BNL-113292-2016-JA

**The Electrochemistry of Fe₃O₄ / Polypyrrole
Composite Electrodes in Lithium-Ion Cells:
The Role of Polypyrrole in Capacity Retention**

**Andrea M. Bruck, Cara N. Gannett, David C. Bock, Paul F. Smith,
Amy C. Marschilok, Kenneth J. Takeuchi, and Esther S. Takeuchi**

Submitted to the Journal of Electrochemical Society

December 2016

Energy and Photon Sciences Directorate

Brookhaven National Laboratory

U.S. Department of Energy

USDOE Office of Science (SC),

Basic Energy Sciences (BES) (SC-22)

Notice: This manuscript has been co-authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The Electrochemistry of Fe₃O₄ / Polypyrrole Composite Electrodes in Lithium-Ion Cells: The Role of Polypyrrole in Capacity Retention

Andrea M. Bruck^a, Cara N. Gannett^{b,c}, David C. Bock^d, Paul F. Smith^a, Amy C. Marschilok^{a,e,*}, Kenneth J. Takeuchi^{a,e,*}, and Esther S. Takeuchi^{a,d,e,*}

^a Department of Chemistry, Stony Brook University, Stony Brook, NY 11790, USA.

^b Department of Chemistry, State University of New York at Geneseo, Geneseo, NY 14454, USA

^c Center for Inclusive Education, Stony Brook University, Stony Brook, NY 11794, USA

^d Brookhaven National Laboratory, Upton, NY 11973, USA

^e Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11790, USA

*corresponding authors: (A.C.M.) amy.marschilok@stonybrook.edu, (K.J.T.) kenneth.takeuchi.1@stonybrook.edu, (E.S.T.) esther.takeuchi@stonybrook.edu

Abstract

Two series of magnetite (Fe₃O₄) composite electrodes, one group with and one group without added carbon, containing varying quantities of polypyrrole (PPy), and a non-conductive polyvinylidene difluoride (PVDF) binder were constructed and then analyzed using electrochemical and spectroscopic techniques. Galvanostatic cycling and alternating current (AC) impedance measurements were used in tandem to measure delivered capacity, capacity retention, and the related impedance at various stages of discharge and charge. Further, the reversibility of Fe₃O₄ to iron metal (Fe⁰) conversion observed during discharge was quantitatively assessed *ex-situ* using X-ray Absorption Spectroscopy (XAS). The Fe₃O₄ composite containing the largest weight fraction of PPy (20wt%) with added carbon demonstrated reduced irreversible capacity on initial cycles and improved cycling stability over 50 cycles, attributed to decreased reaction with the electrolyte in the presence of PPy. This study illustrated the beneficial role of PPy addition to Fe₃O₄ based electrodes was not strongly related to improved electrical conductivity, but rather to improved ion transport related to the formation of a more favorable surface electrolyte interphase (SEI).

Introduction

Li-ion battery (LIB) technology has played a critical role in the widespread adoption of a variety of portable electronic devices. However, due to the applications-driven nature of batteries, especially ambitious capacity and power requirements by potentially new devices, there is an increasing need for the basic understanding of the complicated Li-ion related electrochemistries associated with new electroactive materials. For example, one strategy to increase the capacity of electroactive materials is to use materials capable of multi-electron transfer (such as conversion reactions) resulting in high energy density materials.⁽¹⁾ Towards this end, magnetite, Fe₃O₄, is a promising nanoscale electroactive material with a high theoretical

capacity (926 mAh/g) upon full conversion to Fe metal.(2) Thus, over the past several years, the number of published studies of Fe_3O_4 has been increasing due in part to its high energy density, as well as environmental friendliness and low cost.(3)

Electroactive materials are incorporated into batteries through the fabrication of composite electrodes, where several additives may be used to enhance conductivity and to mechanically bind the components. Typically, an electrically conductive carbon additive (e.g. acetylene black or graphite) and a polymer binder (e.g. polyvinylidene difluoride (PVDF) or polytetrafluoroethylene (PTFE)) are mixed with the electroactive material to form a composite electrode.(3, 4) As mentioned above, future device applications will dictate increases in battery energy density, which may be accomplished by incorporating high capacity electroactive materials into composite electrodes where all the electroactive material is electrochemically accessible and the mass and volume contributions of passive components is minimized. For example, composite electrodes containing single walled carbon nanotubes have shown good capacity retention for up to hundreds of cycles with nanoscaled Fe_3O_4 and $\text{Li}_x\text{V}_3\text{O}_8$ electroactive materials with no additional carbon or binder required.(5-7)

Electrically conducting polymers are intriguing as composite electrode additives since conceptually they can fulfill the roles of both carbon and binder.(8, 9) Prior studies have shown benefit of added conducting polymers in Fe_3O_4 composite electrodes containing carbon and other binders.(10, 11) Chemically driven oxidative polymerization of PPy (using iron chloride, FeCl_3 , as promoter) on 200 nm Fe_3O_4 nanoparticles resulted in a significant increase in reversible capacity (544 mAh/g at 1 A/g for 300 cycles) compared to PPy-free Fe_3O_4 nanoparticles.(12) Delivery of 652 mAh/g at 2 A/g over 500 cycles for 500 nm nanocages Fe_3O_4 -PPy composites prepared via templated synthesis was reported.(13) Notably, both prior studies involved electrodes comprised of at least 10 wt% electrically conductive carbon additive and included a non-conductive polymer binder.

