than by placing the sample in a large and homogeneous temperature field. Second, the cathode (aluminum) and anode (platinum) have different thermal conductances (2 and 0.7 W/cm K, respectively).

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Microelectrode Evaluation of Transition Metal-Aluminum Alloy **Electrodepositions in Chloroaluminate Ionic Liquids**

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ABSTRACT

Chronoamperometric data collected at a 250 µm tungsten microelectrode were analyzed under near-steady-state con-Clinoidal periode the data confected at a 250 µm tangsten increated to be were analyzed under near-steady-state con-ditions to determine the composition of MAl_x alloys (M = Co, Ni, Fe, Cu, and Ag) electrodeposited from 1.5:1.0 AlCl₃:1-ethyl-3-methylimidazolium chloride room temperature ionic liquids. The analysis method relied on the fact that these alloys are produced by an underpotential deposition mechanism. Results were consistent with previous studies showing that the CoAl_x, FeAl_x, and CuAl_x systems tended to produce alloys with $x \approx 1$. Analysis of the NiAl_x data was complicat-ed by kinetic phenomena, while data analysis of the AgAl_x system was precluded by dendritic growth of the electrode-nosit. All the allow systems complex anodic stripping voltametric behavior and the nature of the oxidation posit. All the alloy systems showed complex anodic stripping voltammetric behavior, and the nature of the oxidation processes (e.g., metal anodization, alloy anodization, or selective dealloying) are different for electrodeposits produced in specific potential regimes. Nonlinear curve fitting of the chronoamperometric data to the appropriate short-time and long-time equations gave diffusion coefficients from 3.9×10^{-7} to 8.3×10^{-7} cm² s⁻¹ for the transition metal ions in the ionic liquid electrolyte at ca. 22°C.

Introduction

Ultramicroelectrodes display a number of unique characteristics which are extremely useful for investigating electrochemical processes: minimal distortion of the faradaic response by uncompensated IR, reduction in the contribution of double-layer capacitance to the overall current response, and onset of steady-state currents at long times.¹ To readily achieve these desired properties, the diameter of embedded disk ultramicroelectrodes is typically $\leq 50~\mu$ m. However, somewhat larger disk electrodes (e.g., diameters $\leq 250 \mu$ m), termed simply microelectrodes for purposes of this paper, offer similar benefits if care is taken to analyze the current responses appropriately.²⁻⁴ These microelectrodes are easy and cheap to construct; they exhibit uniform (with some edge enhancement) and reproducible current densities over the electroactive surface, regardless of counter electrode placement; and the entire electrode area is easily observed during in situ optical microscopy investigations.²

Over the past several years, we and others have exploited ultramicroelectrodes and microelectrodes to examine a variety of electrochemical processes in molten salt electrolytes. Many of these studies were performed in room temperature chloroaluminate molten salts to examine the electrochemistry of the melt ions,6 heterogeneous electron-transfer kinetics, $^{7-11}$ homogeneous electrochemical kinetics, $^{8-10}$ halide complexation, 12 alkali metal reduction potentials, 13,14 the deposition-stripping of lithium^{5,15,16} and sodium,^{5,16} and the nucleation-growth of aluminum electrodeposits.4 Ultramicroelectrodes¹⁷ and microelectrodes¹⁸ also have been employed for studies in high-temperature molten salts, where these analytical tools have provided unique insight into processes which are extremely difficult to evaluate with other electrochemical techniques.

Several research groups have reported the electrodeposition of transition metal-aluminum alloys from room temperature chloroaluminate ionic liquids^{19–28} and from alkali metal chloroaluminates melts.^{28–32} Most intriguing are the electrochemical systems in which the transition metal reduction potential is considerably positive of the aluminum metal reduction potential.^{20,23-25,27,31} In these cases, the transition metal-aluminum alloy is formed by a mechanism in which aluminum is incorporated into the alloy through what can be considered either the underpotential deposition (UPD) of aluminum onto the transition metal electrodeposit or the free energy gained by formation of the bimetallic alloys.^{23–25,31} For purposes of this paper, we refer to these systems as "UPD-formed" alloys because they are formed at potentials positive of bulk aluminum deposition; the term does not necessarily define the mechanism of alloy formation.

The compositions of the UPD-formed alloys are a function of the electrodeposition potential^{23-25,27,31} and can be a function of the transition metal ion concentration in the ionic liquid electrolyte.²³ Unfortunately, particularly in the

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room temperature ionic liquid electrolytes, it has proven to be difficult to prepare alloy samples amenable to accurate elemental analysis. Therefore, researchers have employed a number of electroanalytical methods to evaluate the alloy compositions, including chronoamperometry, steady-state rotating disk voltammetry, anodic linear sweep voltamme-try, and rotating ring-disk voltammetry.^{23-25,27,31} In this paper, we report a simple electroanalytical procedure that exploits the near-steady-state current (I_{NSS}) achieved at 250 µm tungsten microelectrode to determine the composition of several UPD-formed aluminum alloys in the 1.5:1.0 AlCl_s:1-ethyl-3-methylimidazolium chloride (EMIC) ionic liquid. This analytical method is extremely easy to implement and can be applied to electrodeposition in more experimentally challenging electrolytes; for example, similar 25 µm tungsten ultramicroelectrodes have been used to study Li/Li(I) and Bi/Bi(III) in LiCl-KCl at 400°C.6

