

Electrochemical Study of Copper in the 1-Ethyl-3-Methylimidazolium Dicyanamide Room Temperature Ionic Liquid

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The potential utility of the air- and water-stable ionic liquid 1-ethyl-3-methylimidazolium dicyanamide (EMI–DCA) for electrochemical application was evaluated with copper(I) chloride. The temperature dependency of the density and absolute viscosity of EMI–DCA were measured over a temperature range from 297 to 343 K, and equations describing the dependencies are presented. Due to the ligand property of the DCA anion, both CuCl and CuCl₂ are soluble in EMI–DCA. Cyclic voltammograms of Cu(I) in EMI–DCA and other two ionic liquids were compared. Cu(I) can be oxidized to Cu(II) or reduced to Cu metal in these solutions. The electrodeposition of Cu on glassy carbon and nickel electrodes involves a three-dimensional progressive nucleation and growth process. Scanning electron microscopy and X-ray diffraction results indicate that the morphology of the copper electrodeposits is dependent on the deposition potential, and compact coatings containing nanocrystalline copper could be obtained by potentiostatic electrolysis at low overpotentials. The low viscosity of EMI–DCA and the high solubility of metal chlorides in it would facilitate the electrodeposition of metals using this ionic liquid.

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Room temperature ionic liquids (ILs) obtained from the combination of anhydrous aluminum chloride and 1-ethyl-3methylimidazolium chloride (EMIC)¹ have been extensively studied as the electrolytes for various electrochemical applications such as high-efficiency batteries and electroplating. Numerous examples on the use of chloroaluminate ILs for the electrodeposition of single metals and alloys have been reported.² Their high moisture sensitivity, however, may complicate the incorporation of these ILs into commercial devices. The applications of the ILs has been greatly accelerated by the discovery of the landmark air- and water-stable ionic liquids such as 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄),³ 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄),⁴ and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMP–TFSI).⁵ New ILs have been continuously developed and studied since then.⁶⁻⁸ Ionic liquids such as $EMI-BF_4$ IL was obtained by combining equal molar quantities of EMI⁺ and BF₄. In other words, it can be considered as a neutral IL. It was found, however, that many metal compounds or metal chlorides do not dissolve well in the neutral IL. From a practical point of view, it is of great interest to search for ILs with good solubility, low cost, low viscosity, and a wide potential window.

Recently, low-viscosity ILs based on the dicyanamide (DCA) anion have been synthesized and characterized. Due to the donor ligand property that is known for the dicyanamide anions,⁹⁻¹² many metal compounds are expected to be soluble in the DCA-based ILs by complexing with DCA anions. This feature would make it easier to prepare a bath solution for electrodeposition.

The electrochemistry of copper species has been studied in several ionic liquids. In the Lewis acidic and basic chloroaluminates, anodic dissolution of copper produces Cu(I), which can be reduced to Cu metal.^{13,14} CuCl is insoluble in the EMI–BF₄ IL but was made soluble when excess chloride ions were introduced to form the chloride-rich IL (denoted as EMI–Cl–BF₄), and Cu metal was obtained by the reduction of the Cu(I).¹⁵ Cu(II) was studied in a trimethyl-n-hexylammonium bis(trifluoromethyl)sulfonyl)amide (TMHA–TFSI) IL using the divalent copper salt, Cu(TFSI)₂, as the Cu(II) source.^{16,17} The solubility of CuCl in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMP–TFSI) IL is very limited, and the Cu(I) was produced by anodic dissolution of a copper electrode for the deposition study.¹⁸ The

CuCl is insoluble in the 1-butyl-3-methylimidazolium hexafluorophosphate (BMI–PF₆) IL. However, copper nanoparticles were electrodeposited by direct electrochemical reduction of the CuCl powders attached to the electrode substrate.¹⁹

Although the DCA-based ILs may be a promising electrolyte for the electrodeposition of metals, there is a paucity in the literature regarding the electrodeposition of metals in this IL system. To explore the utility of this IL system, 1-ethyl-3-methylimidazolium dicyanamide (EMI–DCA) (Scheme 1) was synthesized and employed for the electrochemistry and electrodeposition of copper in this work. Both CuCl and CuCl₂ are soluble in the EMI–DCA.

