investigation of new electrode materials and comprehension of the mechanism of lithium uptake. Herein, we report on the first in operando measurements of electron magnetism on a battery during cycling. We have succeeded in designing a non magnetic cell and have investigated the lithiation mechanism of $FeSb_2$, a high energy density anode material. The stepwise increase of the magnetic moment reveals an increase of amorphous Fe nanoparticle size, while Sb undergoes a reversible alloying with Li.

The rechargeable Li-ion batteries (LIBs) display high energy density which makes them the preferred energy storage device for portable applications.[1] The performance of LIBs depends on materials evolution upon cycling.[2] One of the challenges consists in the investigation of new electrode materials and comprehension of the mechanism of lithium uptake.[3] New ways to get real–time information on the performances of the battery are continuously sought. The development of in-situ (or in operando) characterization techniques brings valuable information on chemical processes since the interpretation of ex situ measurements brings a partial picture of the chemical reactions.[4] The electrode lithiation can be described as an intercalation, insertion, conversion or alloying reaction with lithium. The development of effective conversion and alloying electrode materials is a milestone for the achievement of high energy density LIBs required for electrical vehicles (EVs). As an alternative to graphite, conversion anodic materials display promising characteristics such as high gravimetric and volumetric capabilities.[5]

Conversion reactions, where an electrode material undergoes a phase change, are highly sensitive to kinetics. Each interface is highly reactive, thus application of external potential results in metastable amorphous states far from the thermodynamic equilibrium. These transient states must relax to some new thermodynamic state, thus questioning the use of ex-situ measurements on electrodes. In situ local probe measurements have been recently developed to address the lithiation mechanism, including solid-state nuclear magnetic resonance (SS-NMR),[6] Raman spectroscopy,[7] mass spectrometry,[8] Mössbauer spectrometry,[9] X-Ray diffraction,[10] soft X-ray spectroscopy,[11] or

electron microscopy.[12] In particular, SS-NMR has been used for the characterization of electrode materials[13] and has probed the chemical environment in electrodes in situ,[14] while MRI has allowed mapping batteries in operando,[15] and SS-NMR has been recently applied to paramagnetic solids.[16] Indeed, most of the electrode materials are based on Mn, Fe, Co or Ni. Even silicon, a promising anodic material can be alloyed with a transition metal to improve its cycling ability. The electrodes display a paramagnetic or ferromagnetic at one stage during lithiation or delithiation process which makes electron magnetic measurements highly valuable as shown ex-situ on pristine and cycled electrode materials.[17,18] The presence of transition metals in electrodes opens an avenue for the study of electron magnetic properties to resolve the lithiation mechanism and we have previously reported on the ex-situ measurements of magnetism in conversion materials for anodes.[19,20] Nevertheless, to our knowledge, no publication has reported in operando measurement of electron magnetism in LIBs until now.

In operando electron magnetic measurements should bring quantitative information on the electrochemical processes, in particular when a ferromagnetic phase is formed electrochemically, even on amorphous phases. In this framework, we have isolated the model compound $FeSb_2$ by alloying an active anodic material Sb with a magnetic transition metal Fe, thus undergoing a conversion process into amorphous Fe and nanocrystalline Li_3Sb.[21]

In this communication, we report on the first in-situ measurements of electron magnetism on a battery during cycling. We have succeeded in designing a non-magnetic cell and have investigated the lithiation mechanism of $FeSb_2$, as electrode material. The magnetization has been measured at constant magnetic field or in a sweeping magnetic field in a SQUID magnetometer. The magnetization has been collected for several charge/discharge cycles. These real-time measurements change our perception of lithiation mechanism in $FeSb_2$. After the first cycle, the electrochemical process involves the reversible lithiation on Sb only, while all the changes in magnetic moment are mainly due to nanostructural effects with an evolution of Fe particle size, leading us to a distinct lithiation mechanism.

