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## *In situ* Raman spectroscopy of carbon-coated ZnFe<sub>2</sub>O<sub>4</sub> anode material in Li-ion batteries – Investigation of SEI growth†

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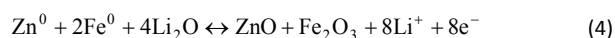
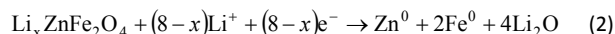
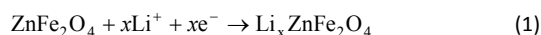
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The (de)lithiation process of carbon-coated ZnFe<sub>2</sub>O<sub>4</sub> has been investigated by *in situ* Raman spectroscopy. Solid electrolyte interphase (SEI) products were detected. Their detection may result from a temporary surface enhancement Raman effect from Zn nanoparticles formed in the conversion reaction at a potential that coincides with SEI formation.

Lithium-ion batteries (LIBs) are electrochemical energy storage devices with a high energy density, as well as lightweight and flexible in design. In addition to be used in the widely within the electronic devices industry, power tools, and progressively automotive applications, they are being investigated as a large scale stationary storage technology.<sup>1,2</sup> However, it is necessary that even greater improvements in terms of power, safety, lifetime, and cost of the LIB are achieved for stationary energy storage applications.<sup>1</sup> The chemical stability and the lithium-ion conductivity are influenced by the passivation layers formed on the electrode surface of LIBs. In particular, the solid electrolyte interphase (SEI) is a multicomponent electron insulator film formed on the anode surface once in contact with the organic-based electrolyte, which has a great influence upon irreversible charge loss, power capability, cycle of life and safety.<sup>3</sup> It consists of a patchwork of insoluble inorganic species and organic layers formed by non-aqueous electrolyte reduction products that prevents further electrolyte decomposition, but crucially still permits Li<sup>+</sup> transport.<sup>3,4</sup> Therefore, it is essential to understand the processes that occur at the electrode/electrolyte interfaces to improve the efficiency of LIBs.

ZnFe<sub>2</sub>O<sub>4</sub> (ZFO) is a non-toxic and cheap anode material for LIBs with a high specific theoretical capacity *ca.* 1000 mAh g<sup>-1</sup>,<sup>5,6</sup> as a result of an alloying conversion reaction.<sup>7</sup>



Large volume changes during the (de)lithiation process, as well as nanoparticle aggregation and poor intrinsic electronic conductivity lead to capacity fading and poor rate capability.<sup>6</sup> These issues are overcome by encapsulating ZFO nanoparticles within a carbon matrix. A non-toxic, simple and environmentally friendly carbon coating of ZFO nanoparticles (ZFO-C) has been described by Bresser *et al.*<sup>5</sup> In the present work the ZFO-C composite during the first discharge-charge cycle is investigated by *in situ* Raman microscopy.

Spinel ZnFe<sub>2</sub>O<sub>4</sub> material has five first order active Raman modes ( $A_{1g} + E_g + 3F_{2g}$ ).<sup>8</sup> The spectrum of the powder presents peaks at 340, 467, 647, 1098 and 1280 cm<sup>-1</sup> (Fig. 1 (i)). The peaks at 340 and 467 cm<sup>-1</sup> are assigned to 2  $F_{2g}$  modes and 647 cm<sup>-1</sup> to  $A_{1g}$  symmetry. The other two modes at 221 cm<sup>-1</sup> ( $F_{2g}$ ) and 246 cm<sup>-1</sup> ( $E_g$ ), are not observed clearly above the signal to noise ratio within the spectrum. The peaks observed at 1098 and 1280 cm<sup>-1</sup> are suspected to be overtone bands.

ZnFe<sub>2</sub>O<sub>4</sub> peaks are absent in the spectrum for the sample after the carbon coating step with sucrose precursor (Fig. 1 (ii)), in agreement with a previous report.<sup>9</sup> Only two bands are observed at 1347 and 1586 cm<sup>-1</sup> that are assigned to the characteristic carbon D and G bands, respectively.<sup>10,11</sup> The D band ( $A_{1g}$  mode) results from a break in the symmetry at the edges or defects in graphene sheets.<sup>10-12</sup> The G band assigned to  $E_{2g2}$  mode is related to the C-C stretching mode within the hexagonal lattice.<sup>10</sup>