Experimental

Apparatus and chemicals.— The EMI–DCA IL was prepared and purified following the previous literature;¹² however, chloroethane rather than iodoethane was used in this study. All electrochemical experiments were performed under a purified nitrogen atmosphere in a glove box (Vacuum Atmospheres Co.), where both the moisture and oxygen contents were maintained below 1 ppm. Anhydrous CuCl and CuCl₂ (99.999%, Strem) were used as received.

All electrochemical experiments were carried out with an EG&G PARC model 273A potentiostat/galvanostat controlled by EG&G model 270 software. Experiments were performed in a three-electrode cell. For cyclic voltammetry, the working electrodes were a platinum electrode, a nickel electrode, or a glassy carbon electrode. A platinum wire (Alfa Aesar, 99.95%) immersed in ferrocene/ ferrocenium (Fc/Fc⁺ = 50/50 mol %) BMP–TFSI solution contained in a glass tube with a porous Vycor tip (Bioanalytical Systems, MF-2042) was used as a reference electrode; therefore, all the potentials reported in this paper are with respect to this reference. The counter electrode was a spiral copper wire which was immersed in the bulk ionic liquid solution. Electrodeposition experiments were conducted on nickel wires.



Scheme 1. Chemical formula of EMI-DCA ionic liquid.

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Figure 1. (Color online) (a) Density of EMI–DCA as a function of temperature. (b) Relationship between the viscosity of EMI–DCA and temperature.

The surface morphology and elemental composition of the copper coatings were investigated with the Philip XL-40FEG fieldemission scanning electron microscope (SEM) and its auxiliary X-ray energy-dispersive spectroscope (EDS). The crystal structure of the copper coatings was also analyzed by the Rigaku D/MAX 2500 diffractometer.

Measurements of density and viscosity.— Density and viscosity measurements were carried out over a temperature range from 297 to 343 K with a calibrated Pyrex glass dilatometer and an Ostwald viscometer, respectively. The detailed description of the construction of the dilatometer and viscometer, as well as the procedures for the measurements, has been reported elsewhere.^{20,21}

Results and Discussion

The temperature dependence of the selected physical properties of EMI–DCA.— The ionic liquid used for physical property measurements was dried under vacuum at 393 K for 24 h before use; the dilatometer and viscometer had to be airtight. The experimental density data for the EMI–DCA ionic liquid displayed a linear dependence on the absolute temperature as shown in Fig. 1a. By using linear regression techniques, the experimental data were fitted to a linear equation of the form

$$\rho = x_0 + x_1 T \qquad [1]$$

where ρ is the density and *T* is the absolute temperature. The fitted values of the coefficients x_0 and x_1 were found to be 1.5431 and -0.0016, respectively, over a temperature range from 297 to 343 K.

The values of the experimental kinematic viscosity, ν , measured with the viscometer described above, were converted to dynamic or absolute viscosities, η , by

$$\eta = \rho \nu \qquad [2]$$

An Arrhenius plot of ln η vs 1/T was constructed from the experimental data and linearity was obeyed. This linear behavior has also been reported recently;²² the viscosity of EMI–DCA was measured over the temperature range from 297 to 343 K. Figure 1b represents

Table I. Physical properties of the selected room temperature ionic liquids.

| Composition | $\rho (g/cm^3)$ | η (cP) | Reference |
|------------------------|-----------------|-------------|------------|
| EMI-DCA | 1.064(297 K) | 22.7(297 K) | This study |
| EMI-BF ₄ | 1.240(295 K) | 37.7(295 K) | 26 |
| EMI-Cl-BF ₄ | 1.2553(303K) | 48.8(303 K) | 15 |
| EMI-TFSI | 1.520(295 K) | 34.0(295 K) | 26 |
| EMI-TfO ^a | 1.38(298 K) | 45(290 K) | 27 |
| EMI–TfA ^a | 1.285(295 K) | 35(298 K) | 27 |
| EMI–BETI ^a | 1.6(295 K) | 61(299 K) | 27 and 28 |
| EMI-AlCl ₄ | 1.29(298 K) | 17(298 K) | 29 |
| BMI-TFSI | 1.429(292 K) | 52.0(293 K) | 26 |
| BMI-BF ₄ | 1.170(303 K) | 233(303 K) | 26 |
| BMI-PF ₆ | 1.370(303 K) | 312(303 K) | 26 |
| BMP-TFSI | 1.379(301 K) | 67.2(301 K) | 22 |

^a TfO = CF₃SO₃, BETI = $C_4F_{10}NO_4S_2$, TfA = CF₃CO₂.

the linear relationship between ln η and 1/T. A linear equation of the form

$$\ln \eta = y_0 + y_1(10^3 \times 1/T)$$
 [3]

where $\ln \eta$ and $10^3 \times 1/T$, was fitted to the experimental data by using linear regression techniques. The fitted values of y_0 and y_1 were -6.0374 and 2.7076, respectively, within a temperature range from 297 to 343 K.