Experimental

All electrochemical studies were performed under an inert atmosphere (He or Ar) inside a Vacuum Atmospheres glove box or in a custom optical electrochemical cell.⁴ Electrochemical experiments were carried out with an EG&G Princeton Applied Research model 273 potentiostat/galvanostat controlled with the EG&G PARC 270 software package operating on a PC platform. In situ optical observations were made with a Nikon Epiphot metallurgical inverted microscope equipped with bright-field/dark-field objectives. Nonlinear least squares regression analyses were performed with Kaleidagraph[®] for Windows[®] running on a 486 PC platform.

For all electrochemical studies, the working electrode was a 250 μ m tungsten disk microelectrode, constructed as previously described.⁴ The CoAl_x studies were performed with Al/Al(III) reference and counter electrodes as described earlier.²⁴ To simplify the experimental setups, all other MAl_x (M = Fe, Ni, Cu, Ag) alloy studies were performed using an M wire reference electrode and a Pt wire counter electrode, both inserted directly into the analyte solution. The M wire reference electrode establishes a reversible couple with its corresponding metal ion [e.g., Ni/Ni(II)] dissolved in the analyte.

Analyte solutions were prepared by dissolving the appropriate anhydrous transition metal chloride in a 1.5:1.0 AlCl₃:EMIC ionic liquid. CuCl (99.995%, Aldrich) was used as received. $CoCl_2 \cdot xH_2O$ (99.999%, Aldrich), NiCl₂·6H₂O (99.9999%, Aldrich), and FeCl₂·4H₂O (99.995%, Aldrich) were dried by heating to 100–120°C under vacuum prior to use. AgCl was prepared from AgNO₃ and KCl, followed by in vacuo heat drying.

Results and Discussion

Chronoamperometric current response at a disk microelectrode.—For a small disk electrode, an extremely useful general expression describing the diffusion-controlled current (I_D) as a function of the time (t) following a potential step has been given by Aoki and Osteryoung²

$$I_{\rm D} = 4nFD(C - C_{x=0}) r[f(\tau)] = 4nFDC r[f(\tau)]$$
[1]

for $C_{x=0} = 0$. In this expression, *n* is the number of electrons involved in the electrochemical process; *F* is the Faraday constant; *D* is the diffusion coefficient of the diffusing species; *C* is the bulk concentration of the diffusing species; $C_{x=0}$ is the concentration of the diffusing species at the electrode surface, which is driven to zero for potentials in the limiting current regime; *r* is the radius of the electrode; and $f(\tau)$ is the function describing the shape of the current response, where $\tau = 4Dt/r^2$. For a stationary disk microelectrode, $f(\tau)$ takes on two forms, depending on the value of τ . For $\tau > 1.44$

$$f(\tau) = 1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} - 0.00646\tau^{-5/2}$$
[2]

and for $\tau < 0.82$

$$f(\tau) = (\pi/4\tau)^{1/2} + \pi/4 + 0.094\tau^{1/2}$$
[3]

Over the range $0.82 < \tau < 1.44$ the curves calculated from Eq. 2 and 3 agree to within 0.5%, allowing extension of Eq. 2 and 3 to $\tau > 0.82$ and $\tau < 1.44$, respectively. As shown later, the diffusion coefficient for the transition metal ions in the room temperature melts is ca. 5×10^{-7} cm² s⁻¹; hence, at the 250 µm diam disk electrodes used in our studies, Eq. 2 and 3 are applicable for t > 64 s and t < 112 s, respectively. However, as shown next, it is not necessary to know the form of $f(\tau)$ to determine the alloy compositions.

We use CoAl_x to illustrate the application of Eq. 1. First, the chronoamperometric diffusion-controlled limiting current response for Co(II) reduction to Co metal, at any time, is given by

$$I_{\rm D}[{\rm Co(II)}] = 4(2)FDCr[f(\tau)]$$
[4]

while the current response during the concurrent reduction of Co(II) and Al(III) to produce a $CoAl_x$ alloy at more negative potentials is given by

$$I_{\rm D}[{\rm Co(II)} + x{\rm Al(III)}] = I_{\rm D}({\rm CoAl}_x) = 4(2 + 3x)FDCr[f(\tau)]$$
[5]

In both Eq. 4 and 5, the diffusion coefficient and concentration terms are those for the Co(II) solute, because the alloy deposition process is diffusion limited in Co(II); that is, reducible Al(III) present as $Al_{2}Cl_{7}^{-}$ is in large excess.²⁴ Also, the condition $C_{x=0} = 0$ is satisfied for both equations as long as measurements are made sufficiently negative of the Co/Co(II) formal reduction potential. Hence, by sampling the current at the same time during the Co metal and CoAl_x alloy chronoamperometric transients, $f(\tau)$ is the same for both Eq. 4 and 5, and the two equations can be combined and rearranged to give

$$x = \text{Al:Co} = \left(\frac{2}{3}\right) [I_{\text{D}}(\text{CoAl}_x) - I_{\text{D}}(\text{Co})] / [I_{\text{D}}(\text{Co})]$$
 [6]