The intensity ratio of the D and G peaks is sensitive to the type and order of carbon material.<sup>11</sup> In the present study, it is possible to distinguish the signal that corresponds to the carbon coating and that of the carbon additive (Fig. 1 (iii)); the D/G peak intensity ratio for ZFO-C and carbon black are 0.32 and 0.86, respectively. Thereby, clear differentiation between the two different types of carbon from Raman analysis of the composite electrode allowed precise

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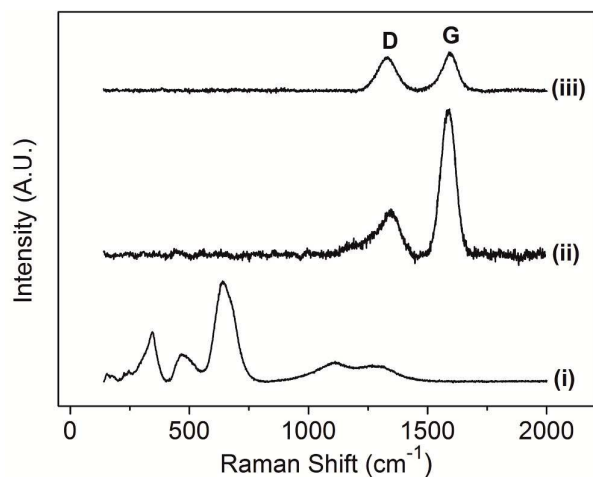
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† Electronic Supplementary Information (ESI) available: Experimental details and further *in situ* Raman investigation of ZnFe<sub>2</sub>O<sub>4</sub>-C, uncoated ZnFe<sub>2</sub>O<sub>4</sub> and ZnO-C., Raman spectrum of 1 M LiPF<sub>6</sub> in EC/DMC electrolyte and TEM image of ZnFe<sub>2</sub>O<sub>4</sub>-C. See DOI: 10.1039/x0xx00000x

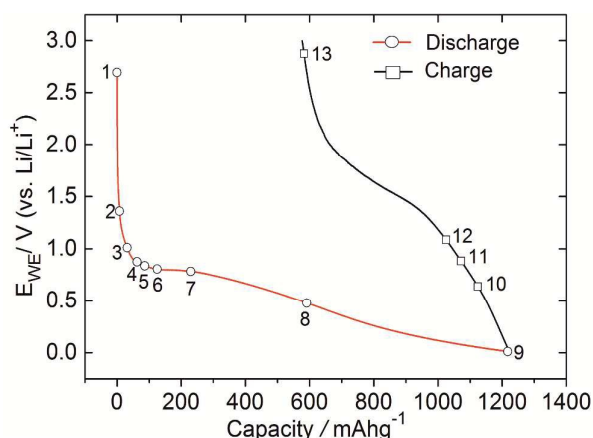


**Fig. 1.** Raman spectra of (i) Uncoated ZFO; (ii) ZFO-C and (iii) Carbon black (Super C65) powders.

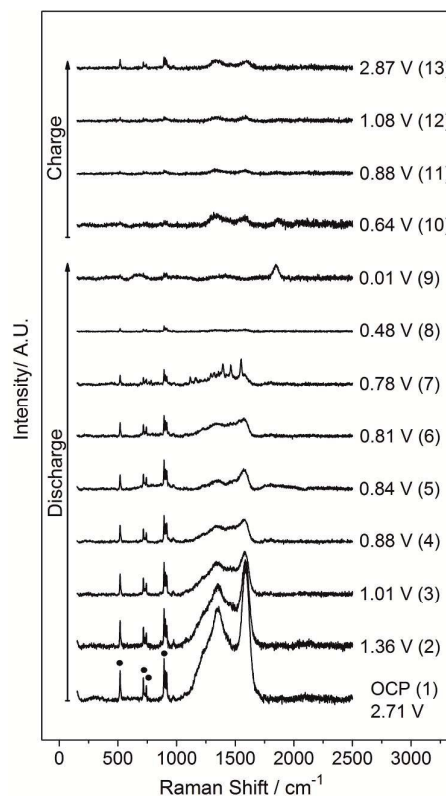
monitoring of ZFO-C only rather than the carbon black conductive additive.

*In situ* Raman spectroscopy of ZFO-C film electrodes was performed in a three-electrode Raman cell containing 1 M LiPF<sub>6</sub> in 1:1 w/w EC/DMC electrolyte. Electrode and cell preparations are described in the electronic supplementary information (ESI<sup>†</sup>).