$FeSb_2$ is a very interesting anodic material for LIB, both for its performance and the ability to study Fe and Sb by Mössbauer

spectrometry.[22] The low polarization value and the highly stable potential stand close to performance of insertion materials at 0.8 V, with better volumetric and gravimetric values than graphite (4100 mA h/cm^3 ; 540 mA h/g for FeSb$_2$ and 820 mA h/cm^3; 372 mAh/g for graphite) and with coulombic efficiency above 97% (Fig. S3, charge/discharge capacity). Previous study has shown that the electrochemical reaction is thought to be a reversible conversion process according to the following chemical equations:[22]

$$FeSb_2 + 4\ Li \leftrightarrow Li_4FeSb_2$$

$$Li_4FeSb_2 + 2Li \leftrightarrow 2\ Li_3Sb + Fe$$
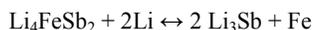
Fe is the only ferromagnetic phase since the ^{57}Fe Mössbauer spectrum of the ternary phase does not show any magnetic ordering; the temporal evolution of magnetic moment should give us a quantitative proof of the validity of the proposed mechanism. On the other hand, recent work on conversion electrode materials has demonstrated the instability of the composite electrode formed at the end of lithiation and the necessity of in situ measurements.[23]

The in situ cell has been designed using diamagnetic raw materials according to the geometrical constraints of a SQUID cryostat with an external diameter of 6.5 mm and a length of 20 mm (Figure 1B), and inserted in a polypropylene straw (Figure 1A). The working electrode consists in FeSb$_2$ formulated on a Cu foil and the counter electrode of Li plated on Cu foil, all details are available in supporting information. The cell is connected in galvanostatic mode at C/5 from 0 V to 1.4 V and cycled at 300 K while the magnetic moment is sampled at constant field (2 T). In a control experiment, the magnetic measurements are performed on a polypropylene cell assembled without FeSb$_2$. The reference sample displays a constant paramagnetic value (Figure S1).
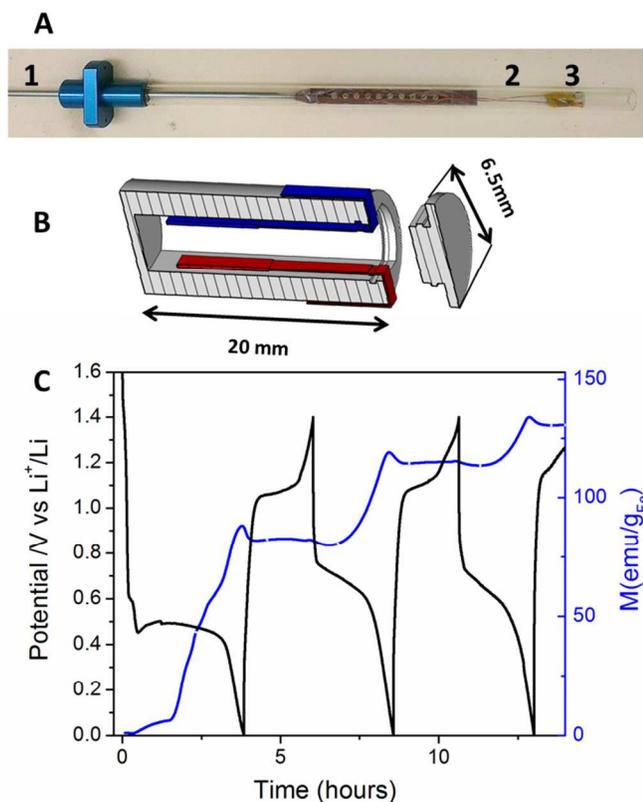
cycling (black) and corresponding magnetic moment at 300 K (blue) (C)

The temporal changes in magnetic moment of FeSb$_2$ follow the periodicity of the potential (Figure 1C). The lithiation process induces a sharp increase of magnetic moment with a maximum found slightly after the start of the delithiation process. The magnetic moment remains almost constant until a new lithiation induces another sharp increase. The stepwise increase of magnetic moment shows damping after 3 cycles. This remarkable behavior is unexpected and resembles the signature of an irreversible phenomenon while the electrochemical processes remains almost steady (Figure 2A).

