***In situ* XANES and EXAFS Analysis of Redox Active Fe Center Ionic Liquids**

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Abstract

In situ X-Ray Absorption Near Edge Spectroscopy (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) techniques are applied to a metal center ionic liquid undergoing oxidation and reduction in a three electrode spectroscopic cell. Determination of the extent of reduction under negative bias on the working electrode and the extent of oxidation are determined after pulse voltammetry to quiescence. While the ionic liquid undergoes full oxidation, it undergoes only partial reduction, likely due to transport issues on the timescale of the experiment. Nearest neighbor Fe-O distances in the fully oxidized state match well to expected values for similarly coordinated solids, but reduction does not result in an extension of the Fe-O bond length, as would be expected from comparisons to the solid phase. Instead, little change in bond length is observed. We suggest that this may be due to a more complex interaction between the monodentate ligands of the metal center anion and the surrounding charge cloud, rather than straightforward electrostatics between the metal center and the nearest neighbor grouping.

Background

Flow batteries are receiving attention recently due to a number of beneficial system design factors that they incorporate, in particular the ability to charge quickly and the ability to uncouple capacity from rate

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4 capability of the battery.[1-3] The design of such systems is simple, requiring only an electronically
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capability of the battery.[1-3] The design of such systems is simple, requiring only an electronically
conductive electrode at either the anode or cathode, as the electrochemical redox reactions occur in the
liquid phase (the anolyte and catholyte, respectively). [4,5] Recharge of the cells is a matter of pumping
away the “discharged” chemistry from the external storage tanks, and pumping “charged” chemistries
back into these tanks, or running the cell in reverse, decreasing the oxidation state of the anolyte and
increasing that of the catholyte under the influence of an applied current and field, see (Figure 1)[6]

Flow batteries are limited in their electrochemical capacity, for a fixed volume, to the specific energy
density of the catholyte and anolyte. Historical flow battery systems relied on chemistries that were
aqueous acid based salt systems, such as the iron-chromium system [7] or the nonaqueous
Ru(bpy)₃(BF₄)₂ systems.[8] Later improvements were observed using such chemistries as vanadium[9]
or zinc bromide.[10] More recently, chemistries such as bromine/polysulfide have also been
investigated.[11] These chemistries suffered from low total electrolyte concentration in the solvent,
limiting the specific energy density of the flow batteries.

Recent progress in redox active ionic liquids, however, has produced ionic liquids with increased energy
density by designing both a redox active anion and cation into the ionic liquid.[12-15] These materials
show increased ability to support higher currents and capacities due to the increased concentration of
redox active constituent in the anolyte and catholyte. However, the viscosity of these ionic liquids is
higher than those of the solvated salt systems, which raises the question of conformational state of
these large cation complex ionic liquids during the change of oxidation state. Additionally, because
these ionic liquids are designed with ligands intended to allow for partial shielding of the redox active
center, the question arises of what kinetic limitations are imposed by the design of the molecule during
electron transfer at either the anodic or cathodic current collectors.

The iron center ionic liquids (ILs) previously reported in the literature are of specific interest due to their low cost, ease of synthesis, and relative environmental stability [16]. These ILs had previously been reported to have significant overpotential for oxidation and reduction, and the question arises as to whether these overpotentials arise due to issues in transport within the electrolyte itself, or due to barriers to electron transfer to and from the redox active site. *Use of soft X-Ray spectroscopic techniques have been applied successfully to probe ligand structure within imidazolium based ILs previously [17].* Here, we present the first evidence that the ligands surrounding the metal center *in the iron center ethanolamine chemistries* are not completely unaffected by the electronic transfer (as would be expected from traditional electrostatics) but instead respond to the oxidation and reduction of the metal center in an unintuitive way.