To further probe the role of the electrically conductive polymer in the mesoscale (bulk) properties of composite electrodes, this study focuses on the Fe_3O_4 conversion reaction and its relationship to the electrically conductive polymer binder, PPy, including a detailed study of composite electrodes with nanoscale Fe_3O_4 and PPy. Two series of electrodes were explored where one group contained additional binders and electrically conductive carbon and a second group that did not. The preparation of Fe_3O_4 -PPy composites has been reported using an additional oxidative initiator with an acidification step to polymerize the pyrrole.(14, 15) In contrast, our preparations used no additional oxidative initiator and Fe^{3+} ions generated from dissolution of Fe_3O_4 in acidic solution acted as the oxidant. Our hypothesis was that the dissolved Fe^{3+} ions may reside in close proximity to the Fe_3O_4 particles and thus the PPy generated would also be in close proximity to the Fe_3O_4 particles.

Herein, we present the role of an electrically conducting polypyrrole generated *in situ* from dissolution of magnetite in acidic conditions and its effect on the conversion reaction in the PPy- Fe_3O_4 composite electrodes with and without added carbon and binder. The electronic state of the PPy with the Fe_3O_4 nanoparticles was investigated using Raman and the overall impedance of the Fe_3O_4 -PPy composite was analyzed using Electrochemical Impedance Spectroscopy (EIS). After galvanostatic cycling, Fe_3O_4 -PPy composite electrodes were

characterized *ex situ* using X-ray Absorption Spectroscopy (XAS) to elucidate the roles of the polymer and carbon additives in terms of capacity retention upon cycling. To our knowledge, this is the first study where the PPy was generated directly from acid dissolution of Fe_3O_4 and the first study where the role of the conducting polymer PPy was investigated comprehensively by comparing carbon and binder containing and carbon free Fe_3O_4 -PPy composites. The results of this study indicate that ion transport facilitated by the presence of PPy in Fe_3O_4 based electrodes was a more critical factor in determining the electrochemistry rather than improved electrical conductivity. The findings reported here are relevant to future studies of composite electrodes using conversion type electroactive materials where the goal of attaining higher energy density and longer cycle life may be furthered by improved ion transport through mediation of the surface electrolyte interphase.

Experimental

Materials synthesis and characterization

Magnetite nanoparticles were synthesized using a co-precipitation method developed previously.⁽¹⁶⁻¹⁸⁾ Briefly, stoichiometric amounts of iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were dissolved in H_2O under $\text{N}_2(\text{g})$ and added dropwise to aqueous triethylamine ($(\text{CH}_3\text{CH}_2)_3\text{N}$). The product was washed and dried *in vacuo*.

PPy was prepared by dissolving *p*-toluenesulfonic acid (HTos) monohydrate ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$) in H_2O . Under stirring, distilled pyrrole ($\text{C}_4\text{H}_5\text{N}$) and then iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) to initiate oxidative polymerization were added and stirred for 18 hours. The Ppy was filtered and isolated as a black solid.

The magnetite-polypyrrole (Fe_3O_4 -PPy) composite material was prepared as follows. As synthesized magnetite was suspended in H_2O . Then *p*-toluenesulfonic acid (HTos) monohydrate ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$) was dissolved in H_2O and added to the suspension and stirred for 15 hours. Distilled pyrrole ($\text{C}_4\text{H}_5\text{N}$) was added to the acidified magnetite suspension, ultrasonicated and stirred for 4 or 24 hrs yielding the Fe_3O_4 -PPy product. The product was then washed with H_2O and dried *in vacuo*.

Crystallite size and sample purity were determined using X-ray powder diffraction (XRD) on a Rigaku Ultima-IV diffractometer with $\text{Cu K}\alpha$ measured in a 2θ range from 5 - 90° with a step width of 0.04° and a scan rate of $5^\circ/\text{min}$. The sample purity was confirmed using the PDF card for magnetite (01-071-6336) and the peaks of interest ($2\theta = 30.2^\circ$) were fit using PeakFit version 4.12 by using a Person VII area function to find the full width at half max then applying the Scherrer equation to calculate crystallite size. The weight percent of polypyrrole was determined using thermogravimetric analysis (TGA) with a Thermal Advantage Release Q series 5.4.0 instrument using an alumina sample cup ramping from 25 - 800°C at a rate of $10^\circ\text{C}/\text{min}$ under air. Raman spectroscopy was used to evaluate the polypyrrole coating on a Horiba Scientific XploRA instrument with a 532 nm laser between 100 - 2000 cm^{-1} . A JEOL JEM 1400 microscope was used for Transmission electron microscope (TEM) imaging. Images were obtained at 120 kV voltage using a Gatan ORIUS SC1000B CCD camera. Inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Thermo Scientific iCAP 6000

series spectrometer was used to evaluate Fe dissolution. The material was pressed into a 13mm in diameter pellet with the thicknesses ranging from 0.35-0.43 mm and placed between two electrodes under constant pressure to measure AC impedance on a Bio-Logic – Science Instruments EC-lab using a sine wave amplitude of 10 mV over a frequency range of 175 Hz – 1 MHz. The impedance data was fit using equivalent circuits using the software ZView version 3.4c.

Ex situ XANES and EXAFS measurements of the Fe K-edge (7.11 keV) were conducted at the Cornell High Energy Synchrotron Source (CHESS) on beamline F3 with a Sagittal Si(111) crystal monochromator in transmission geometry with a Fe reference foil. Fe metal nanoparticles, FeO, α -Fe₂O₃, γ -Fe₂O₃, and Fe₃O₄ standards were measured with pristine samples of the materials. The data collected were aligned, merged, and normalized in Athena.

Electrochemical Characterization

Electrodes were prepared using Fe₃O₄, Fe₃O₄-PPy, or PPy as the active material, 20% carbon, and 10% polyvinylidene fluoride (PVDF) in *n*-methyl-2-pyrrolidone (NMP). The slurry was spread onto copper foil with the final ratios of active material, ketjenblack carbon, and PVDF 7:2:1, respectively. The Fe₃O₄-PVDF electrode was constructed with a ratio of 9:1, Fe₃O₄:PVDF. Electrodes were also generated without additional carbon or binder using the same procedure. Cells were assembled in an Ar(g) filled glovebox with polypropylene separator, Li metal counter electrode, and 1 M LiPF₆ in dimethylcarbonate:ethylene carbonate (7:3) electrolyte. All cells were cycled at a rate of 50 mA/g and 100 mAg/g of Fe₃O₄. The cycling data reported is an average capacity from each cell condition ranging from 2-5 cells. AC Impedance was completed on cells before and after cycling on a Bio-Logic – Science Instruments EC-lab using a sine wave amplitude of 10 mV over a frequency range of 1 mHz - 1 MHz. and was fit using equivalence circuits on ZView version 3.4c.