In a control experiment, the anode material is tested in the same conditions (rate C/5, same electrolyte and separator) in standard coin cell configuration versus lithium metal. The anode exhibits a reversible capacity of 530 mA h/g close to the theoretical limit (540 mA h/g) with two discharge plateaus (0.86 V; 0.78 V) and one charge plateau at 1.02 V. For the sake of consistency, we have plotted the voltage profile collected during the second cycle in real time experiment on the same graph (Figure 2A, red line). The in situ cell reaches the same capacity with a voltage profile similar to the coin cell control experiment (black line). The main discrepancy lies in the higher polarization (potential differences between charge and discharge plateaus), a classical signature for loose pressure between the electrodes in the in situ cell. Therefore, electrochemical processes are highly consistent in ex situ and in situ experiments.


FIGURE 1: Photograph of the insert for SQUID measurement (1), the electrical connections (2) and in situ cell (3) (A); scheme of the in situ cell (B); electrode potential vs lithium during galvanostatic
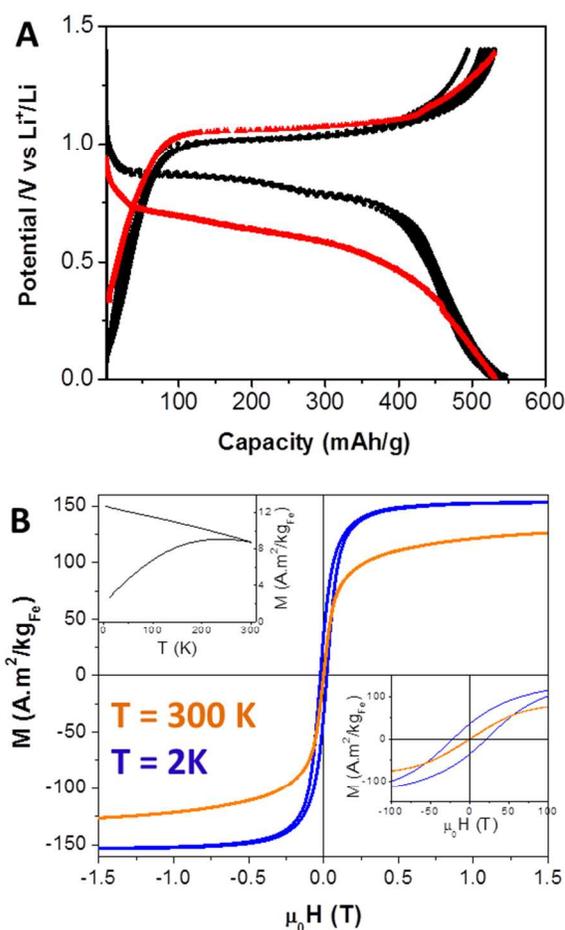
FIGURE 2: Electrode potential vs lithium during galvanostatic cycling for the in-situ cell (red dots) and ex-situ coin cell (black dots) (A); ex-situ magnetic measurements after the 8th delithiation: hysteresis at 2 K (blue) and 300 K (orange), magnification of the hysteresis (right down panel) and ZFC/FC (left upper panel) (B)

