Cyclic Voltammetry and X-ray Absorption Spectroscopy of Nickel Oxide in the Ionic Liquid 1-Ethyl-3-Methyl Imidazolium Chloride/Aluminum Chloride

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Transition metal chlorides have been examined in situ in ionic liquids (ILs) using cyclic voltammetry (CV) but the oxides of these metals have not received as much attention. In this study, the structure of nickel oxide in the ionic liquid, 1-ethyl-3-methyl imidazolium chloride (EMIC) and aluminum chloride has been investigated. The NiO in EMIC/AlCl3 IL was examined with CVs and Extended X-ray Absorption Fine Structure (EXAFS) in both Lewis acidic and basic IL solutions. The CV of NiO in both acidic and basic EMIC/AlCl3 ILs shows similarities with the CV of NiCl2 in these ILs. The EXAFS data for the NiO and anhydrous NiCl2 in these acidic and basic IL solutions are also analogous, indicating that some corresponding molecular structures may have formed and these are discussed in detail.

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Nickel is a commercially important metal and the electrodeposition of nickel and nickel alloys continues to hold high interest. Nickel is used in stainless steels, superalloys, shape memory alloys, and medical applications as well as heat and corrosion protection applications. Thus, it would be beneficial to produce it in the most environmentally friendly fashion and ionic liquids (ILs) can play an important role in achieving this goal. Nickel can be deposited from nickel sulfamate baths but non-aqueous solutions could allow for electroplating different alloys or different microstructures than are possible from aqueous solutions. The composition of the electrolyte and the parameters used in the electrodeposition have a strong effect on the structure and properties of the deposits. Many metals cannot be deposited from aqueous solutions because their potentials fall outside of the electrochemical range of stability for water. Using ILs for the electrodeposition of metals can avoid some of this difficulty because they have a larger electrochemical potential window than water and this could allow for the preparation of some unique alloys. ILs are also appealing because of their very low vapor pressure. Earlier research has shown that nickel metal and nickel alloys can be deposited from nickel chloride dissolved in the IL EMIC/AlCl3 but this depended on Lewis acidity of the IL which in turn affects the structure of the Ni ions that form in the solution.

In order to understand the electrodeposition of the transition metals and their alloys, the structures of several transition metal chlorides have been studied in situ in ionic liquids using EXAFS. However, the oxides of these metals have not received as much attention. When working with the water and air sensitive ILs, there is always a concern about oxygen and moisture contamination and its effect on the properties of the IL. Also, many of the transition metal chlorides are studied in the anhydrous state and thus they are also sensitive to oxygen and moisture contamination in the IL. In this study, we examine the structure of the nickel ions that form in the EMIC/AlCl3 IL when nickel(II) oxide is added to simulate the effect of oxygen contamination. AlCl3 is a Lewis acid and the acidity of the IL can be manipulated by adjusting the ratio of the AlCl3 to the EMIC. The structure of NiO was studied with CVs and EXAFS in both Lewis acidic and Lewis basic EMIC/AlCl3 ILs.

Experimental

Sample preparation.—EMIC and AlCl3 were prepared and purified as described previously. All solution preparations were performed in a Vacuum Atmosphere nitrogen filled drybox, where oxygen and water concentrations were below 1 ppm. By definition, a value of N < 0.5 is basic and N > 0.5 is acidic, where N is the mole fraction of AlCl3 in the melt. Concentrations were based on density calculations determined by Fannin et al. The 102 mM NiCl2 solution in the basic melt was prepared by direct addition of NiCl2 to the N = 0.43 basic melt. NiCl2 dissolves more quickly in a basic IL, so the 27 mM NiCl2 solution in the N = 0.60 acidic IL was prepared by addition of the appropriate amount of AlCl3 to a solution of NiCl2 in the basic IL to change the IL to acidic. The NiO solutions were prepared by adding NiO (Alfa Aesar, 99.9%) to the basic EMIC/AlCl3 melt, N = 0.43, to make a nominal 21 mM Ni(II) solution. The acidic solution, N = 0.60, was prepared with a nominal concentration of 36 mM Ni(II). NiO dissolved very slowly in both acidic and basic melts at ambient temperature, requiring 50 days to completely dissolve as determined by cyclic voltammetry. Voltammetric experiments were carried out at ambient temperature (22°C). The nickel liquid solutions were sealed in 2 ml thick polyethylene bags and were examined with EXAFS.