Application of Eq. 6 does not require knowledge of the solute concentration or of its diffusion coefficient; instead, by simply collecting chronoamperometric data at a potential for pure metal electrodeposition and over the potential range for MAl, alloy production, the compositions of the UPD-formed alloys can be calculated. Although Cottrellian analysis of the chronoamperometric data can also be used to perform a similar compositional determination, it employs linear least squares fitting over a designated time period, and so it only provides an average composition for the electrodeposit formed over the chosen time period.^{24,31} Also, chronoamperometric data at short times can be distorted by nucleation phenomena, kinetic effects, and double-layer charging; therefore, results obtained from Cottrellian procedures can be dependent on the experimentalist's choice of data to analyze (e.g., the time period), giving rise to ambiguities in the analysis procedures.²⁴ To avoid the problems encountered at short times, we apply Eq. 6 only at longer times in the near-steady-state regime where $I_{\rm D}$ becomes $I_{\rm NSS}$; however, in principle, Eq. 6 can be used to monitor the alloy composition throughout the electrodeposition process.

Equation 6 offers a simple means for rapidly screening UPD-formed alloy compositions. In addition, proper application of Eq. 1–3 can provide the diffusion coefficient for the transition metal solute ion from the same chrono-amperometric experimental curves. For the remainder of this paper we illustrate these techniques using several MAl_x systems.

Although we refer to the binary metal electrodeposits as alloys throughout this paper, the exact structures of these electrodeposits are not known. Structural analysis is complicated because the alloys tend toward an amorphous structure as the aluminum content is increased, and ex situ compositional analysis [e.g., scanning electron microscopy/ energy-dispersive spectroscopy (SEM/EDS)] is not straightforward because the chloroaluminate melt is often entrained in the metallic electrodeposit.^{20,24,26} Therefore, the simple in situ analytical procedure described here is extremely valuable for identifying the electrodeposition con-



Fig. 1. SCVs for 81 mM Co(II) in 1.5:1.0 AlCl₃:EMIC. Letters indicate different stripping regions (see text). Switching potentials [V vs. Al/Al(III)]: 0.4, 0.1, -0.1; scan rate 50 mV s⁻¹.

ditions required to produce binary alloys having particular compositions.

Cobalt metal and cobalt-aluminum alloys.—Staircase cyclic voltammograms (SCVs) at a 250 μ m diam tungsten disk microelectrode in 1.5:1.0 AlCl₃:EMIC containing 81 mM CoCl₂ are shown in Fig. 1. As described in our earlier paper, the metal or alloy deposition and stripping processes depend upon the switching potential (E_{λ}) .²⁴ In particular, three distinct stripping waves are observed for electrodeposits which have been previously designated as Co metal $(E_{\lambda} = 0.4 \text{ V}, \text{peak A})$; an alloy of nominal composition CoAl₁ $(E_{\lambda} = 0.1 \text{ V}, \text{peak B})$; and an alloy approaching the composition CoAl₂ $(E_{\lambda} = -0.1 \text{ V}, \text{peak C})$.²⁴

The concurrent appearance and disappearance of distinct peaks at different stripping potentials implies that the chemical nature of the oxidation processes (e.g., metal anodization, alloy anodization, or selective dealloying) are different for the binaries electrodeposited in specific potential regimes. Changes in the kinetics of the stripping process would cause gradual shifts in the stripping peaks and may play a role in the stripping process; however, kinetics are only a perturbation of the more dramatic chemical influences.

Chronoamperometric experiments performed over the potential range 0.5–0.7 V, where only Co metal is deposited, are shown in Fig. 2. For times less than 10 s, the current transients are governed by nucleation and growth phenomena, making standard Cottrellian analysis extremely difficult or impossible to perform. Instead, by continuing to record the current transient at longer times, the



Fig. 2. Chronoamperometric transients for Co metal electrodeposition influenced by nucleation and growth phenomena. Deposition potentials [V vs. Al/Al(III)]: (A) 0.7, (B) 0.6, (C) 0.575, (D) 0.55, (E) 0.525, and (F) 0.5.

