# Ageing mechanisms of conversion-type electrode material studied on iron sulfide thin films

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## ARTICLE INFO

## ABSTRACT

The morphological and chemical modifications induced by repeated cycling of conversion-type negative electrode material were studied for iron sulfide thin films in 1 M-LiClO$_4$/PC by combining AFM, XPS and ToF-SIMS analysis with electrochemical control. The topographical changes were consistent with irreversible swelling of the material caused by repeated volume expansion/contraction. A 3% capacity fading measured after 9 conversion/deconversion cycles resulted mainly from the loss of electroactive material forming pinhole defects in the thin film electrode. Repeated cycling caused increasing accumulation of non deconverted material in the bulk thin film electrode. Repeated cycling also resulted in continuous surface up-take and increasing accumulation of the SEI layer in the bulk thin film electrode, rich in Li$_2$CO$_3$. Formation of a duplex-like structure with organic and inorganic compounds primarily distributed in the outer and inner parts, respectively, was suggested by ToF-SIMS depth profiling of the SEI layer.

## 1. Introduction

Conversion-type materials (M$_a$X$_b$, where M is a transition metal and X is an anion like O, S, F and P) used as negative electrodes in lithium ion-batteries (LIB) show a high theoretical capacity and a good reversibility of conversion/deconversion process attributed to the formation of pure metal nanoparticles embedded in the Li$_n$X matrix upon reduction of M$_a$X$_b$ with Li [1]. As a conversion-type material, iron sulfide (FeS) has a theoretical gravimetric capacity (609 mAh/g) and a potential of conversion/deconversion (1.3 V vs. Li/Li$^+$) higher than those of graphite (372 mAh/g and less than 0.25 V, respectively) [2–4]. The overall conversion/deconversion reaction of FeS is the following:

$$FeS + 2Li^+ + 2e^- \leftrightarrow Li_2S + Fe \qquad (1)$$

Conversion-type materials face problems of huge volume changes and voltage hysteresis upon cycling [5]. Kim *et al.* [6] have reported good capacity retention in all solid state Li-ion batteries at room temperature for a highly milled FeS anode. However FeS powder showed a huge capacity fading in 1 M LiPF$_6$-EC/DMC after 10 charge/discharge cycles at room temperature [2].

To our knowledge, most of the studies performed on FeS until now have addressed its electrochemical performance [2,5,7] with no surface or bulk analysis of the electrode modifications upon cycling. In a recent work, we have studied the mechanism of the conversion/deconversion process of an iron sulfide (troilite, FeS$_{1-x}$, x~0.07) thin film during the 1st discharge/charge cycle using surface and interface analytical techniques [3]. However, the aging performance induced by repeated discharging/charging, and related to volume expansion/contraction and voltage hysteresis, also needs to be understood by performing thorough analytical studies. Moreover, a solid electrolyte interface (SEI) layer is usually formed on the anode material in Li-ion batteries by reductive decomposition of the electrolyte. This SEI layer plays an important role in the electrochemical performance of anode materials. Based on the lithium electrode passivation, Peled [8,9] proposed a model of the SEI with a compact inner layer mainly composed of inorganic compounds and a porous outer layer mainly composed of organic components. This model has been confirmed for alloy-type and intercalation-type materials [10–12] but, according to our knowledge, no studies have been performed on cycled conversion-type materials.

This paper reports on the aging mechanism of thin-film FeS electrode induced by multiple cycling. Surface and bulk chemical and morphological modifications are thoroughly discussed. Cyclic Voltammetry (CV) has been applied to test the electrochemical performance of iron sulfide (FeS) thin films in a half cell with 1 M LiClO$_4$-PC. Surface and bulk analysis before and after cycling were

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performed by means of X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Atomic Force Microscopy (AFM). ToF-SIMS depth profiling was applied. It is well-adapted to analyze the in-depth variation of the chemical composition and the volume changes. Its application allows discussing the relationship between capacity fading and volume changes of the iron sulfide thin film electrode and modification of the SEI layer upon cycling.

## 2. Experimental

The iron sulfide thin film was composed of troilite $FeS_{1-x}$, prepared by thermal sulfidation of the polished pure iron foil (99.5% purity, $26 \times 17 \times 0.05$ mm size, Goodfellow) at $300\,°C$ for 3.5 minutes in 150 mbar $H_2S$. The details concerning sample preparation can be found in our previous paper [3]. The chemical formula of as prepared $FeS_{1-x}$ troilite (where x = 0.07) is hereafter expressed as FeS for simplicity. XPS depth profiling indicates that the thickness of the pristine FeS thin film was about 210 nm. After production the iron sulfide samples were transferred under vacuum (in the quartz tube) to an Ar filled glove box where all the electrochemical measurements were performed in a three-electrode glass cell with metallic Li foils (Aldrich) used as reference and counter electrodes. All the potentials given in this paper are referred to $Li/Li^+$ electrode. The electrolyte was 1 M lithium perchlorate in propylene carbonate (1 M-$LiClO_4$/PC Aldrich). An Autolab (AUT30) potentiostat/ galvanostat was used. Cyclic voltammetry (CV) was performed with a scan rate of 0.5 mV/s between 0.25 and 3 V, starting from the open circuit potential (OCP) in the negative potential direction. After cycling, the specimens were taken out from the test cell at a stable OCP (at delithiated state), washed immediately with non-aqueous acetonitrile, dried in Ar flow and transferred directly in anhydrous and anaerobic conditions from the glove box to the XPS analysis chamber under ultra-high vacuum (about $10^{-9}$ mbar) [13].