Electrochemistry.—The electrochemical experiments were conducted with an EG&G PARC model 283 potentiostat controlled with the EG&G PARC PowerSuite software package. Experiments were conducted at room temperature in a single compartment glass cell using a 1 mm diameter platinum disc working electrode (Cypress Systems) that was polished successively with 1 μm, 0.3 μm and 0.05 μm alumina (Buehler) and a platinum wire was used for the counter electrode. The reference electrode consisted of an aluminum wire immersed in an N = 0.60 EMIC/AlCl3 ionic liquid and isolated from the bulk solution with a Teflon tube containing a Vycor frit. The reference electrode for NiCl2 in the basic melt was a Ag/AgCl electrode using an electrolyte of 0.10 M EMIC in EMI BF4. The potential of this electrode was found to be +0.03 V vs the Al reference using ferrocene. The CV scans were run at 25 mV/s and 50 mV/s and were started at the open circuit potentials (OCP). The OCP for the acidic melt was ~+1.0 V and the OCP for the basic melt was ~0 V.

EXAFS data collection and analysis.—The EXAFS experiments were conducted on beamline X-11A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). All of the EXAFS data were measured at room temperature with the storage ring operating at 2.8 MeV and beam currents in the range of 150 to 260 mA. The monochromator was detuned 20% at 400 eV above the storage ring edge to remove any higher harmonics. Several scans were taken for each sample, and the analysis was carried out on the averaged data. The EXAFS data were collected at the nickel K-edge (8333 eV) in fluorescence mode using a Si(111) double crystal
monochromator and a Ni foil was used as the calibration reference. The EXAFS signal deteriorates above 13k due to the dilute nature of the solutions and data collected at higher k values were not included in the analysis.

The analysis of the X-ray absorption data was carried out using the XDAP data analysis code.  The EXAFS portion of the spectrum, \( \chi(k) \), is initially extracted from the absorption background using a second-order polynomial removal, extrapolated from the pre-edge data. This is followed by the removal of the post-edge background using a cubic spline removal technique. The EXAFS data are then normalized to a per atom basis by dividing through by the step height of the absorption edge. The contribution of an individual shell in the EXAFS data is isolated by carrying out a \( k^n \) (\( n = 1–3 \)) weighted Fourier transform (FT) on the data which transforms it from k to R space, producing a pseudo radial structure function (RSF). The peaks in the RSF correspond to the individual coordination shells in the sample. These peaks are shifted from their true values to lower values of bond distance due to the phase shifts. However, phase correction with the appropriate backscattering element will account for this shift and this technique can be used to identify the backscattering elements. An individual shell can be isolated by carrying out an inverse FT from R-space back to k-space over a range of \( \Delta R \) determined from the nodes in the imaginary portion of the FT on either side of the shell of interest. Using this technique on data for reference compounds with well-defined structural parameters, the phase, \( \phi(k) \), and amplitude, \( A(k) \), functions can be determined. This reference phase and amplitude information are used to determine the structural parameters of an unknown sample by carrying out a non-linear least squares fit in k-space following the isolation of the \( \chi(k) \) from the experimental data. FEFF 5 was used to generate the theoretical spectra that were used in the analysis.

Results and Discussion

Electrochemistry.—The cyclic voltammetric curves for NiCl₂ and NiO in the \( N = 0.60 \) acidic IL are shown in Figures 1a and 1b, respectively and the CV curves for NiCl₂ and NiO in the \( N = 0.43 \) basic IL are displayed in Figures 2a and 2b, respectively. The electrochemical window of stability in the acidic IL extends from 0 V, where the deposition of aluminum occurs, to 2.5 V, where there is chlorine evolution. In the basic IL, it extends from 1 + 1.0 V, where chlorine evolution occurs, to 1 + 1.9 V, where the decomposition of the EMIC begins to occur. It can be seen in the figures that the NiCl₂ solutions have significantly different electrochemical behaviors in the acidic and basic ILs. This is due to the different coordination of the nickel ions with the chloride ions that occurs as the acidity of the IL changes.

