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of Magnetite, Fe₃O₄: Impact on Electrochemistry**

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

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Magnetite is a conversion anode material displaying multi-electron transfer during lithiation and delithiation. The solid electrolyte interphase (SEI) on magnetite, Fe_3O_4 , electrodes for lithium ion batteries was deliberately modified through the use of fluoroethylene carbonate (FEC) electrolyte additive, improving both capacity retention and rate capability. Analysis showed reduction of FEC at higher voltage compared to non-fluorinated solvents with formation of a modified lithium fluoride containing electrode surface.

Magnetite iron oxide, Fe_3O_4 , is a promising conversion-type anode material for next generation lithium systems due to its low cost, natural abundance, and high theoretical capacity (924 mAh/g) due to multiple electron transfer. Practical use of the material has been complicated by phase transformations occurring during cycling and formation of a resistive solid electrolyte interphase (SEI).¹ Anode material alternatives to graphite have benefited from the use of electrolyte additives or co-solvents.² Specifically, fluoroethylene carbonate (FEC) used with Si ,^{3, 4, 5, 6} Sn ,^{7, 8} Co_3O_4 ,⁹ and NiO ¹⁰ provided enhanced cycling stability relative to electrolytes utilizing non-fluorinated carbonate solvents. One previous report utilized FEC as an electrolyte component with Fe_3O_4 at a ratio of 33% and also showed improved capacity retention after 30 cycles, though no mechanistic details were provided.¹¹

The current study probes the role of FEC concentration on the electrochemistry of nano-sized Fe_3O_4 composite electrodes through the use of voltammetry as well as galvanostatic cycling. For the first time, isothermal microcalorimetry measurements are used to probe and understand the decomposition reaction of FEC as a function of potential at the Fe_3O_4 surface. Additionally, this work reports the first direct evidence of a modified SEI composition on Fe_3O_4 electrodes cycled in the presence of FEC, thus providing mechanistic

insight into the improved electrochemical behavior.

The electrochemistry of $\text{Li}/\text{Fe}_3\text{O}_4$ composite electrodes using cyclic voltammetry (CV), galvanostatic cycling, and rate capability testing is shown in Figure 1a-e. Four solvent compositions were tested with 1 M lithium hexafluorophosphate (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. Figure 1a shows the CV curves for the first cycle. All electrolyte compositions demonstrate three well-defined cathodic peaks. The first peak at $\sim 1.6\text{V}$ is ascribed to initial insertion of Li^+ cations into the interstitial octahedral sites of the ccp Fe_3O_4 structure (Fe^{3+} to Fe^{2+}), the second peak at $\sim 1.0\text{V}$ corresponds to additional Li^+ insertion and phase change from spinel Fe_3O_4 to rock-salt FeO , and the third peak at 0.60V is attributed to both the conversion reaction (Fe^{2+} to Fe^0) as well as the formation of solid electrolyte interphase due to electrolyte decomposition at the electrode surface.^{12, 13} During the anodic process, two overlapping peaks centered at $\sim 1.6\text{V}$ and $\sim 1.8\text{V}$ are attributed to oxidation of Fe^0 to Fe^{2+} .¹⁴ It is notable that in cycle 1 the three electrolytes containing FEC display a new cathodic peak at 1.2V . This additional cathodic current is attributed to the reduction of FEC, which has previously been shown to reduce at higher potentials relative to the non-fluorinated carbonates on nano-Si electrodes.⁶ No differences in the anodic curves are observed for cells with or without FEC, indicating that the reduction of FEC on the electrolyte surface appears irreversible. The second CV cycle (Fig. 1b) shows minimal difference among the four electrolyte compositions in the $2.0 - 1.1\text{V}$ range, and the additional peak at 1.2V is no longer observed, suggesting that most significant FEC reduction at the electrode surface occurs during cycle 1.

Galvanostatic cycling results are presented in Fig 1c. The high discharge capacity ($> 1400\text{ mAh/g Fe}_3\text{O}_4$) in cycle 1 is attributed to lithiation of Fe_3O_4 , the carbon in the composite electrode and electrolyte decomposition.^{12, 14} Voltage profiles for cycle 1 (Fig. 1d) indicate that discharge capacity between $2.0 - 1.1\text{V}$ depends on the electrolyte composition, specifically