The stepwise increase of magnetic moment is intriguing and deserves a close investigation of the magnetization as a function of field and temperature. The ex situ measurement is performed directly on the $FeSb_2$ electrode from the coin cell after washing and drying in glovebox. The coin cell is stopped at the end of delithiation process after 8 cycles, the delithiated electrode should consist of paramagnetic $FeSb_2$ if the conversion mechanism is fully reversible. Nevertheless, the electrode displays a ferromagnetic behavior at 2 K with a high magnetic moment (170 Am^2/kg_{Fe}) (Figure 2B) and a superparamagnetic behavior at 300 K while the temperature dependence (Zero Field-Cooled/Field-Cooled or ZFC/FC) is typical of superparamagnetic nanoparticles with a maximum in the ZFC around 250 K (Figure 2B inset). Therefore, the material consists of one phase of nanoscale Fe and one phase consisting mostly of Sb, as already qualitatively demonstrated from Mössbauer spectrometry (Fig. S5).[22] Both phases are amorphous in the delithiated state and in-situ XRD experiments have previously shown the occurrence of a Li_3Sb phase only in the discharged electrode, as shown in the supporting information (Fig. S4).[22]
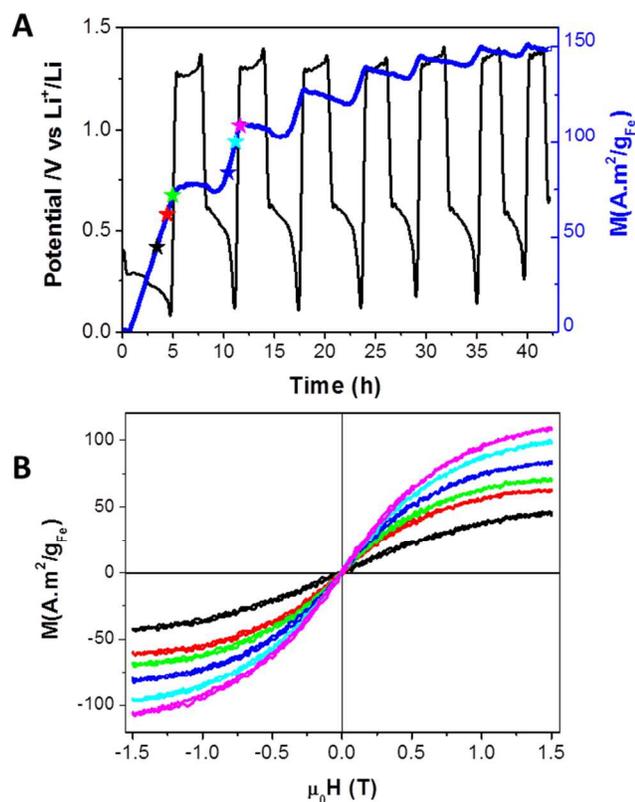

FIGURE 3: Electrode potential vs lithium during galvanostatic cycling for the in-situ cell (plain line) and magnetic moment collected in-situ at 300 K (blue dots) (A); in-situ field dependent magnetic measurements; the different colors correspond to the stars on panel A (B)

To precise these results, we have measured the magnetic moment at constant field during 8 cycles (Figure 3A) and observe the stepwise increase of the magnetization which reaches a plateau after 8 cycles.

Compared to electrochemical cycle which lasts for 10 hours, a magnetic measurement is very fast (about one second) which allows us to scan the field at a define potential (around 10 minutes experiment). On the Figure 3A, the stars mark the potential where the magnetization is measured as a function of the field at 300 K. On figure 3B, the curves display the expected superparamagnetic behavior without hysteresis and the magnetic moment does not saturate even at high field, clearly evidencing the superparamagnetic behavior. These measurements are consistent with the ex situ measurements and demonstrate that low temperature measurements are not needed to confirm the magnetic nature of the materials.