currents approach the near steady state, and the analysis procedures discussed previously are easily applied. This is clearly seen in Fig. 3, where the microelectrode current data sampled at 60 ms intervals for a chronoamperogram collected over the full potential range of interest are transposed and plotted in a current vs. potential format at different sampling time intervals. The curves are therefore equivalent to normal pulse voltammograms collected at different pulse times.³³ In Fig. 3, the current vs. potential curves are presented in four frames, each corresponding to sampling time regimes in which the current responses are similar in behavior. (i) From 0.25 to 1 s, currents for Co metal are nonexistent (0.6–0.4 V) due to slow nucleation of this metal phase; however, the alloy phases are nucleated much more rapidly at the higher overpotentials. In this time regime, no alloy compositional analysis is possible. (ii) From 1 to 5 s, Co metal electrodeposition begins to appear; however, the curves display erratic behavior due to nucleation phenomena which greatly distort the potential region from 0.6–0.4 V. Again, this time regime is useless for alloy analysis. (iii) From 5 to 10 s, the curves begin to display limiting current plateaus similar to normal pulse voltammograms, but they are still too distorted for data analysis. (iv) From 10 to 20 s, the curves resemble normal pulse voltammograms with a prepeak at the start of the Co metal wave; this prepeak is a result of nucleation which delays the expected Cottrell decay at low overpotentials. At sampling times approaching 20 s (indicated in figure), the curves appear as normal pulse voltammograms with characteristics of near-steady-state diffusion control, i.e., the current for each successive curve does not decay as rapidly as expected for Cottrell behavior.³³ Therefore, only in this final time regime can one begin to consider alloy analysis. We believe it is better to use even longer times. such as 120 s, to insure that nucleation and kinetic effects do not perturb the diffusion-controlled analysis; however, based on these results, it is possible to following the CoAl_x electrodeposition process after 10 to 20 s. In fact, this method of transposing chronoamperometric data into current vs. potential data is an effective method for determining the time regime over which Eq. 6 can be applied.

Chronoamperometric curves recorded from 0.525 to 0.0 V are shown in Fig. 4. The two traces for Co metal electrodeposition at 0.525 and 0.5 V overlap completely and are indistinguishable from each other in the figure. As the potential shifts to more negative potentials, $CoAl_x$ alloys are produced, and the currents increase accordingly. At deposition potentials more negative of 0 V, the nucleation and growth of a bulk aluminum metal phase occurs concurrent with the diffusion-limited deposition of a $CoAl_{1.7}$ (vide infra) alloy phase; this is illustrated by the four chronoamperograms in Fig. 5.

Equation 6 was applied to the data in Fig. 4 to determine the CoAl_x alloy compositions at various electrodeposition potentials ($E_{\rm deposit}$). Figure 6 presents both the nearsteady-state currents at t = 120 s (dashed line, left y axis) and x in CoAl_x calculated from Eq. 6 (solid line with open triangles, right y axis) as a function of $E_{deposit}$. The open triangles represent x values calculated for the individual experiments, and these values are tabulated in Table I for selected experiments. Also, the thickness of the alloy electrodeposits were estimated from compositionally weighted densities of the pure metals, and these values are also listed in Table I. The solid triangles represent x values determined from SEM/EDS analysis on thicker alloy samples, as reported previously.²⁴ An x value of zero is indicative of pure Co metal electrodeposition. The nearly horizontal $I_{\rm NSS}$ region from 0.6 to almost 0.4 V in Fig. 6 corresponds to a diffusion-limited current plateau for Co metal electrodeposition; however, this current plateau contains contributions from both linear and nonlinear diffusion terms.³³ After the Co metal current plateau, the $I_{
m NSS}$ values increase as the potential traverses the alloy-forming regions. As seen in Fig. 6, the values of x in $CoAl_x$ display plateauing at alloy compositions of approximately CoAl_{0.8} and CoAl_{1.7}. The first plateau starts and ends at CoAl_{0.6} and CoAl₁, re-

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spectively, while the second plateau starts at $CoAl_{1.6}$ but is interrupted by bulk aluminum electrodeposition at more negative potentials (Fig. 5). The *x* values agree with our earlier assessment of the $CoAl_x$ system; however, the use of Eq. 6 is simple and unambiguous, unlike the problems we encountered when trying to apply the standard Cottrell equation to current transients at larger Pt electrodes.²⁴

The rises and plateaus for x in CoAl_x are more clearly seen in the derivative dx/dE which is plotted with the xvalues in Fig. 7. The value of the derivative function is negative because x increases is the potential becomes more negative. The rising current regions correspond to maxima in the derivative plot and are labeled R1 and R2, while the two plateau regions appear as minima and are labeled P1 $(0.6 \le x \le 1)$ and P2 $(x \ge 1.6)$. To illustrate the general applicability of Eq. 6 for this system, the data in Fig. 4 were also analyzed at t = 30, 60, and 90 s. The resulting x values, including results for t = 120 s, are shown in Fig. 8. The x values at each potential are constant for all times during experiments performed at electrodeposition potentials greater than 0.15 V, while the shorter time analyses begin to deviate to lower x values as the potential becomes more negative of 0.15 V (i.e., beyond the CoAl₁ composition). We believe this deviation is due to nucleation or kinetic phenomena which influence the shorter time data; however, these perturbations are minimal at times approaching the near-steady-state regime. Importantly, Fig. 8 demonstrates the ability of this microelectrode analytical procedure to monitor the alloy composition throughout the deposition process. Based on the



Fig. 3. Plots of current vs. potential for CoAl_x electrodeposition obtained by transposing chronoamperometric data. Resulting "normal pulse" curves are grouped into four time regimes with each curve corresponding to a 60 ms change in sampling time. Currents generally decrease as sampling time increases.