The potential profile of ZFO-C electrode during the first discharge-charge cycle is shown in Fig. 2. The maximum capacity at the end of the discharge process is 1221 mAh g<sup>-1</sup> in agreement with previous studies and with the reactions described in Eq. 1-3.<sup>5, 13</sup> This value is similar to the capacity obtained for the uncoated ZFO film electrode (Fig. S1 in ESI<sup>†</sup>). The Raman spectrum collected at the open-circuit potential (OCP), shown in Fig. 3, presents peaks associated with the electrolyte at 518, 717, 742, 893, 904 and 910 cm<sup>-1</sup> (Fig. S2 in ESI<sup>†</sup>),<sup>14, 15</sup> in addition to D (1347 cm<sup>-1</sup>) and G (1590 cm<sup>-1</sup>) peaks. The lithiation also occurs into the carbon coating, evidenced by the weakened D and G peaks, as the discharge reaction proceeds. These bands disappear into the background at



**Fig. 2.** Potential profile of ZFO-C electrode for the first discharge-charge cycle in 1 M LiPF<sub>6</sub> in 1:1 w/w EC/DMC electrolyte. *In situ* Raman spectra have been collected in the marked points at different stages of the discharge and charge process.



**Fig. 3.** *In situ* Raman spectra of ZFO-C electrode collected at different stages of the discharge and charge cycle in 1 M LiPF<sub>6</sub> in 1:1 w/w EC/DMC electrolyte. Labels: ● electrolyte peaks.

potentials lower than 0.2 V, and rising again during the charging of the cell at potentials above 0.64 V (spectrum 10) in agreement with previous graphite reports.<sup>12</sup> Raman data also highlights that the carbon shell remains mechanically intact after the first discharge-charge cycle, as ZFO band at 647 cm<sup>-1</sup> is not observed after completion of the first de-lithiation step. A decrease in the peak intensity of the D and G bands is observed, when compared to the spectrum at OCP, suggesting that the de-lithiation step was not completely reversible and part of the lithium may still be trapped within the carbon shell. The D/G intensity ratio has increased from 0.32 to 1.12, thus the (de)lithiation steps result in an increase in the disorder of the carbon coating.

The conversion reaction described in Eq. 2 occurs during the discharge plateau at around 0.80 V (see Fig. 2).<sup>7</sup> This process leads to the destruction of the ZFO structure with the formation of metallic zinc and iron particles in a Li<sub>2</sub>O matrix. The zinc is then alloyed with lithium at more negative potentials (Eq. 3).<sup>7, 16</sup> Additional sharp peaks arise at 1118, 1163, 1292, 1319, 1357, 1395, 1463 and 1551 cm<sup>-1</sup> in the Raman spectra collected between 0.80 V and 0.69 V. These bands are related to reduction products of the carbonate solvents that formed the SEI on the carbon coating as explained later in more detail. These peaks associated with SEI products are absent in the spectra collected during *in situ* measurements of uncoated ZFO electrode as shown in Fig. S1 (in ESI<sup>†</sup>). The explanation for this may be the different electrode/electrolyte interface, since the nanoparticles are not

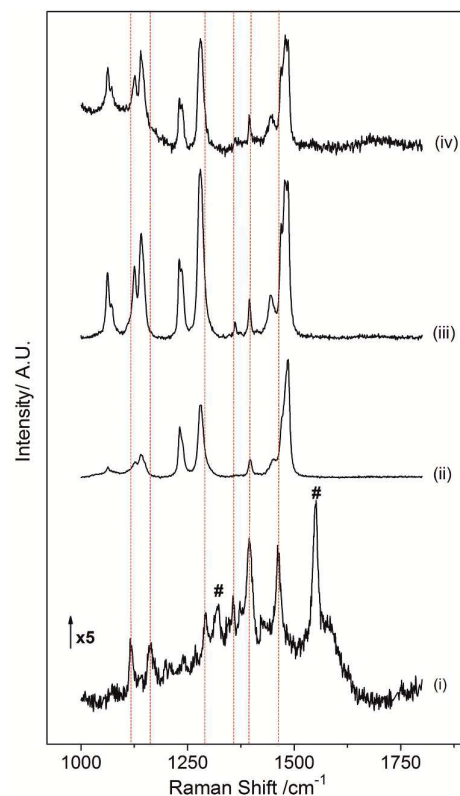
encapsulated in a carbon matrix. Only a band at approximately  $1850\text{ cm}^{-1}$  is observed at potentials lower than 0.69 V. A peak associated with  $\text{Li}_2\text{C}_2$  has been previously reported at this wavenumber position.<sup>17,18</sup> This peak is observed up to 0.64 V in the charge process, potential at which the D and G bands re-appear in the spectra.