The investigation of a battery is always complex since the electrodes are often very reactive and unstable. The main issue remains to ensure that the evolution of magnetic properties relates to an electrochemical process and not to a relaxation of the electrode material at constant potential (CP) or in open circuit (OCV). Recent work on conversion electrode materials has demonstrated the instability of the composite electrode formed at the end of lithiation.[20] Once the external constraint of an electrochemical potential is lifted, chemical relaxation towards more thermodynamically stable phases or microstructures may occur before one could investigate the electrode with ex situ techniques. The in situ cell shows no evolution of the magnetic moment with a cell in open circuit voltage (OCV) (Figure 4A) and at constant potential without electrochemical process. The magnetic moment is constant whether the CP or OCV is applied at the end of the lithiation or delithiation process. The magnetic moment follows only the electrochemical processes and does not vary at CP or OCV.
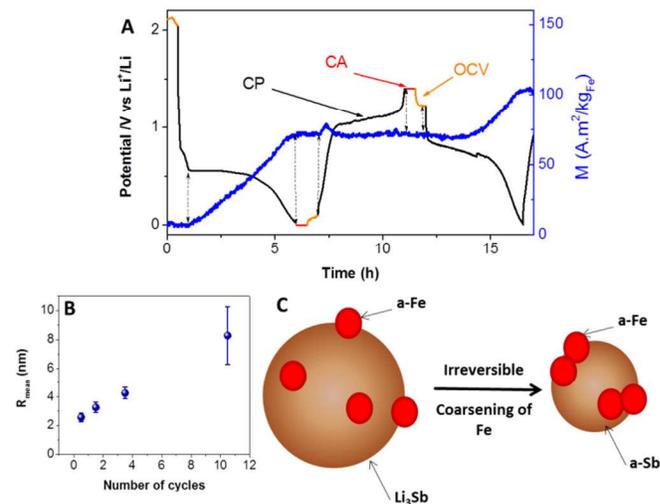

FIGURE 4: Electrode potential vs lithium during galvanostatic cycling for the in situ cell (black line), open circuit voltage (orange line), constant potential (red line) and magnetic moment at 300 K (blue dots) (A); Magnetic particle size calculated from the ex situ ZFC/FC measurements as a function of number of cycles for fully lithiated electrodes (B); Schema of the magnetic size coarsening (C)

To understand the stepwise increase of magnetic moment, we have performed several low temperature hysteresis. Each curve displays the magnetic properties of $FeSb_2$ electrode dried from battery stopped for a specific state of charge/discharge (Figure S2A). During the first lithiation process, the magnetic moment obtained at low temperature increases rapidly to reach the value of 175 Am^2/kg_{Fe}. This magnetic moment is close to the one observed at room

temperature after 8 cycles: 150 Am^2/kg_{Fe} (Figure 3A). From this high magnetic moment, we conclude that the conversion of $FeSb_2$ is already completed after the first lithiation. During in situ measurement at 300 K, the magnetic moment reaches only 70 Am^2/kg_{Fe} as a consequence of superparamagnetism.

To verify this point, we have carried on ZFC/FC measurements on the fully delithiated material at the end of charge after n cycles (Figure S2B). The ZFC/FC curves are characteristic of superparamagnetic behavior with a maximum increasing from T = 10 K to T > 300 K at the end of lithiation process. A numerical analysis of the curves according to a Stoner-Wolfarth model[24] of non-interacting superparamagnetic nanoparticles allows us calculating the actual radius, while modeling the electrode as Fe magnetic nanoparticles diluted in a non-magnetic matrix.[25] Particle size obtained from ZFC/FC keeps increasing linearly upon cycling to more than 8 nm after 10 cycles (Figure 4B). Fe nanoparticles of this size are above the critical radius and their blocking temperature close to 300 K, the electrode material displays a ferromagnetic behavior.

In operando measurements reveals the complexity of the electrode, which relates to the interplay between the electrochemical reaction and the structural evolution. Contrary to the first proposed schema, the electrochemical reaction is a reversible alloying process based almost exclusively on Sb after first lithiation, following the electrochemical mechanism:

$$2\ Li_3Sb + Fe \leftrightarrow 2\ Sb + Fe + 6\ Li$$
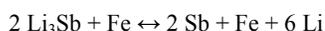
The electrochemical cycle is only based on Sb while Fe phase content remains constant. This mechanism is consistent with the plateau of magnetic moment observed after 8 cycles. Even though Fe does not directly participate in the electrochemical process, the presence of Fe nanoparticles improves the cycling performances of Fe/Sb compared to a Sb electrode with a coulombic efficiency above 97% after the first cycle (500 mAh/g capacity after 50 cycles on Fig. S3).