Fig. 4. Current transients for cobalt metal at (+) 0.525 and (\Box) 0.50 V and for CoAl_x alloy formation at (∇) 0.40, (\times) 0.35, (\triangle) 0.30, (\Box) 0.20, (\diamond) 0.10, and (\bigcirc) 0.0 V.

Fig. 5. Current transients showing the nucleation and growth of aluminum onto a CoAl_x alloy underlayer. Deposition potentials [V vs. Al/Al(III)]: (A) 0.0, (B) -0.05, (C) -0.10, and (D) -0.15.

results in Fig. 8, $CoAl_x$ alloys with $x \le 1$ are homogeneously electrodeposited from t = 30 to 120 s, while alloys with x > 1 are electrodeposited with an apparent increase in aluminum content over this same time period. As discussed earlier, the behavior of the $CoAl_x$ electrodeposition cannot be followed for times much less than 10 s due to nucleation and kinetic phenomena.

Fig. 6. Plots of $\{-, -\}$ $I_{\rm NSS}$ at 120 s and of $\{-\Delta-\}$ x in CoAl_x as a function of deposition potential. Solid triangles represent EDS values from Ref. 24.

Table I. Near-steady-state analysis for the chronoamperometric electrodeposition of CoAl_x at a 250 μm tungsten microelectrode.

$E_{ m deposit}$ [V vs. AI/Al(III)]	$x ext{ in CoAl}_x ext{ from } I_{ ext{NSS}} ext{ at } 120 ext{ s}$	Deposit thickness (µm)
0.50	0.00	0.07
0.40	0.04	0.08
0.35	0.32	0.10
0.30	0.61	0.14
0.25	0.75	0.15
0.20	0.89	0.16
0.15	1.05	0.19
0.10	1.23	0.20
0.05	1.41	0.21
0.00	1.59	0.22
-0.05	1.70	0.24

It is also possible to perform nonlinear curve fitting analysis with Eq. 4 to determine the diffusion coefficient for Co(II) in these systems. The experimental current transients recorded at $E_{deposit} = 0.55$ and 0.50 V (i.e., potentials for Co metal electrodeposition) from 70 to 120 s were initially fit with Eq. 2 [i.e., long-time $f(\tau)$] substituted into Eq. 4 using the Co(II) diffusion coefficient as the adjustable fitting parameter. This procedure gave $D_{Co(II)} =$ $4.4 imes 10^{-7}$ and $4.3 imes 10^{-7}$ cm² s⁻¹ at 0.55 and 0.50 V, respectively. Values of τ calculated from these diffusion coefficients were 0.78 and 1.34 for 70 and 120 s, respectively. These τ values fell into the regime where either Eq. 2 or 3 can be used in Eq. 4; therefore, nonlinear curve fitting was repeated using Eq. 3 [i.e., short-time $f(\tau)$] substituted into Eq. 4. For both 0.55 and 0.50 V data, the fitting procedure with Eq. 3 gave $D_{\text{Co(II)}} = 4.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, in agreement with the values obtained using Eq. 2. Figure 9 shows fits

Fig. 7. Plots of $(-\bullet-) dx/dE$ and $(-\Delta-) x$ in CoAl_x as a function of deposition potential.

Fig. 8. Plots of x in CoAl_x as a function of deposition potential at $t = \{\Delta\}$ 30, $\{\nabla\}$ 60, $\{\Box\}$ 90, and $\{O\}$ 120 s.

Fig. 9. Nonlinear curve fitting analysis (solid line) using Eq. 2 and 4 of the current transients for Co metal electrodeposition. Raw data collected at 50 ms intervals are indicated as points.

obtained using Eq. 2 and 4 and illustrates the slow current decay at relatively long times in the near-steady-state regime. Therefore, this fitting procedure provides a straightforward means for determining diffusion coefficients from the same chronoamperometric data used to calculate alloy compositions. Also, it is noteworthy that the fitting error was less than 0.1% for all analyses, although we estimate an error of approximately 5–10% arising from other experimental uncertainties (e.g., metal ion concentration and electrode radius).

Finally, we demonstrate that the chronoamperometric response for alloy electrodeposition does indeed follow the behavior predicted by Eq. 1. Using $D_{\text{Co(II)}} = 4.4 \times 10^{-7} \text{ cm}^2$ s^{-1} , the combination of Eq. 1 and 2 was fit to different time intervals of the chronoamperometric data using n as the fitting parameter. Nonlinear least squares fitting was performed over time intervals of 60-120 s, 90-120 s, and 110-120 s and at alloy electrodeposition potentials of 0.4, 0.3, 0.2, 0.1, and 0.0 V. The resulting n values were then converted to *x* values in CoAl_{*x*} using x = (n - 2)/3. These *x* values, as well as x values calculated from Eq. 6, are summarized in Table II, and the fits over the time interval 90-120 s are shown in Fig. 10. From Table II it is apparent that the more laborious nonlinear fitting procedures are in agreement with the x values calculated from Eq. 6. Also, the nonlinear least squares fits in Fig. 10 are quite good, although the data do not decay as rapidly as predicted at 0.2 and 0.1 V and are almost constant over this time regime for the

Table II. Values for x in CoAl_x calculated from Eq. 6 at 120 (column 2) and from nonlinear least squares fitting of Eq. 1 and 2 to different chronoamperometric time intervals.