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the FEC concentration, with electrodes cycled with 0 M, 0.4 M, 1.33 M, and 2.66 M FEC showing capacities of 71, 127, 152, and 153 mAh/g in this voltage range. These results show that FEC reduction occurs at potentials > 1 V, in good agreement with the CV results. Assuming a 4 electron reductive decomposition mechanism per molecule of FEC as recently proposed⁵ and that additional capacity in this voltage range is attributed to solely to reduction of FEC, these capacities correspond to reduction of $3.58\text{E-}4$, $5.18\text{E-}4$, and $5.24\text{E-}4$ moles FEC per total electrode mass (including Fe_3O_4 , carbon black, and PVDF.) Notably, concentrations of FEC in the electrolyte of 1.33 M and 2.66 M deliver the same capacity in the voltage range, indicating the amount of FEC reduced during the first discharge did not further increase with increasing concentration. If the same amount of FEC reduction in cycle 1 occurred in each subsequent cycle, all the FEC in a cell would be consumed in 53, 125, and 247 cycles for 0.4 M, 1.33 M, and 2.66 M FEC electrolytes, respectively. However, analysis of voltage profiles of cycles 2 and beyond indicates similar capacities in the 2 – 1.1 V range for the tested electrolytes, in good agreement with the CV results. Thus, full consumption of FEC is expected to occur at cycle numbers which are significantly higher than the estimates based on cycle 1. FEC reduction in the first cycle for the composite electrode was probed. Electrodes were prepared with Fe_3O_4 /PVDF (no carbon black) and carbon black/PVDF (no Fe_3O_4 present) and were discharged in either 0 M FEC or 1.33 M FEC electrolyte. A low rate (50 mA/g) was utilized to enable Fe_3O_4 to be discharged without conductive additive present. Results are presented in Figures S2 and S3. The difference in delivered capacity in the FEC reduction voltage range of 2 V – 1.1 V for electrodes cycled with and without FEC was 15 mAh/g and 350 mAh/g for Fe_3O_4 /PVDF and carbon black/PVDF,

respectively. When normalized vs. surface area of Fe_3O_4 and carbon black (as measured by the BET technique), the delivered capacities between 2 V – 1.1 V are 0.49 mAh/m^2 ($4.6\text{E-}6$ moles FEC/ m^2) and 0.44 mAh/m^2 ($4.0\text{E-}6$ moles FEC/ m^2) for Fe_3O_4 /PVDF and carbon black/PVDF, respectively. Thus, the data indicate that FEC reduces on both Fe_3O_4 and carbon black active surfaces of the composite electrodes to a similar degree where the significant difference in FEC reduction is attributed to the higher surface area of the carbon black compared to Fe_3O_4 . Thus, during cycle 1, FEC is reduced on all the active surfaces of the electrode. The much lower amount of FEC reduction observed after cycle 1 implies a stabilized surface film. With additional cycling, FEC reduction may occur primarily on the Fe_3O_4 particles, which undergo significant volume changes during conversion reactions in each cycle, while SEI formation on carbon black may remain relatively stable after its initial formation. In support of this hypothesis, previous studies have indicated that continuous SEI formation occurs on materials undergoing volume change during reaction including $\text{Si}^{5,15}$ and $\text{Sn}^{7,16}$ as well as FeF_2 .¹⁷ In contrast, the SEI formed using carbonate based electrolytes is relatively stable on carbonaceous anodes,^{18,19} with electrolyte decomposition occurring principally during the first cycle.¹⁹

The concentration of FEC in the electrolyte significantly impacts capacity retention for extended cycling. The electrode cycled with no FEC in the electrolyte delivered $\sim 230 \text{ mAh/g}$ at 100 cycles, corresponding to $\sim 23\%$ capacity retention between cycles 2 – 100. Addition of 0.4 M FEC to the electrolyte results in only a modest improvement to $\sim 350 \text{ mAh/g}$ after 100 cycles. However, cells cycled with 1.33 M FEC exhibited dramatically improved capacity retention, with 100th cycle capacity of $\sim 650 \text{ mAh/g}$ (63% capacity retention), a 280% improvement in capacity over no FEC in the electrolyte. Increasing the FEC

Figure 1: (a,b) CV curves of Fe_3O_4 electrodes with varying amounts of FEC obtained in the voltage range of 0.1 to 3.0 V (vs Li^+/Li) and scan rate of 0.1 mV/s for (a) cycle 1 and (b) cycle 2. The inset in (a) and (b) shows the magnified region 1.0 – 2.5 V during the cathodic scan for cycles 1 and 2. (c) Charge/discharge capacities of the electrodes for 100 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. (d) Voltage profiles for the first cycle for electrodes cycled at C/2. (e) Discharge capacities of the electrodes at various rates for 30 cycles.