The SEI is formed of organic and inorganic electrolyte decomposition products.<sup>4</sup> Some of the organic compounds detected on carbon materials are lithium alkyl carbonate species ( $\text{ROCO}_2\text{Li}$ ) and polymeric species (e.g. polyethylene oxide).<sup>4,19</sup>

Polyethylene glycol/oxide powders with different molecular weights (PEG-1000, PEO-100k and PEO-1M) have been studied by Raman spectroscopy to investigate the origin of the peaks observed during the discharge of ZFO-C electrode between 0.80-0.69 V (Fig. 4). The peak analysis for PEO materials and ZFO-C electrode at 0.78 V are presented in Table 1. There is a spectrum dependence on the chain length within  $800\text{--}1000\text{ cm}^{-1}$  region that corresponds to  $\text{CH}_2$  rocking and wagging coupled with C-O, C-C and C-O-C stretching vibrations.<sup>20</sup> The intensity of the peak at  $840\text{ cm}^{-1}$  increases relative to the intensity of the band at  $860\text{ cm}^{-1}$  as the average molecular weight increases. These peaks are related to  $\text{CH}_2$  rocking and combined CO stretching/ $\text{CH}_2$  rocking, respectively.<sup>20</sup> There is a broadening in the spectrum background for PEO-1M in the region from  $700$  to  $1000\text{ cm}^{-1}$ .

The spectrum collected at 0.78 V during the discharge cycle presents peaks at  $1118$ ,  $1163$ ,  $1292$ ,  $1357$ ,  $1395$  and  $1463\text{ cm}^{-1}$  that can be related to PEG-PEO peaks at  $1125$ ,  $1142$ ,  $1281$ ,  $1361$ ,  $1395$  and  $1445\text{ cm}^{-1}$ . The peak shifts in the *in situ* spectra with respect to PEG-PEO powders could be explained by the complexation with lithium cations in the electrolyte salt during cycling. The peak observed at  $1357\text{ cm}^{-1}$  related to  $1361\text{ cm}^{-1}$  PEO band is only present in the spectrum for PEO-100k, indicating that the polyethylene species formed on the electrode surface may have an average molecular weight in the order of 100k.

One of the main peaks for polyethylene oxide materials appear at  $1480\text{ cm}^{-1}$  with a shoulder at  $1469\text{ cm}^{-1}$  assigned to  $\text{CH}_2$  scissor mode.<sup>20</sup> In the discharge curve only the shoulder is observed at  $1461\text{ cm}^{-1}$ . Two peaks at  $1319$  and  $1551\text{ cm}^{-1}$  are not present in PEO materials (Fig. 4 #). However, symmetric C=O stretch in  $(\text{CH}_2\text{OCO}_2\text{Li})_2$  and asymmetric C=O mode for  $\text{RCOOLi}$  compounds have been reported in SEI studies using FTIR.<sup>4</sup> Therefore, we tentatively assign these peaks to lithium alkyl carbonate species,



**Fig. 4.** Raman spectra of (i) ZFO-C electrode discharged at 0.78V and polyethylene oxide materials (ii) PEG (av. Mw= 1,000), (iii) PEO (av. Mw= 100,000) and (iv) PEO (av. Mw=1,000,000).

that have been widely observed in past SEI studies.<sup>4</sup> These peaks have also been observed in the spectra collected on a ZFO-C particle when the potential was held at different potentials (chronoamperometric methods) as shown in Fig. S3-4 (in ESI†).

The conversion reaction in Eq. 2 leads to the formation of zinc and iron nanoparticles. This reaction occurs approximately at 0.8 V.<sup>7,16</sup> The presence of Zn nanoparticles may enhance the Raman signal, explaining the observation of the peaks for SEI components between 0.80 and 0.69 V. The effect of Zn nanoparticles in the surface-enhancement Raman scattering (SERS) has been described by Yang *et al.* in  $\text{TiO}_2$  nanoparticles doped with Zn.<sup>22</sup> The disappearance of the peaks at potentials below 0.69 V could be

**Table 1.** Raman peak position ( $\text{cm}^{-1}$ ) and full-width at half maximum (FWHM,  $\text{cm}^{-1}$ ) of polyethylene oxide compounds and for ZFO-C electrode at  $E = 0.78\text{ V}$  during the discharge step.