For the XANES/EXAFS measurements, the cells were cycled to 10 cycles and recovered in the charged state or discharged state. The coin cells were opened in an Ar(g) filled glovebox where the electrode was extracted, washed with dimethylcarbonate, dried, then put between polyimide tape for analysis.

Results

Material Characterization.

The parent Fe₃O₄ and Fe₃O₄-PPy composite were imaged by TEM, **Figure 1A, B**. The as prepared Fe₃O₄ material in absence of PPy is ~9 nm in dimension with evidence of aggregation, **Figure 1A**. In the presence of 20% PPy, **Figure 1B**, the 9 nm Fe₃O₄ particles are closely affiliated with the PPy that is visible in the image consistent with the initial hypothesis. The preparation of the Fe₃O₄-PPy composite is illustrated in schematic form in **Figure 1C**.

XRD patterns were collected after each synthesis to ensure purity of all materials. The background was subtracted and the patterns corresponded well to the magnetite structure (PDF # 01-071-6336) as shown in **Figure 2A**. After the PPy reaction resulting in Fe₃O₄-PPy composites containing 6 wt% or 20 wt% of PPy there are no additional peaks or significant peak shifting in

the XRD indicating no major structural changes in the magnetite occurred. The crystallite size of the magnetite, 9 ± 1 nm along the (220) plane, remained constant during the polymerization process and no PPy peaks are present in the XRD after the polymerization, consistent with the XRD of pure PPy which shows no crystalline peaks and only a broad amorphous peak between 10 - 30° , **Figure 2A**.

Thermogravimetric analysis (TGA) was used to quantify the amount of PPy in the Fe_3O_4 -PPy composites. Pure magnetite shows approximately 2.5wt% loss below 250°C attributed to surface water. In the samples with PPy added, an additional weight loss is observed between 250 - 625°C as shown in **Figure 2B** attributed to PPy decomposition consistent with previous literature and the mass loss profile of pure PPy. (12, 19-21) The amount of PPy in the Fe_3O_4 -PPy composites was determined from this mass loss in this region with Fe_3O_4 +6wt% PPy having an average weight percent of 6 ± 1 wt% PPy and the Fe_3O_4 +20wt% PPy had an average weight percent of 21 ± 1 wt% PPy.

Raman spectroscopy was used to characterize the Fe_3O_4 , PPy, and Fe_3O_4 -PPy composite materials. Specifically, Raman was used to confirm the presence of conducting polymer by looking for vibrational modes indicative of the oxidized state of PPy. The peaks associated with PPy in **Figure 2C** are 940 , 977 , 1054 , 1241 , 1334 , 1399 , and 1580 cm^{-1} . Peaks indicating short conjugation length of PPy are 1054 , 1241 , and 1334 cm^{-1} . (22) The frequencies at 940 , 977 , 1399 , and 1580 cm^{-1} are associated with the $\delta_{\text{C-H}}$, δ_{ring} , $\nu_{\text{C-C}}$, and $\nu_{\text{C=C}}$, respectively. The frequencies are within the range of previously reported polaronic and bipolaronic states of PPy indicating an intrinsic electrically conductive network. (23) The 6 wt% sample shows increased intensity of the PPy peaks with decreased intensity of the iron oxide peaks, with the 20 wt% PPy sample following the same trend. The Pure PPy spectrum shows a peak at 386.5 cm^{-1} which could be residual iron hydroxide from the iron chloride used in the polymerization of the pure pyrrole monomer that was incorporated into the structure. In **Figure 2C**, the spectrum of pure magnetite shows the characteristic frequencies of the E_g , T_{2g} , and A_{1g} vibrations at 386 , 505 , and 666 cm^{-1} , respectively. (24) The E_g and T_{2g} peaks appear to be shifted from the literature values of 310 and 540 cm^{-1} and could suggest a hydrated surface based on the Raman of hydrated iron oxides which show E_g , T_{2g} , and A_{1g} vibrations at 370 - 385 , 480 - 548 , and 710 cm^{-1} , respectively. (25)

AC impedance was measured for the as-synthesized Fe_3O_4 , PPy and the Fe_3O_4 -PPy composite materials pressed into pellets free from carbon or binder additives. The Bode plots of the pellets are shown in **Figure 3** where the Fe_3O_4 has the largest overall impedance and the Fe_3O_4 +20 wt% PPy and Pure PPy have the lowest overall impedance. The pure Fe_3O_4 and Fe_3O_4 +6 wt% PPy show behavior consistent with an RC parallel circuit with resistor values of $5 \times 10^5 \pm 2 \times 10^4\ \Omega$ and $2 \times 10^4 \pm 2 \times 10^2\ \Omega$, respectively. Pure PPy and Fe_3O_4 +20 wt% PPy show only a resistor component, with values of $99 \pm 1\ \Omega$ and $62 \pm 1\ \Omega$, respectively. These values for the pure PPy material are comparable in magnitude to prior reports, however the morphology of the PPy and doping level can vary substantially between different syntheses altering the intrinsic conductivity of the polymer. (26-28) For the Fe_3O_4 +20 wt% PPy sample, the elimination of the capacitor component and decrease in the resistor value suggest an electrically conductive network propagates electron transfer throughout the pellet.