content from 1.33 M to 2.66 M did not result in further appreciable improvement of capacity retention at 100 cycles. This is similar to the results observed for excess capacity in the first cycle where 1.33 M and 2.66 M FEC containing cells delivered similar capacity in the 2.0 – 1.1 V range. The improvement in reversible capacity was further investigated by cycling carbon black / PVDF electrodes (no Fe_3O_4) under the same conditions using 0 M and 1.33 M FEC electrolytes. (Figure S1). The carbon black electrodes showed no capacity dependence on FEC concentration after cycle 1, indicating that the improved capacity retention with FEC addition is primarily due to enhanced reversibility of the Fe_3O_4 active material. The improved capacity retention was reflected in the rate capability results (Fig. 1f) where the sample with addition of 1.33 M FEC delivered ~ 800 mAh/g at a 2C rate.

Isothermal microcalorimetry (ICM) measurements were performed on $\text{Li}/\text{Fe}_3\text{O}_4$ cells during lithiation for the first 5 cycles to provide insight into electrolyte decomposition and associated SEI formation in the presence of FEC. Fig. 2. shows the discharge profiles, Fig. 2a, heat flow, Fig. 2b, and total heat evolved, Fig. 2c, from the cells with 0 M FEC and 1.33 M FEC as a function of capacity during cycle 1 lithiation, while the data for cycles 2 and 5 are presented in the supplemental information in Figures S4 and S5. In cycle 1, the differences in heat flow are attributed to differences in electrolyte reactivity as the cells were otherwise the same. For the cell discharged with the standard electrolyte, heat flow peaks at 40 mAh/g (1.5 V), 100 mAh/g (1.0 V), and 300 mAh/g (0.8 V) are attributed to heat evolved during initial lithium intercalation¹³, initiation of phase change to a rock salt structure¹³, and onset of SEI formation from electrolyte decomposition on the electrode surface²⁰, respectively. Evident differences are observed in the cell utilizing 1.33 M FEC, with a significant increase in heat generation within the ca. 2.0 – 1.0 V voltage range, in good agreement with the CV results. The striking difference in the heat signature for the cell having FEC additive provides strong evidence that FEC reduction on the electrode surface occurs at a higher voltage relative to EC/DMC, resulting in a modified SEI composition. During the 2nd – 5th lithiation, similar heat flow and total heat evolved as a function of capacity for cells with and without FEC are observed. Thus, the data support the assertion that FEC is primarily reduced during the first cycle.

Electrodes cycled 100x in cells with 0 and 1.33 M FEC were recovered and analyzed by XRD (Fig. 3). The electrode cycled in standard electrolyte showed peaks 33.6 2-theta and 56.6 2-theta, corresponding to Li_2O , and a peak at 44.7 2-theta, corresponding to Fe^0 metal. Phase fractions identified by Rietveld analysis were 0.53 and 0.47 for Li_2O and Fe^0 respectively. The electrode was analyzed in the charged state where the data indicate that after 100 cycles a significant amount of iron metal formed during the reduction process does not re-oxidize to iron oxide. This outcome is consistent with the poor capacity retention of the electrode (ca. 300 mAh/g after 100 cycles). The electrode cycled in 1.33 M FEC electrolyte showed additional peaks at 38.7 2-theta, 44.9 2-theta and 65.4 2-theta, corresponding to a LiF phase with a

Figure 2. (a) Voltage profiles of $\text{Li}/\text{Fe}_3\text{O}_4$ coin cells with either 0 M or 1.33 M FEC in the electrolyte during 1st 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.

cubic crystal structure ($Fm\bar{3}m$). The phase fractions of Fe^0 , Li_2O , and LiF by Rietveld analysis are 0.12, 0.66, and 0.22, respectively, with LiF having a crystallite size of ~ 9 nm. The phase fraction of Fe^0 is appreciably lower compared to the electrode cycled in 0 M FEC, at 0.16 vs. 0.53, indicating significantly more Fe^0 atoms are re-oxidized in the 100x charged state, which is supported by the comparably higher electrochemical reversibility of the electrode. The significant fraction of Li_2O observed by diffraction suggests that the iron centers have oxidized to a FeO -like state,^{12, 13} since oxidation of Fe^0 to FeO rather than Fe_3O_4 would result in 1 mole of additional Li_2O for every initial mole of Fe_3O_4 (Equations 1, 2). This argument is further supported by the reversible capacity of the electrode after 100 cycles (~ 650 mAh/g), which is reasonable given the theoretical reversible capacity between

Figure 3. (a) XRD patterns of Fe_3O_4 electrodes cycled with either (a) 0 M or (b) 1.33 M FEC in the electrolyte. (c) Peak positions of refined phases.