$E_{ m deposit}$	<i>x</i> at 120 s	<i>x</i> 60–120 s	<i>x</i> 90–120 s	<i>x</i> 110–120 s
0.4	0.04	0.04	0.06	0.06
0.3	0.61	0.63	0.64	0.65
0.2	0.89	0.88	0.91	0.92
0.1	1.23	1.21	1.25	1.27
0.0	1.59	1.50	1.57	1.61

Fig. 10. Nonlinear least squares fits to $CoAl_x$ chronoamperometric data over the 90–120 s time interval. Electrodeposition potentials are indicated on the figure.

0.0 V electrodeposition. This latter observation is most likely caused by the electrodeposition of a roughened, or dendritic, alloy electrodeposit. Such a deposit gives rise to a gradual increase in the electroactive area, which in turn counters the small current decay expected under these near-steady-state conditions. The effects of surface roughening are mitigated, however, because as the chronoamperometric currents approach near-steady-state conditions, the diffusion layer takes on a hemispherical geometry with a radius that is expected to be larger than the features of the roughened surface. Therefore, Eq. 1 (with Eq. 2 or 3) and 6 are applicable even when the surface is not ideally flat. Importantly, there is no need to perform the more laborious nonlinear least squares analyses; instead, Eq. 6 is simple to apply and does not require determination of the diffusion coefficient for the limiting ion, i.e., Co(II) in this case. Also, as discussed earlier, fitting of the chronoamperometric data over a time interval assumes that the electrodeposit maintains a constant composition throughout the deposition process; however, this may not be true. Instead, single time analysis using Eq. 6 allows prediction of the variability in electrodeposit composition (see Fig. 8).

Iron metal and iron-aluminum alloys.—Staircase cyclic voltammograms at a 250 μ m diam tungsten disk microelectrode in 1.5:1.0 AlCl₃:EMIC containing 50 mM FeCl₂ are shown in Fig 11. The reference electrode was an iron wire inserted directly into the analyte melt; consequently, potentials are referenced to the Fe/Fe(II) couple. For all five voltammograms, a 10 s hold was performed at the switching potential prior to scan reversal. For voltammo-

Fig. 11. SCVs for 50 mM Fe(II) in 1.5:1.0 AlCl₃:EMIC. Letters indicate different stripping regions (see text). Switching potentials [V vs. Fe/Fe(II)] with 10 s holds: -0.45, -0.5, -0.55, -0.65, and -0.75; scan rate 200 mV s⁻¹.

Fig. 12. Plots of (- - -) $l_{\rm NSS}$ at 120 s and (- Δ -) x in FeAl_x as a function of deposition potential.

grams with $E_{sw} = -0.45$, -0.5, and -0.55, a reduction wave for Fe(II) was not easily observed; however, stripping peaks designated A and B in Fig. 11 were obtained. At more negative switching potentials, a reduction wave became apparent, and the new stripping peak C appeared. Based on the three distinct stripping peaks, it appears that the FeAl_x system is similar to the CoAl_x system in that it exhibits at least three chemically distinct oxidation phenomena which are dependent upon the composition of the electrodeposit.

Chronoamperometric data for the FeAl, system were collected for 120 s over the Fe and $FeAl_x$ electrodeposition potential range. The current transients were perturbed by nucleation phenomena at all potentials studied, similar to that reported previously for the Co and CoAl, system.²⁴ However, even though the chronoamperometric transients exhibited a nucleation-derived peak up to 40 s after the initial potential step, the use of $I_{\rm NSS}$ values at 120 s in Eq. 6 mitigates any detrimental effects these perturbations have on the compositional analysis. Therefore, the $I_{\rm NSS}$ values at 120 s are shown in Fig. 12, and values calculated for x in $FeAl_r$ using Eq. 6 are summarized in Fig. 12 and in Table III. The potential for Fe metal electrodeposition was taken as -0.35 V because it corresponds to the beginning of the first current plateau for Fe(II) reduction in Fig. 12. As reported for $CoAl_x$, ²⁴ the FeAl_x system appears to favor an *x* value of 1; however, *x* values from 0 up to at least 1.55 are accessible. These compositional results are in agreement with numbers obtained by Mitchell and Hussey in similar FeAl_x systems.³⁴

In addition to recording the chronoamperometric responses, anodic stripping voltammetry (ASV) was performed on each 120 s electrodeposit to provide insight into

Table III. Near-steady-state analyses for the chronoamperometric electrodeposition of FeAl_x and NiAl_x alloys at a 250 µm tungsten microelectrode.