XPS analysis was performed with a VG ESCALAB 250 spectrometer of Thermo Electron Corporation. An Al Kα monochromatized radiation (hν = 1486.6 eV) was employed as X-ray source. Magnetic lens was not used during the analysis, owing to magnetism of samples. The spectrometer was calibrated against the reference binding energies (BE's) of clean Cu (932.6 eV), Ag (368.2 eV), and Au (84 eV) samples. The photoelectron take-off angle was 90° for all analyses. Survey spectra were recorded with a pass energy of 100 eV, and high resolution spectra of the C1s, O1s, Fe2p, S2p, Li1s core level regions and valence band (VB) region were collected with a pass energy of 20 eV. The data processing (peak fitting and decomposition) was performed with the Advantage software provided by Thermo Electron, using a Shirley type background and Gaussian/Lorentzian peak shapes with a fixed ratio of 70/30 [14]. The BE's of the C1s and O1s spectra were corrected with reference to the carbon peak for -$CH_2$-$CH_2$- bonds set at 285.0 eV.

Following XPS analysis, the samples were transferred to the ToF-SIMS analysis chamber using a vacuum vessel. ToF-SIMS negative ion depth profiling was carried out for the pristine and cycled samples. A pulsed 25 keV $Bi^+$ primary ion source was used over a $100\,\mu m \times 100\,\mu m$ area for analysis with the same sample current of $1\,\mu A$ for all samples. Depth profiling was performed by sputtering with a 1 keV $Cs^+$ ion gun giving a 70 nA target current over a $300\,\mu m \times 300\,\mu m$ area for all samples. Data acquisition and post-processing analyses were performed using the Ion-Spec software.

AFM topographic imaging was performed *ex situ* with the Agilent 5100 system in tapping mode at a resonant frequency of the cantilever of about 250 kHz. A silicon tip mounted on a cantilever with a force constant of 1.2–3.5 $Nm^{-1}$ (Applied Nanostructure, Inc.) was employed. All the AFM images were treated with Gwyddion 2.3



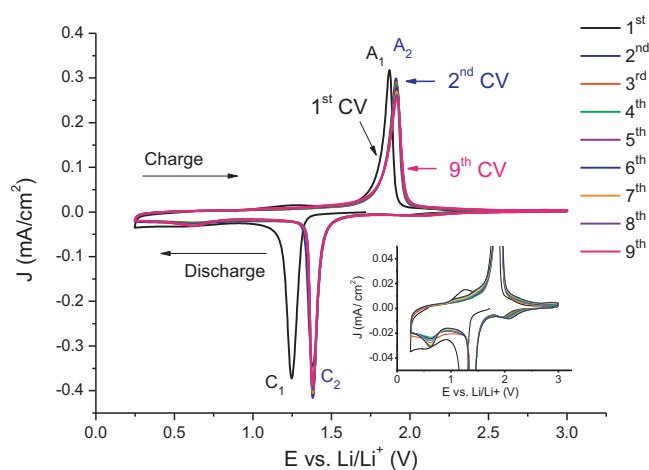**Fig. 1.** Cyclic voltammograms (1st to 9th) of iron sulfide thin film in 1 M $LiClO_4$-PC (scan rate = 0.5 mV/s). Current density variations are magnified in the inset.

software. The pitted surface fraction of FeS thin film after 9 CV was calculated with the Image-Pro plus 6.0 v software.

## 3. Results and discussion

### 3.1. Electrochemical properties of iron sulfide thin film

Fig. 1 presents the first nine discharge/charge cycles (CVs) performed on the FeS thin film electrode. The cathodic/anodic peaks are attributed to the conversion/deconversion reaction (equation 1). In the 1st CV the peaks $C_1/A_1$ are observed at 1.25/1.87 V, in agreement with our previous work [3]. In the 2nd CV a shift to more positive potentials, $C_2/A_2$ at 1.38 V/1.91 V is observed but no further shift is observed in the subsequent cycles (3rd to 9th CVs). Obviously, owing to surface and bulk modifications, the conversion potential shows more hysteresis between the 1st and 2nd CVs than in the following cycles, as observed previously [2,5]. The current densities of the cathodic and anodic peaks decrease slightly upon cycling indicating capacity fading. However, even after 9 CVs the charge density decrease calculated from the anodic peak is only 3% compared to the 1st cycle.

Upon discharge a broad cathodic wave is observed between 0.84 V and 0.25 V (inset of Fig. 1). It is mostly attributed to the reductive decomposition of electrolyte resulting in formation of a SEI layer. Since the current density in this potential region is larger in the 1st CV than in the following cycles, the SEI layer formation mostly occurs during this cycle. However it persists in the subsequent cycles as shown by a small cathodic peak at ∼ 0.62 V. A small anodic peak at ∼1.27 V in the 1st CV shifts to more positive potential at ∼1.45 V in the following cycles accompanying the shift of the major cathodic and anodic peaks (inset of Fig. 1). In our previous paper [3], we attributed this small peak to the formation of intermediate compounds. However, it is difficult to identify the exact chemical components, which can be formed at this potential. The previous XPS analysis has shown non-significant quantity of disulfide components [3]. The presence of disulfide in a form of $Li_2S_2$ compound was observed previously by Zhang [15].

Owing to the formation of the SEI layer during the first discharge process, the coulombic efficiency measured by the charge ratio of the A to C peaks is only 87% for the 1st CV. In the following cycles (CVs), it remains stable to around 106%. This overvalued coulombic efficiency is due to a calculation of the charge limited solely to the C and A peaks, whereas further conversion reaction also occurs