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FeO and Fe metal.

The most noteworthy distinction between electrodes cycled with and without FEC is the presence of LiF on the surface of the electrode. This finding provides direct chemical evidence of a modified solid electrolyte interphase (SEI) on the electrode surface through use of the FEC additive. The finding here is consistent with LiF previously observed on the surface of Si anodes cycled in FEC found to be associated with improved cycling stability, yet is not dependent on affiliation of Si and F.^{3, 21} Furthermore, the findings here affirm that interfacial control of the Fe₃O₄ electrode is critical for improving its electrochemical stability, as has been reported for composite electrodes based on Fe₃O₄ and other oxides.²²

In summary, fluoroethylene carbonate (FEC) was evaluated as an electrolyte component for improving the electrochemical reversibility of nanocrystalline Fe₃O₄ composite electrodes. Electrodes cycled with 1.33 M FEC in the electrolyte exhibited a significant enhancement in capacity retention with a 280% increase in capacity relative to non FEC containing electrolyte after 100 cycles. CV and galvanostatic discharge indicated that FEC reduction occurs at voltages between 2.0 and 1.0 V, above that of other carbonate solvents in the electrolyte. Isothermal microcalorimetric results provided direct thermal evidence of FEC decomposition on the electrode surface in this voltage range, and that reduction of FEC causes significantly higher levels of heat generation relative to cells with no FEC present in the first reduction. The formation of crystalline LiF was affirmed by XRD on electrodes cycled with FEC containing electrolyte. Thus, the improved electrochemical results are attributed to a solid electrolyte interphase layer that forms at higher voltages, prior to the reduction of the non-fluorinated carbonate solvents, and has a modified composition compared to SEI formed in conventional electrolyte. Parallels drawn between Fe₃O₄ and Si electrodes, which both undergo dramatic volume changes during (de)lithiation²³ (ca. 90% for Fe₃O₄, ca. 300% for Si), suggest that the modified film formed in the presence of FEC is able to better accommodate the large volume changes during cycling than the native SEI formed in non-fluorinated carbonate solvents.

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Conflict of interest

There are no conflicts to declare.