	$E_{doposit}$	
x in FeAl_x	[V vs. Ni/Ni(II)]	x in NiAl_x
0.00	-0.325	0.00
0.06	-0.35	0.02
0.16	-0.375	0.06
0.45	-0.40	0.12
0.66	-0.45	0.23
0.86	-0.50	0.33
0.95	-0.55	0.45
0.98	-0.60	0.48
1.08	-0.65	0.50
1.23	-0.70	0.53
1.55	-0.75	0.63
2.65	-0.775	0.79
6.42	-0.80°	$\sim \! 14^{\rm b}$
	$\begin{array}{c} x \text{ in FeAl}_x \\ \hline \\ 0.00 \\ 0.06 \\ 0.16 \\ 0.45 \\ 0.66 \\ 0.86 \\ 0.95 \\ 0.98 \\ 1.08 \\ 1.23 \\ 1.55 \\ 2.65 \\ 6.42 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

^a Codeposition of bulk Al metal. ^b Calculated from 120 s data.

Fig. 13. ASVs for Fe and FeAl_x electrodeposits made at [(−−−), peak A only] −0.35, [(−−−), peak B only] −0.50, and [(- - -), peaks A and C only] −0.75 V.

peaks A, B, and C seen in Fig. 11. Anodic scans were performed by sweeping positively at 50 mV s⁻¹ from the opencircuit potential of the electrodeposits. The ASV potential scans, illustrated in Fig. 13, displayed the same stripping peaks as seen in Fig. 11; however, the constant potential deposition aided in peak assignment. Therefore, the ASV experiments provided the following information: (i) peak A gradually broadened and shifted from 0.062 to 0.018 V as E_{deposit} varied from -0.35 to -0.45 V; (ii) peak B appeared for electrodeposits produced at -0.475 to ca. -0.65 V, while peak A was a shoulder or was completely absent in this potential range; and (iii) peak A reappeared and peak C appeared for electrodeposits produced at -0.70 to -0.80 V, while peak B was absent in this potential range. At -0.85 V, bulk aluminum began to electrodeposit concurrently with the FeAl_x alloy. As discussed previously for CoAl_x, the three anodization peaks most likely correspond to three chemically distinct stripping phenomena. In the case of $FeAl_x$ alloys electrodeposited between -0.70 and -0.80 V, the presence of both peaks A and C points toward a selective dealloying of aluminum, as previously discussed for the $CoAl_x^{24,25}$ and $NiAl_x^{23}$ systems. By comparing the results in Fig. 12 and Table III with the stripping behavior observed for the ASV experiments, it is apparent that the ASV stripping peaks correlate with distinct compositional regions in Fig. 12. Therefore, we tentatively assign the following compositional ranges for each of the stripping peaks—peak A: $0 \le x \le 0.16$; peak B: $0.3 \le x \le 0.95$; and peak C: $1 \le x \le 1.55$.

Nonlinear curve fitting was used to fit Eq. 1–3 to the chronoamperometric transient recorded at -0.35 V for Fe(II) reduction to Fe metal. Data from 70 to 120 s were employed to lessen contributions from nucleation perturbations. In this time regime, both long-time (Eq. 2) and short-time (Eq. 3) formulas for $f(\tau)$ are applicable. Using n = 2, C = 50 mM, and the Fe(II) diffusion coefficient as the adjustable fitting parameter, analysis gave $D_{\text{Fe(II)}} = 3.9 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for both $f(\tau)$ formulas.

Nickel metal and nickel-aluminum alloys.—To prepare the Ni(II) analyte solution, sufficient anhydrous NiCl₂ was added to a 1.5:1.0 AlCl₃:EMIC melt to produce a 34 mM solution; however, only a portion of the NiCl₂ dissolved, and so, the saturated Ni(II) concentration was used to analyze the NiAl_x system. Importantly, application of Eq. 6 does not require knowledge of the metal ion concentration.

Staircase cyclic voltammograms recorded in the Ni(II) melt are shown in Fig. 14 with potentials referenced to the Ni/Ni(II) couple. Although electrodeposits were produced over the potential range from -0.3 to -0.4 V, a well-defined reduction wave was not observed until the potential was negative of -0.4 V. Stripping peak A is associated with the anodization of Ni metal or possibly NiAl_x alloys having low aluminum content. Anodization of the NiAl_x alloys pro-

Fig. 14. SCVs for saturated Ni(II) in 1.5:1.0 AlCl₃:EMIC. Letters indicate different stripping regions (see text). Switching potentials [V vs. Ni/Ni(II)] with 10 s holds: -0.4, -0.5, -0.6, -0.7, and -0.8; scan rate 50 mV s⁻¹.

duced negative of -0.4 V gave rise to stripping peaks B and C, again indicative of selective aluminum dealloying. The stripping behavior was confirmed with ASV experiments and is consistent with a previous study on NiAl_r alloys.²³

Chronoamperometric currents measured at 120 s did not show consistent behavior across the entire potential range of interest (vide infra); therefore, data collection was extended to 300 s. The $I_{\rm NSS}$ values at 300 s are shown in Fig. 15, and values calculated for x in NiAl_x using Eq. 6 are summarized in Fig. 15 and in Table III. The potential for Ni(II) reduction was taken from the first current plateau at -0.325 V. Deposition potentials were limited to -0.775 V because Al metal began to electrodeposit along with the alloy phase at -0.80 V. Therefore, the UPD-formed NiAl_x alloy begins to form at a potential approximately 0.45 V positive of bulk Al metal, which agrees with the UPD shift of ca. 0.4 V reported for Al on Ni.²³

Using $I_{\rm NSS}$ currents recorded at 120 s, the *x* values for NiAl_{*x*} were within ±0.02 of the corresponding values calculated at 300 s for potentials from -0.325 to -0.5 V; however, for potentials from -0.55 to -0.70 V, the *x* values at 120 s displayed random scatter with an average value of 0.49 (±0.04).