Electrochemistry. The electrochemistry of the composites was tested for various electrode compositions: as-synthesized Fe_3O_4 with 10wt% PVDF binder (Fe_3O_4 -PVDF), composites of Fe_3O_4 +6wt% PPy (Fe_3O_4 +6wt% PPy) and Fe_3O_4 +20 wt% PPy (Fe_3O_4 +20wt% PPy) prepared with no additional carbon or binder and those with electrically conductive carbon and binder for the electrodes (Fe_3O_4 -C-PVDF, Fe_3O_4 +6wt% PPy-C-PVDF, Fe_3O_4 +20wt% PPy-C-PVDF). A cell with an electrode using polypyrrole, carbon, and binder was also constructed for comparison (PPy-C-PVDF).

Figure 4 shows the voltage profiles versus electron equivalents during reduction for Fe_3O_4 and the composites with and without added carbon in the electrode for the 1st, 2nd, 10th, and 20th cycles. Overall, cycle 1 and 2 capacities for the samples with carbon show the trend of Fe_3O_4 -C-PVDF > Fe_3O_4 +6wt% PPy-C-PVDF > Fe_3O_4 +20wt% PPy-C-PVDF where the difference in delivered capacity between cycle 1 and cycle 2 is 603 mAh/g (5.2 electron equivalents), 445 mAh/g (3.9 electron equivalents) and 382 mAh/g (3.3 electron equivalents), respectively. The samples without carbon show the same trend of cycle 1 and 2 capacities for Fe_3O_4 -PVDF > Fe_3O_4 +6wt% PPy-PVDF > Fe_3O_4 +20wt% PPy-PVDF with cycle 1 and 2 capacity difference values of 515 mAh/g (4.5 electron equivalents), 493 mAh/g (4.3 electron equivalents) and 205 mAh/g (1.8 electron equivalents), respectively. Notably, the samples containing added carbon show much higher cycle 10 capacities than those with no added carbon. The samples including electrically conductive carbon delivered cycle 10 capacities of 725 mAh/g (6.3 electron equivalents), 584 mAh/g (5.0 electron equivalents), and 424 mAh/g (3.6 electron equivalents) for Fe_3O_4 -C-PVDF, Fe_3O_4 +6wt% PPy-C-PVDF, and Fe_3O_4 +20wt% PPy-C-PVDF, respectively. The electrodes without carbon additives delivered cycle 10 capacities of 26 mAh/g (0.2 electron equivalents), 80 mAh/g (0.7 electron equivalents), and 22 mAh/g (0.2 electron equivalents) for Fe_3O_4 -PVDF, Fe_3O_4 +6wt% PPy and Fe_3O_4 +20wt% PPy, respectively. The PPy-C-PVDF electrode delivered a 10th cycle capacity of 74 mAh/g (0.6 electron equivalents).

The specific capacities versus cycle numbers to 20 cycles are shown in **Figure 5A** with the results for Fe_3O_4 free PPy electrodes provided for reference. The samples containing electrically conductive carbon retain capacity better than samples without electrically conductive carbon. **Figure 5B** shows data normalized to cycle 2 capacity to illustrate capacity retention for cycle testing under discharge of 50 mA/g and 100 mA/g. The Fe_3O_4 -C-PVDF sample retained 78% the second cycle capacity when cycled at 50 mA/g. However, under 100 mA/g current, only 58% capacity retention was observed. In a similar fashion, the Fe_3O_4 +6wt% PPy-C-PVDF sample retained 83% and 51% capacity when cycled at 50 and 100 mA/g, respectively. In contrast, the Fe_3O_4 +20wt% PPy-C-PVDF sample showed capacity retention of 91% under both 50 and 100 mA/g discharge rates. The cycle number versus capacity plots at 100 mA/g are shown in **Figure S1**.

The electrochemical impedance spectra (EIS) of the coin cells was measured before cycling, after 10 cycles in the charged state, and after 10 cycles in the discharged state after cycling at 50 mA/g. The EIS data were fit to an equivalent circuit model with a DC electrolyte resistance and ohmic resistances element (R1), charge-transfer resistor (R2) and constant phase element (CPE) in parallel with the R2, and a Warburg element as shown in **Figure 6** with the values shown in **Table 1**. The charge transfer resistor (R2) varied considerably among the electrodes enabling us to examine the effect of PPy. In the electrodes with added carbon all of

the pristine materials showed a charge transfer resistance of less than 20 Ω . The pristine Fe_3O_4 -PVDF electrode has a resistance of 426 Ω while the pristine Fe_3O_4 +6wt% PPy and Fe_3O_4 +20wt% PPy electrodes had significantly smaller value of 8.7 and 21 Ω , respectively. Therefore, the PPy does maintain electronic conductivity in the pristine electrode. The 6wt% PPy composite had a similar resistance to the electrode containing carbon (Fe_3O_4 +6wt% PPy-C-PVDF) with a pristine R2 value of 8.1 Ω . The R2 of Fe_3O_4 +20wt% PPy-C-PVDF was 14 Ω , lower than the Fe_3O_4 +20wt% PPy only electrode illustrating the contribution of the electrically conductive carbon. Notably, the pristine sample PPy-C-PVDF showed a R2 of 15 Ω , similar to the pristine Fe_3O_4 +20wt% PPy-C-PVDF.

After charge and discharge of all electrodes containing carbon the R2 was below 40 Ω where the highest R2 was observed for the charged Fe_3O_4 -C-PVDF at 37 Ω (**Table 1**). The Fe_3O_4 +20wt% PPy-C-PVDF and PPy-C-PVDF had similar R2 values when charged while the Fe_3O_4 +6wt% PPy-C-PVDF has the lowest R2 in the charged state of 19 Ω . In the discharged state, the Fe_3O_4 -C-PVDF and Fe_3O_4 +6wt%-C-PVDF had similar values of 22 and 18 Ω , respectively.