Experimental

Spectroscopic cells were machined from Teflon with an 18 mm window through the center of the cell, three tapped ¼" feedthroughs for electrode connections and four through holes for clamping the cell. An O-ring groove was machined around the active region of the cell, including the x-ray window. Unteflonized Toray Paper (Cabot Corporation) 0.050 mm thick was used as the working electrode (WE) that was shaped to cover the entirety of the x-ray transparent window. Platinum mesh (Alfa Aesar) was used as a counterelectrode (CE), and was cut to as large an area as possible that fit within the cell sealing region. The reference electrode (RE) was fritted Ag/AgCl in 0.5M 1-ethyl-3-methyl-imidazolium chloride (EMIC) in 1,2-dimethyl-3-propyl-imidazolium bis(trifluoromethylsulfonyl) imide (DMPI-Im), as previously reported[18]. The X-ray transparent windows for the cell were made from 0.025mm thick Kapton™ tape, pressed against the flat sealing surface of the cell. A single 2" diameter Vespel O-ring was used for the seal (see Figure 2). Electrical contacts to the cell were made with a 6.35 mm 316L stainless steel rod (McMaster-Carr) polished on the contact end, and inserted through 6.35 mm (1/4")

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4 Teflon Swagelok fittings to make contact with either the working or counterelectrode. To ensure good
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6 wetting between the reference, counter, and working electrode, a separator support (open cell
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8 cellulose, VWR) was added to the cell to ensure a salt bridge between WE and CE, which are coplanar in
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10 this design. The cellulose support also bridged to the reference electrode frit to allow for wetting of the
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12 frit by the ionic liquid under all conditions. The total volume of ionic liquid within the cell during test
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14 was ~1 mL.
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19 Electrochemical measurements were conducted using a VoltaLab PGZ100 electrometer. Cyclic
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21 voltammograms were performed at room temperature at 5 mV/sec unless otherwise noted. The
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23 chronoamperometric poisoning potential experiments were conducted at either +600mV vs. Ag/Ag⁺ for
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25 oxidation, -350 mV vs. Ag/Ag⁺ for a mixed state, or at -800mV vs. Ag/Ag⁺ for reduction. Currents were
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27 measured by poisoning the working electrode at the reference potential for a long period of time (>10
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29 minutes), and then stepping to the poisoning potential and recording the oxidative or reductive currents.
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34 For the characterization of the local electronic and atomic structure of the metal center, synchrotron
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36 based x-ray absorption fine structure spectroscopy (XAFS) measurements were performed. The XAFS
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38 spectra were acquired at the bend magnet beamline X19A at the National Synchrotron Radiation Light
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40 Source, Brookhaven National Laboratory. A double crystal Si(111) monochromator was used and
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42 detuned by 40-50% for reduction of harmonics. Three ion gas chambers were used to record in
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44 transmission mode the incident (filled with N₂), transmitted (filled with Ar/He), and reference (filled with
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46 Ar/He) beam. A Fe foil was placed after the second ion chamber for energy calibration (Fe K-edge:
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48 7.112 keV). In addition, the Fe foil as well as Fe₂O₃ and FeO standards (prepared via the scotch tape
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50 method) were used for direct comparison to the electrochemical samples. All measurements were
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52 performed in transmission mode. Spectra were taken at different steps of the chronoamperometric
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54 poisoning routine as described above. Once the current had decayed to 10% of the initial value, the cell
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was removed from the electrometer and placed directly in the beamline hutch for x-ray measurements. In general 3-5 scans were taken per electrochemical step and subsequently averaged during data processing.

XAFS data processing and analysis was done using the IFEFFIT suite of programs.[19] Initial estimates of the threshold energy values (E_0) were obtained via the inflection point in the normalized absorption edges. A Hanning window was applied to a selected k-range to obtain the Fourier transformed extended XAFS (EXAFS) data. The k-space data were weighted by k^2 and Fourier transformed between 3-9 $\text{\AA}^{-1}$. In general, the quality of the EXAFS data precludes rigorous fitting of the data, but inspection of the data, especially in terms of the first shell scattering contributions, is useful in understanding the chemistry of the ionic liquid during electrochemical treatments.

The electrolyte was prepared as described in the literature [12], but is briefly recreated here. A 2.00 g sample of recrystallized $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ (Aldrich) was added to a 2.51 g solution of $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ in a 20 mL scintillation vial and thoroughly mixed for several minutes. The solution was then heated in a glass vial, thoroughly mixed for several minutes, and then heated to 150 °C while stirring for an additional 10 min. Purity was confirmed by FT-IR on a Thermo iS5 spectrometer equipped with a Smart Orbit (Diamond) ATR accessory.