Table I compares the absolute viscosity and density for some selected room temperature ILs. As can be seen, the viscosity of EMI–DCA is relatively low and comparable to the alkyl-substituted imidazolium-based ionic liquids that employ BF_4^- , PF_6^- , and $TFSI^-$ as the anions. Although the charge in the DCA anion was mainly centered on the amide nitrogen, delocalization across the whole molecule is likely, and it is expected to produce a weak ion–ion interaction, which is important for producing ILs with a low melting point and low viscosity.¹² The much lower viscosity of EMI–DCA IL implies a more efficient mass transport and higher conductivity.

Voltammetric studies.— Figure 2 shows the electrochemical window expressed by linear scan voltammograms of the neat EMI–DCA, EMI–TFSI, and EMI–Cl–BF₄ recorded at a glassy carbon electrode. Because the cathodic limit of the ionic liquids is due to the reduction of the EMI⁺ cation, all three ILs exhibit a similar cathodic limit near -2.4 V. The anodic limit of the ionic liquids is determined by the electrochemical oxidation of the DCA⁻, TFSI⁻, and Cl⁻, respectively. The EMI–DCA exhibits an anodic limit near



Figure 2. Staircase linear scan voltammograms recorded at a GC electrode at 313 K for (A) EMI–DCA, (B) EMI–Cl–BF₄, and (C) EMI–TFSI melts. The scan rate was 50 mV s⁻¹.



Figure 3. Staircase cyclic voltammograms recorded at a Pt electrode at 313 K for 50 mM Cu(I) in (A) EMI–DCA, (B) EMI–Cl–BF₄, and (C) EMI–TFSI. Scan rate was 50 mV/s.

1.1 V, which is less positive than that of the EMI–TFSI (1.8 V) but more positive than that of the EMI–Cl–BF₄ (0.5 V). This figure also suggests that if there was any chloride impurities present in the EMI–DCA, oxidation of chloride impurities would be observed near 0.5 V.

Up to 1.1 M of CuCl and 0.9 M of CuCl₂ can be dissolved in the EMI-DCA ionic liquid at room temperature. Similar to previous studies reported for copper species in other ionic liquids, ^{16,17} it was found that, while the Cu(I) solution is stable in the presence of copper, Cu(II) reacts with Cu to produce Cu(I). Shown in Fig. 3A is the cyclic voltammogram recorded on a polycrystalline Pt electrode of a 50 mM Cu(I) solution in an EMI-DCA ionic liquid prepared by the direct dissolution of CuCl into the ionic liquid. For comparison, Fig. 3B and C illustrates the cyclic voltammogram of a 50 mM Cu(I) solution in the chloride-rich EMI–Cl–BF₄ and the EMI–TFSI ionic liquid, respectively. Note that because the solubility of CuCl in the EMI-TFSI ionic liquid is very limited, Cu(I) solution has to be generated by anodic dissolution. However, CuCl dissolves readily in the EMI-Cl-BF4 ionic liquid. All three voltammograms exhibited two redox couples. When the potential was initially scanned from the rest potential toward the positive direction, Cu(I) was oxidized to Cu(II) at wave a2 and the Cu(II) was re-reduced back to Cu(I) at wave c2 when the potential scan was reversed. When the potential was initially scanned from the rest potential toward the negative direction, Cu(I) was reduced to Cu metal at wave c1 and the deposited Cu metal was reoxidized back to Cu(I) at wave a1 when the potential scan was reversed. As seen in these voltammograms, the redox potentials of both the Cu(II)/Cu(I) and Cu(I)/Cu(0) couples in the EMI-DCA and EMI-Cl-BF₄ ionic liquids occurred at potentials more negative than those observed in the EMI-TFSI ionic liquid, consistent with the fact that the DCA⁻ and Cl⁻ anions are more basic coordination ligands that complex with the Cu(II) and Cu(I) more strongly than the TFSI⁻ anion does. It can also be seen that the peak potential separation between the cathodic peak and the anodic peak for the Cu(II)/Cu(I) couple in the EMI–DCA ionic liquid was much less than that observed in the EMI-TFSI ionic liquid. Furthermore, the peak current for the reductions of $\text{Cu}(\text{II})/\text{Cu}(\bar{\text{I})}$ and Cu(I)/Cu(0),respectively, in the EMI-DCA IL was higher than that in the EMI-TFSI and EMI-Cl-BF4 ILs. These results may be ascribed to the more facile charge-transfer kinetics in the EMI-DCA IL, and the lower viscosity of the EMI-DCA IL compared to that of the EMI-TFSI and EMI-Cl-BF₄ ILs. While the reduction potential of the Cu(I)/Cu(0) reaction in the EMI–DCA IL was slightly more negative than that in the EMI–Cl–BF₄ IL, the oxidation potential of the Cu(I)/ Cu(II) reaction in the EMI-DCA IL was more positive than in the EMI-Cl-BF₄ IL. This may indicate that, while Cu(I) is more stable in EMI-DCA IL, Cu(II) is more stable in EMI-Cl-BF₄. These re-