Without PPy or electrically conductive carbon, the Fe_3O_4 -PVDF sample showed a high resistance of 210 Ω in the charged state, **Table 1**. The sample with 6wt% PPy showed an increase of ~130 Ω after cycling. This increase was even larger for 20wt% composite which had an increase of ~371 Ohms between the pristine and charged material after 10 cycles.

XANES. Ex-situ X-ray Absorption Near Edge Structure (XANES) was used to investigate the observed differences in the electrochemistry of the Fe_3O_4 -PPy composites with and without additional carbon and binder. XANES was a useful tool for this study as it probes the oxidation state of the metal center and does not require high levels of crystallinity. In **Figure 7**, the absorption edge of the electrodes with carbon and binder are shown after 10 cycles in the discharged (**Figure 7A**) and charged (**Figure 7B**) state of the cells cycled at 50 mA/g. The spectra of reference materials magnetite (orange), Fe metal (yellow) and FeO (grey) are shown in the figure. In the discharged state, the samples all show edge positions at lower energy than Fe_3O_4 consistent with the samples having reduced iron centers, in agreement with previous XAS investigations of discharged Fe_3O_4 .(29, 30) Notably, the Fe_3O_4 -C-PVDF and Fe_3O_4 +6wt% PPy-C-PVDF sample had spectra that were similar and indicating an oxidation state close to that of Fe^0 . In contrast, the Fe_3O_4 +20wt% PPy-C-PVDF sample indicated iron at an oxidation state less reduced compared to the other two samples with an intermediate oxidation state. These observations are consistent with the observed discharge capacities observed for each sample type.

After 10 cycles, where the samples were isolated in the charged state, the edge positions of the electrode compositions containing carbon approach the magnetite edge, indicating a higher oxidation state of Fe present in the charged state of the electrodes. The Extended X-ray Absorption Fine Structure (EXAFS) k^2 weighted-R-space spectra for the charged electrodes are presented in **Figure 7C**. Even though the iron oxidation state is high, from the EXAFS spectra, it is evident that the local atomic structure of the charged products differed from that of the magnetite reference material, consistent with the moderate functional capacity for the carbon containing electrodes. In contrast, the electrodes that were constructed without carbon delivered

less than 1 electron equivalent after 10 cycles and the XANES Fe edge as shown in **Figure S2**. The edge energies are summarized in **Table S1**. Both the discharged and charged state of the carbon free samples are similar to the Fe metal absorption edge, consistent with the small capacity observed during cycling for these samples.

Discussion

Polymerization Mechanism: The chemical oxidation of polypyrrole has been studied previously and is depicted as the oxidation step in the reaction scheme in **Figure 8**.(31) Variations in pH and solvent have also been investigated and showed that a higher acidity is favorable to prepare electrically conductive polypyrrole (PPy).(32, 33) Therefore, *p*-toluenesulfonic acid (HTos) was used in excess to maintain the pH at ~ 1.5 , promoting Fe^{n+} dissolution from Fe_3O_4 and initiate oxidative pyrrole polymerization. Slow dissolution of magnetite may generate hematite ($\alpha\text{-Fe}_2\text{O}_3$) and wustite (FeO) as products.(34, 35) In this study neither of those phases were observed in the XRD or Raman of the solid Fe_3O_4 -PPy composite product. Therefore, we propose that any dissolved magnetite results in the direct formation of the Fe^{z+} in the acidic solution as shown in the dissolution step, **Figure 8**. The reduction step occurs as the dissolved Fe^{3+} is reduced to Fe^{2+} . The balanced overall reaction indicates that for every 7 Fe^{3+} ions that are dissolved 3 pyrrole monomers should react to form the electrically conductive PPy, resulting in a 2.33 Fe/pyrrole ratio. After a 4 hr reaction $5.3 \pm 1.1\%$ of the magnetite dissolved in the reaction solution resulting in a measured ratio of Fe/py 1.5 ± 0.4 , where the Fe content was monitored by inductively coupled plasma-optical emission spectroscopy (ICP-OES). After 24 hours $12.2 \pm 0.7\%$ of the magnetite dissolved and the Fe/py ratio was 2.2 ± 0.3 , within error of the 2.33 nominal value based on the scheme shown in **Figure 8**.

Electrochemical behavior: The overall reaction of Fe_3O_4 to Fe metal is an 8 e^- reaction and has been previously characterized with additional electron equivalents attributed to solid electrolyte interphase, SEI, formation. (36-38) The electron equivalents delivered in the 1st, 2nd, 10th, and 20th cycle for each sample configuration are shown in **Figure 4**. After 10 cycles, the Fe_3O_4 -PVDF shows 0.9 e^- equivalents, indicating that the conversion of Fe_3O_4 to Fe^0 is irreversible in that electrode condition. The Fe_3O_4 -C-PVDF has far superior cycling capability delivering 6.3 e^- equivalents after 10 cycles, showing the conversion efficiency of the electrode is higher with carbon present.

The addition of PPy to the Fe_3O_4 electrode is intended to provide additional electronic conduction pathways within the electrode. Interestingly, however the interaction of the electrode with the electrolyte was impacted by the presence of PPy. The difference in capacity between cycles 1 and 2 decreased with increasing PPy content in the electrode, indicating a lower irreversible capacity with more PPy present. For example, the first and second cycle discharge capacities of the Fe_3O_4 -C-PVDF electrode were 1404 mAh/g (12.1 electron equivalents) and 801 mAh/g (6.9 electron equivalents) respectively, equivalent to an overall capacity difference of 603 mAh/g (5.2 electron equivalents), while the Fe_3O_4 +6wt% PPy-C-PVDF and Fe_3O_4 +20wt% PPy-C-PVDF electrodes showed smaller capacity differences from the first to second cycle of 445 mAh/g (3.9 electron equivalents) and 382 mAh/g (3.3 electron equivalents). The smaller

difference in capacity between the first and second cycle with higher levels of PPy provides evidence that SEI generation decreases with an increased amount of PPy.