The main magnetic signature of the electrodes results from nanostructural change in the Fe and Li_xSb phases. The formation of nanoscale Fe is observed already in the first lithiation and can be considered as an almost complete reaction as demonstrated by the magnetic moment measured at 2 K (Figure S2A). Since the particles are very small (R_{mean} = 3 nm), the room temperature magnetic moment does not reach the saturation in the in-situ measurements. Magnetic particle size does not vary at constant potential (at least for 30 minutes) allowing for field dependent magnetic measurements. Upon cycling, the steady growth of Fe nanoparticles is observed in situ by the stepwise increase of magnetic moment. This phenomenon results mainly from the particle magnetic size increase and can be explained by the volume expansion during the alloying process of Sb with Li (Figure 4C).[26] The magnetic moment "waves" are dampened upon cycling when the average magnetic particle size reaches the critical value for superparamagnetic behavior. Further analysis of the detailed relationship between each variation of the magnetic moment and an electrochemical reaction will be carried on by the elaboration of a nanocomposite Fe/Sb material with specific ratio and particle size.

Conclusions

The in operando electron magnetic measurements on LIB allow us revisiting the electrochemical mechanism of the high energy density anodic material $FeSb_2$. The plateau reached by the magnetic moment during in situ monitoring implies the reversible lithiation on Sb only, while the stepwise increase of magnetic moment at room temperature is caused by the increase of Fe particle size on the first order. In operando electron magnetism brings macroscopic and quantitative data on the amorphous Fe nanostructures formed during cycling. The investigation of real time characterization techniques enables the collection of information at the nanoscale, required to elucidate electrochemical mechanism. Since most of the electrode materials are based on 3d transition metals with high electron magnetic moment, we believe in-situ electron magnetic measurements will bring valuable information on conversion or alloying mechanism to forecast more efficient electrodes.

Notes and references

[a] Department of Chemistry, Bar Ilan Institute of Nanotechnology and Advanced Materials (BINA), Ramat Gan 52900, ISRAEL.
[b] Department of Physics, Bar Ilan Institute of Nanotechnology and Advanced Materials (BINA), Ramat Gan 52900, ISRAEL.
[c] Institut Charles Gerhardt UMR CNRS 5253, ALISTORE European Research Institute (3104 CNRS) − AIME, Université Montpellier 2, CC1502, place E. Bataillon, 34095 Montpellier cedex 5, FRANCE.

† Electronic Supplementary Information (ESI) available: Experimental details, control experiments of in operando magnetic measurements and prolonged cycling. This material is available free of charge via the Internet at http://pubs.acs.org. See DOI: 10.1039/c000000x/

1. M. Armand and J.-M. Tarascon, *Nature*, 2008, **451**, 652–657.
2. V. Etacheri, R. Marom, R. Elazari, G. Salitra, and D. Aurbach, *Energy Envi. Sc.*, 2011, **4**, 3243.
3. J. B. Goodenough, *Acc. Chem. Res.*, 2013, **46**, 1053–1061.
4. S. F. Amalraj and D. Aurbach, *J. Sol. Stat. Electrochem.*, 2011, **15**, 877–890.
5. a) M. V Reddy, G. V Subba Rao, and B. V. R. Chowdari, *Chem. Rev.*, 2013, **113**, 5364–457; b) L. Ji, Z. Lin, M. Alcoutlabia, X. Zhang *Energy Environ. Sci.*, 2011, **4**, 2682-2699 c) J. Chen *Materials* 2013, **6**, 156-183.
6. M. Letellier, F. Chevallier, C. Clinard, E. Frackowiak, J.-N. Rouzaud, F. Béguin, M. Morcrette, and J.-M. Tarascon, *J. Chem. Phys.*, 2003, **118**, 6038–6045.
7. K. Dokko, M. Mohamedi, N. Anzue, T. Itoh, and I. Uchida, *J. Mater. Chem.*, 2002, **12**, 3688–3693.
8. L. Gireaud, S. Grugeon, S. Pilard, P. Guenot, J.-M. Tarascon, and S. Laruelle, *Anal. Chem.*, 2006, **78**, 3688–98.
9. R. Fong, C. H. W. Jones, and J. R. Dahn, *J. Power Sources*, 1989, **26**, 333–339.
10. A. S. Andersson, B. Kalska, L. Haggstrom, and J. O. Thomas, *Sol. State Ionics*, 2000, **130**, 41–52.
11. X. Liu, D. Wang, G. Liu, V. Srinivasan, Z. Liu, Z. Hussain, and W. Yang, *Nat. Comm.*, 2013, **4**, 2568.
12. J. Y. Huang, L. Zhong, C. M. Wang, J. P. Sullivan, W. Xu, L. Q. Zhang, S. X. Mao, N. S. Hudak, X. H. Liu, A. Subramanian, H. Fan, L. Qi, A. Kushima, and J. Li, *Science (80-.).*, 2010, **330**, 1515–1520.
13. C. P. Grey and N. Dupré, *Chem. Rev.*, 2004, **104**, 4493–512.
14. E. Blanc, M. Leskes, and C. P. Grey, *Acc. Chem. Res.*, 2013, **46**, 1952–1963.
15. S. Chandrashekar, N. M. Trease, H. J. Chang, L. Du, and C. P. Grey, *Nat. Mater.*, 2012, **11**, 311–316.