PEG-1,000		PEO-100,000		PEO-1,000,000		ZFO-C electrode (discharge E= 0.78V)	
Peak	FWHM	Peak	FWHM	Peak	FWHM	Peak	FWHM
1125 <sup>a</sup>	21	1125 <sup>a</sup>	10	1125 <sup>a</sup>	13	1118	7
-	-	1142 <sup>b</sup>	13	1142 <sup>b</sup>	14	1163	10
1281 <sup>c</sup>	14	1280 <sup>c</sup>	13	1281 <sup>c</sup>	11	1292	9
-	-	1361	6	-	-	1357	12
1397	9	1395	5	1395	6	1395	14
1476 <sup>d</sup>	19	1445 <sup>d</sup>	11	1445 <sup>d</sup>	16	1463	13

a) Coupled C-C stretching/ $\text{CH}_2$  wagging<sup>20</sup>; b) Coupled C-C/C-O-C stretching<sup>20</sup>; c) Twisting ( $\text{CH}_2$ ) asymmetric<sup>21</sup> and d) Bending ( $\text{CH}_2$ ) asymmetric.<sup>21</sup>

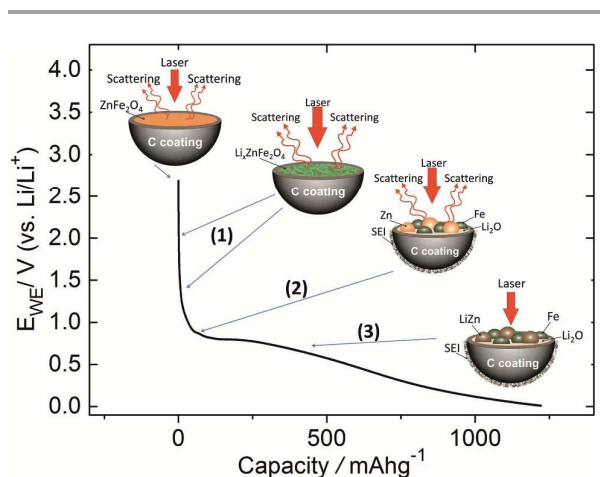
explained by the formation of LiZn alloys in accordance with Eq. 3 and/or increase of the SEI thickness. This is schematically shown in Scheme 1. Di Cicco *et al.*, has estimated the SEI thickness for ZFO-C material by soft X-ray spectroscopy (XAS).<sup>13</sup> In accordance with the thickness calculations as a function of the capacity, the SEI would be approximately 34 nm thick at 0.69 V and this thickness could inhibit the SERS effect.

Although the active material is encapsulated inside of a 2 nm-carbon shell (Fig. S5 in ESI<sup>†</sup>), the Raman enhancement by Zn nanoparticles is still observed. This phenomenon could be considered analogous to shell-isolated nanoparticles enhanced Raman spectroscopy (SHINERS). In this technique the amplification of the signal is produced by gold nanoparticle with an ultrathin silica shell deposited on the substrate.<sup>23</sup> Furthermore, similar Raman enhancement showing PEO-type films have been observed on carbon-coated ZnO electrodes (Fig. S6 in ESI<sup>†</sup>).

In conclusion, carbon-coated ZFO has been investigated by *in situ* Raman spectroscopy during the first discharge-charge. Raman spectrum of ZFO-C nanoparticles only presents the D and G bands related to the homogeneous carbon coating. *In situ* Raman spectra show that not only the lithiation occurs in ZFO nanoparticles, but also in the carbon coating. As a consequence of this, the D and G bands disappear at potentials lower than 0.2 V and they re-appear during the charging step at potentials higher than 0.64 V.

The carbon coating remains mechanically intact after the first cycle, however, the D and G peak intensity is lower indicating that the de-lithiation is not fully reversible and lithium ions remain trapped in the carbon matrix. The D/G intensity ratio is also larger, suggesting an increase in the disorder of the coating after the first (de)lithiation process.

SEI components on the carbon coating were assigned from the Raman data as polyethylene oxide type and organic alkyl carbonate species. The observation of these compounds may be due to the SERS effect from the Zn nanoparticles formed from the conversion reaction during the lithiation process.



**Scheme 1.** Representation of the scattering phenomenon of ZFO-C during conversion-alloying reaction in the lithiation process at different potentials.

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