After 10 cycles, the Fe_3O_4 +6wt% PPy delivered only 0.6 e^- equivalents. The carbon containing sample, Fe_3O_4 +6wt% PPy-C-PVDF, delivered 5.0 e^- at the 10th cycle. The increase in discharge capacity in the presence of the electrically conductive carbon indicates that the carbon improves the electrically conductive network and PPy alone is not as effective. This same trend is observed in the sample containing 20wt% PPy where the carbon containing sample delivers higher capacity and shows the best capacity retention of the group over 50 cycles, **Figure S3**.

After cycling, the XANES absorption edge for the Fe_3O_4 +20wt% PPy-C-PVDF sample in the charged state is more similar to the oxidation state of magnetite edge than the other electrode compositions, **Figure 7B**. However, the Extended X-ray Absorption Fine Structure (EXAFS) k^2 weighted-R-space spectra, **Figure 7C**, indicate that the atomic structure of the recharged iron is significantly different than the Fe_3O_4 standard, which consists of major peaks centered at 1.3 Å (contributions from nearest neighboring oxygen atoms for octahedrally and tetrahedrally coordinated Fe atoms) and 2.6 Å with a broad shoulder at 3.1 Å (contributions from neighboring iron atoms and second coordination shell oxygen atoms). The recharged material, in contrast, has a single major peak at 1.2 Å, with the amplitude of the second shell peak greatly reduced. The spectra are indicative of the Fe atoms being in a highly disordered Fe-O like state where neighboring iron atoms are only a small contribution to the observed amplitude.⁽³⁹⁾ Thus, while the XANES data indicate that the charged electrodes have high oxidation state (between 2+ and 3+), EXAFS shows that the Fe atoms after recharge exist in a disordered oxide phase that is structurally different from Fe_3O_4 . Although the Fe_3O_4 +20wt% PPy-C-PVDF composite charges to an oxidation state similar to that of magnetite, it does not fully discharge to Fe metal.

The capacity retention of the Fe_3O_4 +20wt% PPy-C-PVDF was the best for the group. High capacity retention of the Fe_3O_4 +20wt% PPy-C-PVDF sample can be rationalized by ion transport facilitated through lowered SEI formation resulting from electrolyte decomposition which has been implicated as a significant contributor to capacity fade for conversion materials.⁽³⁹⁾ The role of the PPy in providing favorable electrochemistry of composite electrodes containing conversion materials is related to its ability to provide favorable ion transport rather than its role in increasing electrical conductivity.

Conclusion

Samples of Fe_3O_4 with 6% and 20% PPy were used to prepare electrodes with and without added carbon. The samples with added carbon demonstrated lower charge transfer resistance and improved capacity retention on cycling. Ex-situ X-ray Absorption Near Edge Structure (XANES) was used to characterize pristine and cycled samples in both the charged and discharged condition. In the discharged state, XANES results of Fe_3O_4 -C-PVDF and Fe_3O_4 +6wt% PPy-C-PVDF samples showed oxidation states close to Fe^0 . The Fe_3O_4 +20wt% PPy-C-PVDF sample indicated more oxidized iron. In the charged state, the carbon containing samples showed a Fe oxidation state approaching that of a disordered Fe_3O_4 . Notably, the electrode samples with no carbon present indicated that the Fe oxidation state remained close to Fe^0 shown schematically in Figure 9.

In light of the electrochemical and spectroscopic data the role of PPy in the Fe₃O₄-PPy and Fe₃O₄-C-PPy electrodes can be described as follows. The 6% PPy in the electrodes resulted in lower charge transfer resistance for fresh and cycled electrodes. The 20% PPy resulted in increased charge transfer resistance. In contrast, the irreversible capacity, difference between cycle 1 and 2 discharge capacity, decreased in the presence of PPy where the 20% PPy showed lower irreversible capacity relative to the 6% sample and PPy-free samples. Electrodes with only Fe₃O₄-PPy and no carbon showed impedance values 8 – 10 times higher than electrodes with carbon affirming that PPy alone does not form a sufficiently conductive electrode.

While the PPy may contribute to electrical conductivity, it is worth noting that the samples without carbon did not cycle effectively. Thus, an important contribution of PPy in conversion electrodes has been elucidated where the beneficial effect of PPy in capacity retention in addition to improved electrical conductivity is improved ion transport due to the formation of a more favorable SEI. The findings reported here provide insight into the advancement of high capacity conversion type electroactive materials where both energy density and cycle life may be enhanced by improved ion transport achieved through mediation of the surface electrolyte interphase.

Acknowledgements

This work was supported as part of the Center for Mesoscale Transport Properties, an Energy Frontier Research Center supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under award #DE-SC0012673 for financial support. This research used resources of the Cornell High Energy Synchrotron Source (CHESS) beamline F3. A. M. B. acknowledges the support of the National Science Foundation Graduate Research Fellowship under grant No. 1109408. C.N.G. acknowledges support from the National Science Foundation funded Research Experience for Undergraduates Site: Nanotechnology for Health, Energy and the Environment at Stony Brook University. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

References

1. 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, *Advanced Energy Materials*, **6**, n/a (2016).
2. A. Abraham, L. M. Housel, C. N. Lininger, D. C. Bock, J. Jou, F. Wang, A. C. West, A. C. Marschilok, K. J. Takeuchi and E. S. Takeuchi, *ACS Central Science*, **2**, 380 (2016).
3. A. M. Bruck, C. A. Cama, C. N. Gannett, A. C. Marschilok, E. S. Takeuchi and K. J. Takeuchi, *Inorg. Chem. Front.*, **3**, 26 (2016).