For NiCl₂ in the \( N = 0.60 \) acidic melt, there is a broad reduction peak at 0.32 V seen in Figure 1a which is attributed to the reduction of Ni²⁺ to Ni metal. It has been shown by others that the under-potential deposition (UPD) of aluminum also occurs in this region. The first small oxidation peak at 0.6 V is attributed to the stripping of the small amount of UPD aluminum metal that was deposited during the reduction process. The large oxidation peak at 0.94 V in the acidic IL is attributed to the stripping of the Al-Ni alloy that forms in the UPD of the aluminum. The second large peak at 1 + 0.04 V is attributed to the stripping of nickel metal or possibly a nickel alloy with low aluminum content. In the \( N = 0.43 \) basic melt, Figure 2a shows that nickel(II) undergoes reduction at 1.14 V, which is greatly shifted from the +0.32 V observed in the acidic melt in Figure 1a. This behavior clearly shows the effect of complexation of the Ni(II) by chloride in the basic melt and supports the EXAFS finding of higher chloride complexation of Ni(II) in the basic melt, which is discussed below.

The NiO solutions also display very different electrochemical behaviors in the acidic and basic ILs; however, its behavior in both solutions is very similar to the behavior of the NiCl₂ in the corresponding solutions because both the NiCl₂ and NiO form similar ions when dissolved in these ILs. When nickel chloride is dissolved in basic EMIC/AlCl₃, the solution turns blue. With nickel oxide in this basic IL, although it dissolves very slowly, the solution also turns blue and this further corroborates that the Ni has become coordinated with chloride ions in this solution. A comparison of the results for NiCl₂ and NiO in the basic melts in Figures 2a and 2b, shows that the form of the voltammograms is the same. After stirring for 50 days at ambient temperature, the peak current density in Figure 2b, corrected for the different concentrations, is the same as that in Figure 2a, signifying complete conversion to the chloride in 50 days. The voltammograms are then essentially identical, confirming that NiO is eventually converted completely to Ni(II) ion complexed by chloride in the basic melt. Voltammograms of solutions prepared by dissolving NiCl₂ in the basic melt remained unchanged after a similar amount of time, showing that NiCl₂ is stable in this system, with no evident decomposition of the ionic liquid. The fate of the oxide ion is not known, but it likely reacts with the AlCl₄⁻ in the melt. A similar comparison for NiCl₂ and NiO in the acidic melt in Figures 1a and 1b, using the peak current densities for the oxidation peak at +0.94 V, shows that the conversion of NiO to the nickel complex is much less complete than in the basic melt after 50 days stirring at ambient temperature. This supports the finding of multiple species for NiO in the acidic melt by EXAFS, only one of which displays the voltammogram produced by addition of NiCl₂ to the acidic melt. The low concentration of free chloride ions in the acidic melt is evidently responsible for this low extent of conversion. The NiO solutions display only one stripping peak in the acidic IL at a potential in between the two peaks seen for the NiCl₂ in the acidic IL at 0.99 V. This behavior may be due to
the lower concentration of the nickel complex undergoing reduction to form the alloy.

**X-ray absorption spectroscopy.**—Data were collected for NiO and anhydrous NiCl₂ powder samples for reference standards to be used in the analysis of the IL samples. A representative example of the raw EXAFS data for the NiO powder standard are shown in Figure 3a. The EXAFS chi data for the NiO powder standard are shown in Figure 3b and the k³ weighted FT of the data is shown Figure 3c. The radial structure function of the oxide shows several shells. The first shell is the nickel–oxygen interaction and the second shell is the nickel–nickel interaction. The shells that are at greater distances are additional oxygen and nickel interactions, but they also include multiple scattering contributions. The EXAFS data for the NiCl₂ powder standard are shown in Figure 4a and the k³ weighted FT of the data is shown Figure 4b. The radial structure function of the chloride shows two primary shells. The first shell is the nickel–chlorine interaction and the second shell is the nickel–nickel interaction. The EXAFS data for NiO dissolved in the N = 0.43 basic IL are shown in Figure 5a and the k³ weighted Fourier transform of the data is shown Figure 5b. There is a single peak in the radial structure function, indicating a single shell around the central nickel atom. The Fourier transform was phase corrected with both the chloride shell from the NiCl₂ standard, shown in Figure 6a, and oxide shell from the NiO standard, shown in Figure 6b, in order to determine which element was contributing to the backscattering. When the FT is phase-corrected with the correct backscattering atom, the peak in the imaginary part corresponds to the maximum of the positive peak in the magnitude of the FT. As can be seen in Figure 6a, the backscattering atoms must be primarily from a Ni–Cl interaction where the two peaks are mostly in phase. There is a slight shift in the phase making the imaginary peak slightly off center. This could be possibly due to a small quantity of unreacted NiO or a small amount of a partially reacted species such as NiOCl or NiOCl₂ contributing to the data.