Results and Discussion

Cyclic voltammetry for the spectroscopic cell in the presence of the ionic liquid is shown in Figure 3. The Toray™ paper used for the working electrode in this spectroscopic cell was relatively thick for X-ray beam penetration purposes (0.050 mm), but allowed a significant wetting of the electrolyte into the region being interrogated by the x-ray beam. This carbon paper was chosen for the cell specifically to increase the amount of fluid in the path of the beam to allow for clearer x-ray absorption near edge

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4 structure spectroscopy (XANES) and EXAFS data to be collected from the ionic liquid. While the
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6 relatively large wetted area of the electrode in the window would normally provide high currents and
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8 facile diffusion kinetics, the coplanar nature of the cell design resulted in a very small cross section for
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10 ionic transport to the cathode. As a result, the currents observed in the cell were much smaller than
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12 those observed previously[12], on the order of those currents observed during the electrochemical
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14 evaluation of the material reported previously on a much smaller (3 mm) glassy carbon disk.
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19 The limitations of cell structure on the diffusion of the ions within the electrolyte, combined with the
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21 pore structure for the working electrode, result in a cell structure that is heavily dependent on diffusion
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23 to the working electrode. Because of these transport limitations, it is not unexpected that the redox
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25 peak observed in the polished electrode is only weakly visible in the spectroscopic cell curve. The peaks
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27 associated with the oxidation and reduction of the iron center are also appreciably offset from the
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29 equilibrium case, and for several of the observed cyclic voltammograms, were not strongly observed
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31 until much higher (on oxidation) or lower (on reduction) potentials than in the equilibrium test set.
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36 Since the interest was in the structure of the oxidized or reduced form of the ionic liquid, however, the
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38 cells were poised at either high oxidative potential (+600 mV vs. Ag/Ag+) or at very reducing potentials (-
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40 800 mV vs. Ag/Ag+) and allowed to come to equilibrium through the use of chronoamperometry. Initial
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42 currents on poisoning at a potential were allowed to decay until a value of 10% of the initial value of the
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44 current was observed before the ionic liquid was interrogated with the x-ray beam.
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49 The equilibrium state of the ionic liquid in terms of oxidation state was expected to be the fully oxidized
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51 (Fe^{+3}) state due to the availability of oxygen in the atmosphere. The ionic liquid was synthesized and
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53 stored in contact with air, as well as during cell preparation (no special precautions were taken to keep
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55 the ionic liquid from air during cell setup). The XANES spectra of the ionic liquid in the resting state
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57 compared to a known oxidation state for iron is shown in Figure 4. The K-edge for iron in Fe_2O_3 lies at
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4 7126 eV, in good agreement with the published value [20]. Similarly, the edge for the iron in the ionic
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6 liquid lies at the same value, indicating that the iron is fully oxidized when exposed to atmosphere.
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10 Fe K-edge XANES was also measured for a number of controls for both iron in the +3 state (Hematite,
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12 Fe_2O_3) and in the +2 state (Wustite, FeO). These oxides give the position of the Fe K-edge so that the
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14 oxidation state of the iron in the ionic liquid can be compared to these. As the ionic liquid is reduced in
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16 the spectroscopic cell, the Fe K-edge shifts to a lower value in response (inset Figure 5). Since the
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18 reduction is expected to be a formal charge transfer at the metal site of the cation, this shift is not
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20 unexpected, and maps well to the idea that the ionic liquid cation is in fact seeing a formal charge
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22 transfer to the iron site. A complete change in oxidation state of the IL is not seen, however, but instead
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24 a mixture of +2 and +3 oxidation states are observed (Figure 5). This most likely occurs from a restricted
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26 diffusion issue because the IL is too far away from the electrode to accept an electron during the
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28 timescale of the experiment. It makes sense, however, that cations close enough to diffuse to the
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30 electrode and undergo reduction will do so, even in the diffusionally restricted architecture of the
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32 spectroscopic cell.
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39 The Fourier transformed EXAFS data were examined to determine if the nearest bond distances from
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41 the iron center were changing during oxidation and reduction. Again, standards of iron oxides in the +2
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43 and +3 state were run to set the boundaries of the expected oxidation states. From simple charge
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45 arguments alone, it was expected that, as the oxidation state of the iron center went from +2 to +3, the