4. J. Tucek, K. C. Kemp, K. S. Kim and R. Zboril, *ACS Nano*, **8**, 7571 (2014).
5. C. Ban, Z. Wu, D. T. Gillaspie, L. Chen, Y. Yan, J. L. Blackburn and A. C. Dillon, *Adv. Mater. (Weinheim, Ger.)*, **22**, E145 (2010).
6. A. Marschilok, C.-Y. Lee, A. Subramanian, K. J. Takeuchi and E. S. Takeuchi, *Energy Environ. Sci.*, **4**, 2943 (2011).
7. A. C. Marschilok, C. P. Schaffer, K. J. Takeuchi and E. S. Takeuchi, *J. Compos. Mater.*, **47**, 41 (2013).
8. A. C. Marschilok, C. P. Schaffer, K. J. Takeuchi and E. S. Takeuchi, *Journal of Composite Materials*, **47**, 41 (2013).
9. A. C. Marschilok, S. Zhu, C. C. Milleville, S. H. Lee, E. S. Takeuchi and K. J. Takeuchi, *Journal of The Electrochemical Society*, **158**, A223 (2011).
10. Y. H. Kwon, M. M. Huie, D. Choi, M. Chang, A. C. Marschilok, K. J. Takeuchi, E. S. Takeuchi and E. Reichmanis, *ACS Appl. Mater. Interfaces*, **8**, 3452 (2016).
11. Y. H. Kwon, K. Minnici, M. M. Huie, K. J. Takeuchi, E. S. Takeuchi, A. C. Marschilok and E. Reichmanis, *Chemistry of Materials*, **28**, 6689 (2016).
12. J. Zhao, S. Zhang, W. Liu, Z. Du and H. Fang, *Electrochim. Acta*, **121**, 428 (2014).
13. J. Liu, X. Xu, R. Hu, L. Yang and M. Zhu, *Adv. Energy Mater.*, Ahead of Print (2016).
14. L. Gai, X. Han, Y. Hou, J. Chen, H. Jiang and X. Chen, *Dalton Trans.*, **42**, 1820 (2013).
15. A. Chen, H. Wang, B. Zhao and X. Li, *Synth. Met.*, **139**, 411 (2003).
16. S. Zhu, A. C. Marschilok, E. S. Takeuchi and K. J. Takeuchi, *Electrochem. Solid-State Lett.*, **12**, A91 (2009).
17. S. Zhu, A. C. Marschilok, E. S. Takeuchi, G. T. Yee, G. Wang and K. J. Takeuchi, *Journal of The Electrochemical Society*, **157**, A1158 (2010).

18. M. C. Menard, A. C. Marschilok, K. J. Takeuchi and E. S. Takeuchi, *Electrochim. Acta*, **94**, 320 (2013).
19. W. Chen, X. Li, G. Xue, Z. Wang and W. Zou, *Appl. Surf. Sci.*, **218**, 215 (2003).
20. J. Deng, Y. Peng, C. He, X. Long, P. Li and A. S. C. Chan, *Polym. Int.*, **52**, 1182 (2003).
21. Y. Mao, Q. Kong, B. Guo, L. Shen, Z. Wang and L. Chen, *Electrochim. Acta*, **105**, 162 (2013).
22. Y. Furukawa, S. Tazawa, Y. Fujii and I. Harada, *Synth. Met.*, **24**, 329 (1988).
23. M. J. L. Santos, A. G. Brolo and E. M. Girotto, *Electrochim. Acta*, **52**, 6141 (2007).
24. O. N. Shebanova and P. Lazor, *Journal of Solid State Chemistry*, **174**, 424 (2003).
25. M. Hanesch, *Geophysical Journal International*, **177**, 941 (2009).
26. K. L. Lopez Maldonado, P. de la Presa, M. A. de la Rubia, P. Crespo, J. de Frutos, A. Hernando, J. A. Matutes Aquino and J. T. Elizalde Galindo, *J. Nanopart. Res.*, **16**, 1 (2014).
27. P. Montoya, F. Jaramillo, J. Calderon, S. I. Cordoba de Torresi and R. M. Torresi, *Electrochim. Acta*, **55**, 6116 (2010).
28. L. Qie, L.-X. Yuan, W.-X. Zhang, W.-M. Chen and Y.-H. Huang, *J. Electrochem. Soc.*, **159**, A1624 (2012).
29. 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, *Advanced Energy Materials*, DOI 10.1002/aenm.201502471 (2016).
30. M. C. Menard, K. J. Takeuchi, A. C. Marschilok and E. S. Takeuchi, *Physical Chemistry Chemical Physics*, **15**, 18539 (2013).
31. Y. Tan and K. Ghandi, *Synth. Met.*, **175**, 183 (2013).
32. R. Qian, Q. Pei and Z. Huang, *Makromol. Chem.*, **192**, 1263 (1991).

33. G. Sabouraud, S. Sadki and N. Brodie, *Chem. Soc. Rev.*, **29**, 283 (2000).
34. A. E. Chastukhin, A. D. Izotov, I. G. Gorichev and A. M. Kutepov, *Theor. Found. Chem. Eng.*, **37**, 398 (2003).
35. W. W. Frenier and F. B. Growcock, *Corrosion (Houston)*, **40**, 663 (1984).
36. C. Hendricks, N. Williard, S. Mathew and M. Pecht, *J. Power Sources*, **297**, 113 (2015).
37. J. Fontcuberta, J. Rodriguez, M. Pernet, G. Longworth and J. B. Goodenough, *J. Appl. Phys.*, **59**, 1918 (1986).
38. J. B. Goodenough and Y. Kim, *Chem. Mater.*, **22**, 587 (2010).
39. D. C. P. Bock, C.; Knehr, K. W.; Wang, J.; Zhang, W.; Wang, F.; Wang, J.; West, A.C.; Marschilok, A. C.; Takeuchi, K. J.; Takeuchi, E. S, *ACS Applied Materials and Interfaces*, **8**, 11418 (2016).