A single shell analysis using the nickel chloride reference was performed on the data which yielded a good fit, confirming that the contribution from another backscattering ion other than the chloride ions is small. The single shell fits in k-space and phase-corrected R-space are compared with the experimental data in Figures 7a and 7b, respectively. The analysis indicates that there is an average of 4.6 chlorine atoms in the coordination shell. Earlier studies on nickel chloride dissolved in similar basic ionic liquids indicated that the coordination of chlorides was four while it was found to be six in acidic melts. Gale et al. also found the nickel ion to be tetrahedrally coordinated.
Figure 4. (a) EXAFS spectrum for anhydrous NiCl₂ powder. (b) FT of the spectrum. The first shell is the Ni - Cl interaction and the second shell is the Ni – Ni interaction.

Figure 5. (a) EXAFS spectrum for NiO in the basic IL. (b) FT of the spectrum.

Figure 6. Phase-corrected Fourier transforms for NiO in the basic IL. (a) Phase-corrected with the chloride shell from NiCl₂. (b) Phase-corrected with the oxide shell from NiO.

Figure 8. (a) EXAFS spectrum for NiO in the acidic IL, N = 0.60. (b) FT of the spectrum.

as NiCl₄²⁻ in the basic AlCl₃/1-butylpyridinium chloride IL. Aqueous solutions of NiCl₂ are also known to have the nickel tetrahedrally coordinated as NiCl₄²⁻ in the presence of excess chloride, which makes the solution Lewis basic. EXAFS is an averaging technique and collects data for all of the nickel interactions. The nickel is expected to be primarily tetrahedrally coordinated and it is possible that some nickel atoms are coordinated with either five or six chloride ions. Niobium chloride dissolved in a similar basic melt is coordinated by five chloride ions in a square pyramid structure. As mentioned above, nickel chloride will coordinate with six chloride ions in an acidic IL. Nickel chloride is also a Lewis acid and it is not well understood how the reaction of the nickel oxide to form the nickel chloride will affect the acidity of the ionic liquid. The Δk and ΔR parameters used in the analysis are given in Table I and the results of the fit are shown in Table II.

The Ni-Cl bond distance was found to be 2.31 Å, which compares well with the bond distance of 2.28 Å found for NiCl₂ dissolved in a basic ionic liquid. A similar reaction has been shown to occur in the gas phase with NiO and AlCl₃. Rao et al. postulated the reaction to be:

\[
6\text{NiO} (s) + 4\text{AlCl}_3 (g) = \text{NiAl}_2\text{O}_4 (s) + 5\text{NiCl}_2 (g) + 2\text{AlOCl} (g)
\]

based on their measurements. The reaction in the basic ionic liquid appears to be different as there is no evidence of NiAl₂O₄ and the reactants are AlCl₄⁻ and Cl⁻. From the EXAFS results, the reaction appears to go almost completely to nickel chloride, and this is likely due to the excess free chloride ions in the basic melt. Schafer et al. have shown that other transition metal oxides will also react with AlCl₃ in the gas phase to either fully or partially chlorinate the metal ions.

The EXAFS data for NiO dissolved in the acidic IL, N = 0.60, are shown in Figure 8a. The k³ weighted Fourier transform, shown in
Figure 7. (a) Fit in k-space for NiO in the N = 0.43 basic ionic liquid using the NiCl₂ reference. (b) Phase-corrected Fourier transform of the fit in the basic IL.

Figure 8. (a) EXAFS spectrum for NiO in the N = 0.60 acidic IL. (b) FT of the spectrum.