Notes and references

- S. H. Lee, S.-H. Yu, J. E. Lee, A. Jin, D. J. Lee, N. Lee, H. Jo, K. Shin, T.-Y. Ahn, Y.-W. Kim, H. Choe, Y.-E. Sung and T. Hyeon, *Nano Lett.*, 2013, **13**, 4249-4256; W. M. Zhang, X. L. Wu, J. S. Hu, Y. G. Guo and L. J. Wan, *Adv. Funct. Mater.*, 2008, **18**, 3941-3946; S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R. P. Zaccaria and C. Capiglia, *J. Power Sources*, 2014, **257**, 421-443.
- A. M. Haregewoin, A. S. Wotango and B. J. Hwang, *Energy Environ. Sci.*, 2016, **9**, 1955-1988; K. Xu, *Chem. Rev. (Washington, DC, U. S.)*, 2014, **114**, 11503-11618.
- N. S. Choi, K. H. Yew, K. Y. Lee, M. Sung, H. Kim and S. S. Kim, *J. Power Sources*, 2006, **161**, 1254-1259; V. Etacheri, O. Haik, Y. Goffer, G. A. Roberts, I. C. Stefan, R. Fasching and D. Aurbach, *Langmuir*, 2012, **28**, 965-976; T. Jaumann, J. Balach, M. Klose, S. Oswald, U. Langklotz, A. Michaelis, J. Eckert and L. Giebeler, *Phys. Chem. Chem. Phys.*, 2015, **17**, 24956-24967; K. Schroder, J. Avarado, T. A. Yersak, J. C. Li, N. Dudley, L. J. Webb, Y. S. Meng and K. J. Stevenson, *Chemistry of Materials*, 2015, **27**, 5531-5542.
- S. Dalavi, P. Guduru and B. L. Lucht, *J. Electrochem. Soc.*, 2012, **159**, A642-A646; L. Ma, J. Xia, X. Xia and J. R. Dahn, *J. Electrochem. Soc.*, 2014, **161**, A1495-A1498; C. C. Nguyen and B. L. Lucht, *J. Electrochem. Soc.*, 2014, **161**, A1933-A1938.
- R. Jung, M. Metzger, D. Haering, S. Solchenbach, C. Marino, N. Tsiouvaras, C. Stinner and H. A. Gasteiger, *J. Electrochem. Soc.*, 2016, **163**, A1705-A1716.
- C. Xu, F. Lindgren, B. Philippe, M. Gorgoi, F. Björefors, K. Edström and T. Gustafsson, *Chem. Mater.*, 2015, **27**, 2591-2599.
- K. Eom, J. Jung, J. T. Lee, V. Lair, T. Joshi, S. W. Lee, Z. Q. Lin and T. F. Fuller, *Nano Energy*, 2015, **12**, 314-321.
- D. M. Seo, C. C. Nguyen, B. T. Young, D. R. Heskett, J. C. Woicik and B. L. Lucht, *J. Electrochem. Soc.*, 2015, **162**, A7091-A7095; Z. Z. Yang, A. A. Gewirth and L. Trahey, *ACS App Mater Inter*, 2015, **7**, 6557-6566.
- K. C. Klavetter, S. Garcia, N. Dahal, J. L. Snider, J. P. de Souza, T. H. Cell, M. A. Cassara, A. Heller, S. M. Humphrey and C. B. Mullins, *J. Mater. Chem. A*, 2014, **2**, 14209-14221.
- K. H. Seng, L. Li, D. P. Chen, Z. X. Chen, X. L. Wang, H. K. Liu and Z. P. Guo, *Energy*, 2013, **58**, 707-713.
- C. C. Zhao, Y. Ma, C. Shen and W. Q. Han, *J. Nanosci. Nanotechnol.*, 2016, **16**, 950-955.
- D. C. Bock, C. Pelliccione, K. W. Knehr, J. Wang, W. Zhang, F. Wang, J. Wang, A. C. West, A. C. Marschilok, K. J. Takeuchi and E. S. Takeuchi, *ACS Applied Materials and Interfaces*, 2016, **8**, 11418 - 11430.
- W. Zhang, D. C. Bock, C. J. Pelliccione, Y. Li, L. Wu, Y. Zhu, A. C. Marschilok, E. S. Takeuchi, K. J. Takeuchi and F. Wang, *Adv. Energy Mater.*, 2016, **6**, 1502471.
- C. N. He, S. Wu, N. Q. Zhao, C. S. Shi, E. Z. Liu and J. J. Li, *ACS Nano*, 2013, **7**, 4459-4469.
- Y. Oumellal, N. Delpuech, D. Mazouzi, N. Dupre, J. Gaubicher, P. Moreau, P. Soudan, B. Lestriez and D. Guyomard, *Journal of Materials Chemistry*, 2011, **21**, 6201-6208.
- S. Zhang, M. He, C.-C. Su and Z. Zhang, *Current Opinion in Chemical Engineering*, 2016, **13**, 24-35.
- M. Sina, R. Thorpe, S. Rangan, N. Pereira, R. A. Bartynski, G. G. Amatucci and F. Cosandey, *J. Phys. Chem. C*, 2015, **119**, 9762-9773.
- K. Xu, *Chemical Reviews*, 2014, **114**, 11503-11618; V. A. Agubra and J. W. Fergus, *J. Power Sources*, 2014, **268**, 153-162.
- R. Fong, U. Vonsacken and J. R. Dahn, *J. Electrochem. Soc.*, 1990, **137**, 2009-2013.
- P. Verma, P. Maire and P. Novak, *Electrochim. Acta*, 2010, **55**, 6332-6341.
- X. L. Chen, X. L. Li, D. H. Mei, J. Feng, M. Y. Hu, J. Z. Hu, M. Engelhard, J. M. Zheng, W. Xu, J. Xiao, J. Liu and J. G. Zhang, *Chemsuschem*, 2014, **7**, 549-554.
- Y. Shi, J. Zhang, A. M. Bruck, Y. Zhang, J. Li, E. A. Stach, K. J. Takeuchi, A. C. Marschilok, E. S. Takeuchi and G. Yu, *Advanced Materials*, 2017, **29**, n/a-n/a; Y. Shi, X. Zhou, J. Zhang, A. M. Bruck, A. C. Bond, A. C. Marschilok, K. J. Takeuchi, E. S. Takeuchi and G. Yu, *Nano Lett.*, 2017, **17**, 1906-1914.
- G.-H. Lee, J.-G. Park, Y.-M. Sung, K. Y. Chung, W. I. Cho and D.-W. Kim, *Nanotechnology*, 2009, **20**, 295205/295201-295205; H. Wen, M. Karulkar and A. Drews, *ECS Trans.*, 2017, **77**, 365-372.

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We report the first chemical and thermal evidence of solid electrolyte interphase modification on Fe₃O₄ electrodes via FEC electrolyte additive.