Figure 4. Staircase cyclic voltammograms of 50 mM M Cu(I) in EMI–DCA recorded at (A) GC and (B) Ni electrodes at 313 K. Scan rate was 50 mV/s.

sults demonstrate that the type of the anions in the ILs can play an important role in the chemical behavior of the metal species.

Diffusion coefficients of Cu(I) and Cu(II) species, respectively, were estimated using data taken from chronoamperometry experiments of 50 mM Cu(I) and Cu(II) solutions, respectively, on Pt and GC electrodes. For the Cu(I) species, the potential was stepped from the open-circuit potential (OCP) of the Cu(I) solution to 0.10 V,



Figure 5. Comparison of the dimensionless experimental curves derived from current–time curves shown in the insets with the theoretical models for 3D nucleation/growth process. Insets: current–time transients of the chrono-amperometric experiments recorded at GC and Ni electrodes for 50 mM CuCl in EMI–DCA ionic liquid at 313 K.

where the oxidation reaction was diffusion limited. For the Cu(II) species, the potential was stepped from OCP to -0.28 V, corresponding to the limiting currents for the reduction of Cu(II). For both species the current was found to follow the Cottrell behavior, and the diffusion coefficients were calculated using the Cottrell equation.²³ Consistent with the lower viscosity of EMI–DCA IL, the diffusion coefficient found for Cu(I) and Cu(II) in EMI–DCA were 2.13×10^{-6} and 2.06×10^{-6} cm² s⁻¹, respectively, which were significantly larger than those reported in EMI–Cl–BF₄ [2.3 × 10⁻⁷ and 1.5×10^{-7} cm² s⁻¹ for Cu(I) and Cu(II), respectively].¹⁵

Cyclic voltammograms of copper species were also recorded at nickel and glassy carbon electrodes as shown in Fig. 4. The same redox couples observed in Fig. 3A were observed in these voltammograms except that the Cu(I)/Cu(II) redox couple could not be observed at the Ni electrode because Ni was oxidized at a potential less positive than the oxidation of Cu(I). Unlike at the Pt electrode, the deposition of copper at the Ni and GC substrates requires a nucleation overpotential, as clearly indicated by the presence of the "nucleation loop" in the voltammograms. To study the nucleation process, chronoamperometry experiments were carried out in quiescent solutions containing 50 mM Cu(I). These experiments were carried out by stepping the potential of the working electrode from where no reduction takes place to potentials sufficiently negative to initiate the nucleation/growth process after a short induction time, t_0 . Typical current-time transients resulting from these experiments are shown in the insets in Fig. 5. The transients exhibited the classic shape for a nucleation process; after the capacitive current decay, the current increased slowly until a current maximum, $i_{\rm m}$, was reached at time $t_{\rm m}$. The nucleation/growth process has been classified as either "instantaneous" or "progressive." The instantaneous model refers to the situation in which all nucleation sites are activated at the beginning of the potential step, whereas the progressive model refers to the situation in which the nucleation sites gradually become activated as the chronoamperometric experiment proceeds. To distinguish between the two nucleation/growth models, the data taken from the chronoamperometric experiments were compared to the theoretical dimensionless $(i/i_m)^2$ vs (t/t_m) curves developed by Sharifker et al.²⁴ for three-dimensional (3D) instantaneous and progressive nucleation, respectively. Before the fitting, the experimental *t* and t_m were corrected to $t'(=t - t_o)$ and $t'_m(=t_m - t_o)$. The experimental and theoretical plots of $(i/i_m)^2$ vs (t'/t'_m) are shown in Fig. 5. It is apparent that the electrodeposition of Cu at both electrodes involves a 3D-progressive nucleation/growth process. According to Scharifker's model, the product $i_m^2 t$ should be independent of the applied deposition potential, and can be related to the concentration and diffusion coefficient of Cu(I) species as Eq. 4