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47 Fe-O bond distance would decrease, reflecting the higher Coulombic attraction between the positively
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49 charged iron and the negatively charged oxygen. In the case of the iron oxides, this is observed
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51 experimentally, as the nearest bond distance for iron in the +2 state is longer than that of the Fe-O bond
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53 distance in the +3 state. (Figure 6)
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4 Because the local environment for the iron center in the ionic liquid is similar to that found in the oxides
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6 (both Hematite and Wustite exhibit octahedral coordination of oxygen around the iron), it was expected
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8 that the same behavior would be observed in the ionic liquid. In the case of the fully oxidized ionic
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10 liquid, this was borne out by the EXAFS measurements, with the nearest neighbor bond distances
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12 matching well to the Hematite bond distances. However, as the ionic liquid was reduced, the EXAFS
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14 data showed a slight shortening of the Fe-O bond distance, very different than that of the Wustite bond
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16 length. Having a closer coordination shell of negatively charged oxygen when the iron is reduced may
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18 help to explain at least partially why there did not seem to be an asymmetric response to oxidation and
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20 reduction of the ionic liquid when measured against the glassy carbon electrode. Previous observations
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22 of cyclic voltammetry in the literature[12] observed a symmetric oxidation and reduction peak for the IL.
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24 However, if the interatomic bond distances were increased for the reduced state of the iron, one would
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26 predict that there would be some additional polarization resistance to electron transfer from the
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28 electrode to the redox site, when compared to the oxidized state of the iron center, which would lead to
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30 a nonsymmetric redox curve. The fact that the cyclic voltammograms do not show this additional
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32 polarization to the reduced state correlates well to the EXAFS data that seems to be indicating that
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34 there is overall little change in the local structure of the iron center on either oxidation or reduction.
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37 Nevertheless, this observed decrease in bond distance with reduction of the iron center is unexpected,
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39 and there is not sufficient evidence from the measurements to fully understand why this effect has
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41 occurred. However, the structure of the ligands in the ionic liquid, together with the role of the anion,
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43 may offer some possible explanation. Previously, it was determined that the nature of the ligands
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45 around the iron center is monodentate[12]. This was based on the fact there was a 6:1 ligand to metal
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47 stoichiometry and the complex was stable (as observed by thermogravimetric analysis) well past the
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49 boiling point of the free ligand. In addition, there were more pronounced blue shifts in the hydroxyl
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51 frequencies than the amine (from infrared spectroscopy), suggesting coordination was primarily through
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the oxygen and not the nitrogen. Using these data, we envision that each iron center is surrounded by a cloud of hydroxyl and amine functional groups that are electronically active and likely polarized by the charged central metal (Figure 7). We hypothesize that the interaction of the charge compensating anionic cloud is confounded by the charge centers on the ligands (both the amine and hydroxyl centers). As the iron center is reduced, it may be that the charge compensating anions interact more strongly with the hydroxyl and amine charges located in the outer sphere, and these contributions to molecular structure may play a larger role than the iron center in reconfiguring the ligand structure. Thus, even though the formal charge state on the iron changes, the strong interactions with the outer sphere charges hold the ligands in locally the same position as in the oxidized state. Although there is insufficient evidence to make this claim based on these data alone, such a mechanism would explain the observed lack of local structure change near the iron center.

Conclusions:

Examination of *in situ* Fe K-edge XANES data during charge/discharge of Fe center ILs, is suggestive of partial charging, indicating that only a certain amount of IL near the working electrode changes oxidation state. It is likely that the cell architecture necessary to provide good access to the X-ray beam resulted in increased ohmic drops in the cell and higher oxidation/reduction overpotentials when compared with literature values. Transport limitations within the cell would limit how much of the ionic liquid could access the electrode in a given amount of time, resulting in the observed mixed charge state of the iron center in the reduced state.

Fe K-edge EXAFS seems to indicate that a simple dependence of Fe-O interatomic distance on Fe oxidation state solely due to electrostatics is not occurring, and that more complex ligand-Fe center interactions are in play. We propose that increased interactions between the surrounding ion cloud and the ligands may be playing a role in reversing the Fe-O bond distance trends with oxidation, normally

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4 caused by simple electrostatic interactions. Instead, an increase in bond distance with oxidation of the
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6 iron center is observed. Closing of the ligand shell during reduction could explain sluggish oxidative
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8 kinetics, which was also observed both here and in previous work.
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