Table I. Fourier transform parameters used for isolating the Ni – O, Ni – Cl and Ni – Ni contributions from the experimental compounds.

| Sample                      | Shell     | Δk (Å⁻¹) | ΔR (Å) |
|-----------------------------|-----------|----------|--------|
| NiO in basic melt, N = 0.43 | Ni - Cl   | 2.0–13.0 | 0–2.82 |
| NiO in acidic melt, N = 0.60| Ni - O    | 3.2–12.4 | 1.30–1.96|
|                            | Ni - Cl   | 3.2–13.0 | 1.80–2.48|
|                            | Ni - Ni   | 2.5–13.0 | 1.98–3.08|

Figure 8b, shows multiple peaks which are not seen in the data for NiO in the basic IL. This indicates that there are scattering contributions from multiple species as compared to the basic IL. The peaks at a distance less than 1.5 angstroms are contributions from atomic EXAFS\(^{35,36}\) and were not analyzed. There are three peaks of primary importance located between 1.5 and 3.0 Å in the FT in Figure 8b which has not been phase-corrected. Phase correcting the FT indicates that the first peak is due to oxide, the second is due to chloride and the third is due to nickel and this is discussed below. These multiple shells are likely to consist of unreacted NiO with some contributions possible from NiCl₂, NiOCl and/or NiOCl₂. The peaks were analyzed one shell at a time and that analysis was used to subtract the contributions of that shell from the chi file using the difference file technique.\(^{21,37}\) The nickel shell was analyzed first because it has the largest magnitude. The analysis of the nickel shell indicated 9.7 atoms in the shell and this is primarily due to the unreacted NiO. NiO has a complement of 12 nickel atoms in the first nickel shell. The number is reduced because of the averaging of all of the EXAFS contributions from Ni constituents. The fits in k-space and R-space are very good, shown in Figures 9a and 9b, respectively. In R-space, the imaginary peak is mostly in phase with the positive magnitude and the small misalignment could be due to some overlapping with the adjacent chloride shell. The bond distance was found to be 2.98 Å which is close to the

Table II. EXAFS parameters determined for the NiO in the acidic and basic ionic liquids.

| Sample                      | Shell | N (+/- 10%) | R (Å +/- 0.02 Å) | Δσ² (Å⁻² +/- 5%) | E₀ (eV +/- 10%) | SSR |
|-----------------------------|-------|-------------|-----------------|-----------------|----------------|-----|
| NiO in basic melt, N = 0.43 | Ni - Cl | 4.6         | 2.31            | −0.0012         | 1.80           | 35  |
| NiO in acidic melt, N = 0.60| Ni - O | 3.0         | 2.11            | −0.0012         | −3.41          | 6.9 |
|                            | Ni - Cl | 1.2         | 2.43            | −0.0037         | −1.83          | 14  |
|                            | Ni - Ni | 9.7         | 2.98            | 0.00058         | −5.35          | 65  |

N: coordination number, R: bond distance, Δσ²: mean square relative displacement, E₀: inner potential correction, SSR: sum of the square of residuals between the experimental and the calculated spectra, indicating goodness of fit.
Ni-Ni bond distance of 2.95 Å in NiO crystal. The results of the fit are shown in Table II. The nickel contributions were subtracted from the chi file and the chloride shell was analyzed next.

The analysis of the chloride shell indicated 1.2 chloride ions. This low number is likely due to the low extent of reaction in the acidic melt and is possibly from a nickel oxychloride entity. The acidic melt lacks the free chloride ions that the basic IL has and the free Cl$^-$ could be necessary to drive the chloride complexation reaction to completion. The fits for the chloride shell in k-space and R-space are shown in Figures 10a and 10b, respectively. The symmetrical alignment of the imaginary and positive magnitude peaks indicates that this shell contains only the chloride ion. The chloride contributions were also subtracted from the chi file and the oxide contributions were analyzed. The fits for the oxide shell in k-space and R-space are shown in Figures 11a and 11b, respectively. The analysis of the oxide shell indicated 3.0 oxide ions at a bond distance of 2.11 Å, while in crystalline NiO, the Ni-O bond distance is 2.08 Å and the coordination number is 6.0. The results are shown in Table II. These Ni-O bonds are at least partially due to unreacted NiO and the low coordination numbers for both the nickel and oxygen indicates a small particle size for the remaining unreacted NiO.

To further examine the deconstruction of the chi by subtracting the different backscattering contributions, the calculated chi files for the individual Ni, Cl and O contributions were summed together and compared to the original data. Figure 12a shows the inverse transform of the three shells that were analyzed and compares it with the sum of the calculated files for the Ni, Cl and O contributions, illustrating a good fit. The Fourier transforms of the two spectra are shown in
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