16. D. S. Middlemiss, A. J. Ilott, F. C. Strobridge, and C. P. Grey, *Chem. Mater.*, 2013, **25**, 1723–1734.

17. C. M. Julien, a. Ait-Salah, a. Mauger, and F. Gendron, *Ionics (Kiel).*, 2006, **12**, 21–32.

18. N. a. Chernova, G. M. Nolis, F. O. Omenya, H. Zhou, Z. Li, and M. S. Whittingham, *J. Mater. Chem.*, 2011, **21**, 9865–9875.

19. S. Boyanov, M. Womes, L. Monconduit, and D. Zitoun, *Chem. Mater.*, 2009, **21**, 3684–3692.

20. S. Boyanov, D. Zitoun, M. Ménétrier, J. C. Jumas, M. Womes, and L. Monconduit, *J. Phys. Chem. C*, 2009, **113**, 21441–21452.

21. J. Xie, X. B. Zhao, G. S. Cao, M. J. Zhao, Y. D. Zhong, and L. Z. Deng, *Mater. Lett.*, 2003, **57**, 4673–4677.

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

23. 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.

24. E. Stoner and E. Wohlfarth, *Phil. Trans. R. Soc. A*, 1948, **240**, 599–642.

25. M. Respaud, J. Broto, H. Rakoto, A. Fert, L. Thomas, B. Barbara, M. Verelst, E. Snoeck, P. Lecante, A. Mosset, J. Osuna, T. Ely, C. Amiens, and B. Chaudret, *Phys. Rev. B*, 1998, **57**, 2925–2935.

26. A. Darwiche, C. Marino, M. T. Sougrati, B. Fraisse, L. Stievano, and L. Monconduit, *J. Am. Chem. Soc.*, 2012, **134**, 20805–11.

Among all rechargeable electrochemical energy storage devices available today, lithium-ion batteries (LIBs) display the highest energy density. Nevertheless, a breakthrough is needed to extend the range of portable devices and transportation vehicles. As an alternative to the commercially available graphite, conversion anodic materials display promising characteristics such as high gravimetric and volumetric energy densities.

Conversion reactions, where an electrode material undergoes a phase change, present several unique characteristics which make them an interesting scientific topic and also a technological challenge. Each interface is highly reactive; the metastable phases formed during cycling of the battery relax to more stable states, thus questioning the use of ex-situ measurements on electrodes. In situ local probe measurements have been recently developed to understand the lithiation mechanism. In this communication, we report on the first in-situ measurements of electron magnetism on a battery during cycling. $FeSb_2$, a very interesting anodic material for LIB, display a high energy density and allows the investigation of its structural evolution during cycling through magnetic measurement.