$$i_{\rm m}^2 t = 0.2598(nFC)^2 D$$
 [4]

where *n* is the number of charge transferred per Cu(I), *F* is the faradaic constant, *C* is the concentration of Cu(I), and *D* is the diffusion coefficient. The $i_m^2 t$ product obtained from the experimental *i*-*t* transients varied between 12 and 16 with an average of 14.2, whereas the product estimated using the diffusion coefficient determined from the Cottrell equation was 12.9. The 3D-progressive nucleation/growth process was also observed in a previous investigation for the electrodeposition of copper on GC electrode in basic chloroalumintate ionic liquids.¹⁴

Electrodeposition and characterization of copper.— Electrodeposition of Cu was performed in EMI–DCA containing 50 mM Cu(I) using bulk controlled-potential electrolysis experiments on nickel wires (surface areas = 0.08 cm^2). In the electrodepositing experi-



Figure 6. SEM micrographs of the copper electrodeposits that were prepared on nickel wires at 313 K by electrolysis of solutions of 50 mM CuCl in EMI-DCA at -1.55, -1.65, -1.70, and -1.80 V. The charge passed during the electrolysis was 300 mC.



Figure 7. (A) SEM micrographs of the as-deposited copper that was prepared at 313 K by electrolysis of a solution of 50 mM CuCl in EMI–DCA at -1.65 V. The charge for the electrolysis was 300 mC. (B) EDS profile of the sample shown in (A).

ments, a spiral wire of Cu was directly immersed in the electrolytic solution as the counter electrode in order to compensate for the consumption of the Cu(I) species. After each electrolysis experiment the Cu-deposited sample was rinsed thoroughly with deionized water, dried, and examined by SEM, EDS, and X-ray diffraction (XRD). Figure 6 depicts SEM images of typical as-deposited Cu samples. This figure shows that the electrodeposits produced at lower overpotentials (-1.55 and -1.65 V), at which the deposition rate is low, have a dense, fine-grained, and compact surface containing hemispherical nodules. As the deposition potential is made pro-



Figure 8. (a) XRD patterns (Cu K α) of Cu-deposited Ni-wire samples shown in Fig. 7A. (\bullet):Cu and (\blacksquare):Ni. (b) The fwhm of the Cu(111) peak.

gressively more negative to -1.75 and -1.80 V, the deposits become less compact and less uniform; cauliflower structures of different sizes are observed. The formation of cauliflowers is apparently due to the increased deposition rate. The micrograph of the surface in higher magnification shown in Fig. 7A reveals that the nodules are the cluster of Cu nanocrystals with average sizes of about 40–100 nm. EDS analysis of the sample shown in Fig. 7B indicates that it is free of the ionic liquid residual. The XRD patterns of a typical Cu-deposited sample are shown in Fig. 8. This figure clearly shows the characteristic diffraction patterns of crystalline Cu. From the full-width at half-maximum (fwhm) of the Cu(111) peak, the averaged grain size of Cu was estimated using Scherrer's equation²⁵ to be about 40 nm. This value agrees well with the SEM micrograph shown in Fig. 7A.