Figures

Figure 1: TEM images of (A) Fe₃O₄ nanoparticles and (B) Fe₃O₄ nanoparticles with 20wt% PPy are shown with (C) a schematic of the acidification then polymerization step of Fe₃O₄ nanoparticles to the Fe₃O₄-PPy composite. Fe₃O₄ (grey), polypyrrole (blue).

Figure 2: (A) XRD patterns (B) TGA and (C) Raman spectra of A: Fe₃O₄, B: Fe₃O₄+6wt% PPy, C: Fe₃O₄+20wt% PPy, and D: PPy.

Figure 3: Bode plots for the pressed pellets of A: Fe₃O₄, B: Fe₃O₄+6wt% Ppy, C: Fe₃O₄+20wt% Ppy, and D: Ppy taken between 1 MHz-175 Hz.

Figure 4: Voltage curves at 50 mA/g for (A) $\text{Fe}_3\text{O}_4\text{-C-PVDF}$, (B) $\text{Fe}_3\text{O}_4\text{+6wt\% PPy-C-PVDF}$, (C) $\text{Fe}_3\text{O}_4\text{+20wt\% PPy-C-PVDF}$, (D) $\text{Fe}_3\text{O}_4\text{-PVDF}$, (E) $\text{Fe}_3\text{O}_4\text{+6wt\% PPy}$, and (F) $\text{Fe}_3\text{O}_4\text{+20wt\% PPy}$.

Figure 5: (A) Cycle number versus specific capacity of electrodes containing additional carbon and binder (solid circles) and electrodes without additional carbon added (diamonds). The active material is Fe_3O_4 (black), $\text{Fe}_3\text{O}_4\text{+6wt\% PPy}$ (red), $\text{Fe}_3\text{O}_4\text{+20wt\% PPy}$ (blue), and PPy (green) at 50 mA/g. (B) Capacity retention relative to the second cycle is shown where closed circles are at a rate of 50 mA/g and open circles are at a rate of 100 mA/g for the carbon and binder containing electrodes.

Figure 6: Equivalent circuit used to fit coin cell impedance data.

Sample	Electrochemical Condition	R1	R1 error	R2	R2 error	CPE1-T	CPE1-T error	CPE1-P	CPE1-P error
Fe ₃ O ₄ -C-PVDF	pristine	1.8	1.07	8.6	0.04	2.83E-05	8.64E-07	0.8245	0.0037
	discharged	0.6	0.07	22.3	0.24	4.08E-05	1.50E-06	0.7931	0.0047
	charged	0.8	0.12	37.3	0.49	3.26E-05	1.64E-06	0.8130	0.0065
Fe ₃ O ₄ +6wt% PPy-C-PVDF	pristine	0.7	0.04	8.1	0.02	5.18E-05	1.19E-06	0.7928	0.0022
	discharged	1.1	0.02	18.7	0.15	6.32E-05	2.99E-06	0.7406	0.0046
	charged	1.1	0.03	19.9	0.23	4.50E-05	2.71E-06	0.7685	0.0059
Fe ₃ O ₄ +20wt% PPy-C-PVDF	pristine	0.8	0.02	13.5	0.08	3.92E-05	1.70E-06	0.7783	0.0041
	discharged	2.6	0.02	27.8	0.11	4.11E-05	1.02E-06	0.7641	0.0025
	charged	5.7	0.02	29.8	0.12	4.53E-05	9.86E-07	0.7564	0.0023
Ppy - C - PVDF	pristine	1.1	0.01	32.2	0.2	3.76E-05	1.02E-06	0.8035	0.0027
	discharged	0.7	0.02	28.4	0.15	7.66E-05	4.15E-06	0.7252	0.0055
	charged	0.9	0.02	31.0	0.52	6.11E-05	5.91E-06	0.7020	0.0102
Fe ₃ O ₄ -PVDF	pristine	1.1	15.93	425.7	23.08	3.34E-05	2.51E-06	0.8401	0.0139
	discharged	1.5	0.10	80.4	3.60	7.79E-05	7.60E-06	0.6800	0.0101
	charged	1.5	0.03	215.5	10.40	6.28E-05	1.67E-06	0.7001	0.0047
Fe ₃ O ₄ +6wt% Ppy	pristine	1.1	0.90	8.7	0.17	4.63E-05	3.47E-06	0.7970	0.0081
	discharged	1.0	0.06	86.5	3.33	1.17E-04	7.04E-06	0.6546	0.0066
	charged	2.6	0.11	139.8	9.42	7.66E-05	4.31E-06	0.7178	0.0120
Fe ₃ O ₄ +20wt% Ppy	pristine	0.5	0.70	21.8	1.05	6.10E-05	6.44E-06	0.7596	0.0135
	discharged	0.9	0.04	208.5	19.47	5.30E-05	2.98E-06	0.7376	0.0116
	charged	0.9	0.04	393.2	16.52	2.86E-05	1.42E-06	0.8175	0.0098

Table 1: R1, R2, CPE1-T, and CPE1-P values of the pristine, charged and discharged samples after 10 cycles.

Figure 7: The XANES Fe edge of the Fe_3O_4 -C-PVDF (black), Fe_3O_4 +6wt% PPy-C-PVDF (red), and Fe_3O_4 +20wt% PPy-C-PVDF (blue) (A) discharged state (B) charged state after 10 cycles at 50 mA/g. (C) Fe K-edge k^2 weighted $|\chi(R)|$ comparison of 0 wt%, 6 wt%, and 20 wt% Ppy-C-PVDF electrodes in the charged state. Reference spectra for Fe_3O_4 (orange), Fe metal (green) and FeO (grey) are shown.

Figure 8: The oxidation, dissolution, reduction, and overall redox reaction of Fe_3O_4 in acidic conditions in the presence of pyrrole is shown.

Figure 9: Schematic of the charged state of the electroactive material in the electrode after 10 cycles with and without carbon.