Conclusion

The viscosity of the EMI–DCA IL is lower than the BF_4 , PF_6 , and TFSI-based ILs and exhibits the Arrhenius temperature dependence. CuCl and CuCl₂ are very soluble in the EMI–DCA IL. The reduction potentials observed for the Cu(II)/Cu(I) and Cu(I)/Cu(0) redox couples in the DCA-based ILs are different from those reported in EMI–TFSI and EMI–Cl–BF₄ ILs. Metallic copper coating could be obtained on a Ni substrate by the potentiostatic reduction of Cu(I). The morphology of the as-deposited Cu coating depends on the deposition potential. SEM and XRD results indicate that the electrodeposits contained nanocrystalline Cu. The results observed in this study reveal that DCA-based ILs would be useful electrolytes for electrodeposition.

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References

- J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, *Inorg. Chem.*, 21, 1263 (1982).
- G. R. Stafford and C. L. Hussey, in *Advances in Electrochemical Science and Engineering*, R. C. Alkire and D. M. Kolb, Editors, Wiley-VCH, Weinheim (2001), Vol. 7, p. 275.
- 3. J. S. Wilkes and M. J. Zaworotko, J. Chem. Soc., Chem. Commun. 1992, 965.
- P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. De Souza, and J. Dupont, Polyhedron, 15, 1217 (1996).
- D. R. MacFarlane, P. Meakin, J. Sun, N. Amini, and M. Forsyth, J. Phys. Chem. B, 103, 4164 (1999).
- 6. F. Endres, Phys. Chem. Chem. Phys., 3, 144 (2002).
- 7. A. P. Abbott and K. J. McKenzie, Phys. Chem. Chem. Phys., 8, 4265 (2006).

- 8. Electrochemical Aspects of Ionic Liquids, H. Ohno, Editor, John Wiley & Sons, New York (2005).
- 9. S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray, and R. Robson, J. Chem. Soc.,
- Chem. Commun., 1998, 439.
 J. L. Manson, C. R. Kmety, Q. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein, and J. S. Miller, Chem. Mater., 10, 2552 (1998).
- 11. M. Kurmoo and C. J. Kepert, New J. Chem., 22, 1515 (1998).
- 12. D. R. MacFarlane, S. A. Forsyth, J. Golding, and G. B. Deacon, Green Chem., 4, 444 (2002).
- 13. B. J. Tierney, W. R. Pitner, J. A. Mitchell, and C. L. Hussey, J. Electrochem. Soc., 145, 3110 (1998).
- 14. J. J. Lee, B. Miller, X. Shi, R. Kalish, and K. A. Wheeler, J. Electrochem. Soc., 148, C183 (2001).
- 15. P.-Y. Chen and I.-W. Sun, Electrochim. Acta, 45, 441 (1999).
- 16. K. Murase, K. Nitta, T. Hirato, and Y. Awakura, J. Appl. Electrochem., 31, 1089 (2001).
- 17. T. Katase, K. Murase, T. Hirato, and Y. Awakura, J. Appl. Electrochem., 37, 339 (2007).
- 18. S. Zein El Abedin, A. Y. Saad, H. K. Farag, N. Borisenko, Q. X. Liu, and F. Endres,

Electrochim. Acta, 52, 2746 (2007).

- 19. L. Yu, H. Sun, J. He, D. Wang, X. Jin, X. Hu, and G. Z. Chen, Electrochem. Commun., 9, 1374 (2007).
- 20. J. R. Sanders, E. H. Ward, and C. L. Hussey, J. Electrochem. Soc., 133, 325 (1986).
- 21. J. R. Sanders, E. H. Ward, and C. L. Hussey, J. Electrochem. Soc., 133, 1526 (1986).
- 22. M.-J. Deng, P.-Y. Chen, and I.-W. Sun, Electrochim. Acta, 53, 1931 (2007). A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York (1980), Chap. 5.
- 24. B. Scharifker and G. Hills, Electrochim. Acta, 28, 879 (1983).
- 25. B. D. Cullity and S. R. Stock, Elements of X-Ray Diffraction, Prentice-Hall, Englewood Cliffs, NJ (2001), Chap. 5.
- 26. R. Hagiwara and Y. Ito, J. Propul. Power, 105, 221 (2000).
- S. J. Zhang, N. Sun, X. Z. He, X. M. Lu, and X. P. Zhang, J. Phys. Chem. Ref. Data, 35, 1475 (2006).
- 28. I. Romero-Sanz, I. Aguirre-de-Carcer, and J. Fernandez de la Mora, J. Propul. Power, 21, 239 (2005).
- A. A. Fannin, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes, and J. L. Williams, *J. Phys. Chem.*, 88, 2614 (1984).