Under the electrodeposition conditions used here, NiAl_x appears to favor an alloy composition of ca. NiAl_{0.5}; however, higher aluminum contents can be achieved at more negative potentials. Pitner et al. demonstrated that the compositions of the NiAl_x alloys are a function of the exact experimental conditions [e.g., Ni(II) concentration and current density)] and that the alloying process is influenced by nucleation and kinetic phenomena.²³ Therefore, even in rather complicated systems, the application of I_{NSS}

Fig. 16. SCVs for 59 mM Cu(1) in 1.5:1.0 AlCl₃:EMIC. Letters indicate different stripping regions (see text). Switching potentials [V vs. Cu/Cu(1)] with 10 s holds: -0.5, -0.6, -0.7, and -0.75; scan rate 100 mV s⁻¹.

appears to be a useful technique as long as currents are recorded at sufficiently long times to allow the deposition process to be completely under diffusion control.

Copper and silver metals and copper-aluminum alloys.— Staircase cyclic voltammograms at 250 µm tungsten microelectrodes in 1.5:1.0 AlCl₃:EMIC containing 59 mM Cu(I) and 44 mM Ag(I) are shown in Fig. 16 and 17, respectively. Copper and silver wires were used as reference electrodes, respectively. Aluminum metal electrodeposition began at -0.80 V vs. Cu(I)/Cu and at -0.84 V vs. Ag/Ag(I). Cathodic waves for the reduction of Cu(I) and Ag(I) to their metals were easily observed, and scan reversal gave rise to welldefined stripping waves. In the case of Cu(I), scans to more negative potentials displayed a second reduction wave at ca. -0.6 V, corresponding to CuAl_x alloy formation. In the case of Ag(I), a reduction wave at -0.8 V was observed which we tentatively assign to the formation of AgAl_x alloys; however, we have not been able to calculate the composition of this material using the near-steady-state approach.

During Cu and CuAl_x anodization experiments (i.e., SCV scan reversal and ASV of chronoamperometric electrodeposits), stripping peak A in Fig. 16 was present during Cu metal anodization, while peaks A, B, and C were all present during the anodization of the CuAl_x alloy. Anodization of Ag metal gave rise to a well-defined stripping peak in region A of Fig. 17. Scan reversal at potentials within the Al metal electrodeposition wave produced new peaks labeled B and C (see expanded curve in Fig. 17) and caused the

Fig. 15. Plots of (- - -) I_{NSS} at 300 s and (-- Δ --) x in NiAl_x as a function of deposition potential.

Fig. 17. SCVs for 44 mM Ag(I) in 1.5:1.0 AICl₃:EMIC. Letters indicate different stripping regions (see text). Switching potentials [V vs. Ag/Ag(I)] with 10 s holds: -0.8, -0.9, and -0.95; scan rate 100 mV s⁻¹.

Fig. 18. Plots of (- - -) I_{NSS} at 120 s and (- Δ -) x in CuAl_x as a function of deposition potential.

stripping behavior in region A to develop multiple peaks or to broaden. Although the stripping behavior in both systems points toward selective dealloying of aluminum, at this time we do not speculate further on the nature of the stripping peaks.

Chronoamperometric data for the CuAl_x system were collected for 120 s over the Cu and CuAl, electrodeposition potential range. Unlike the cobalt, iron, and nickel systems, the current transients showed minimal nucleation effects. The I_{NSS} values and the values for x in CuAl_x are presented in Fig. 18. Diffusion-controlled reduction to Cu metal is clearly apparent from the current plateau from -0.1 to -0.5 V. The UPD-formed CuAl_x alloys begin to form at -0.5 V and reach a composition of CuAl_{0.9} before bulk Al electrodeposition at -0.8 V. The values for x in CuAl_x are also tabulated in Table IV. The behavior of the copper system seen at the microelectrode is consistent with that reported by Tierney et al.²⁷

Efforts to obtain $I_{\rm NSS}$ values for the silver system were thwarted by a continual slow rise in the near-steady-state current with time. In situ optical studies⁴ of this phenomena revealed long Ag metal dendrites growing from the periphery of the tungsten microelectrode. The growth of these dendrites into solution increased the effective electrode area by pushing through the diffusion layer, ultimately causing the overall current to increase. Therefore, a necessary condition for proper application of the nearsteady-state analysis is the avoidance of excessive den-dritic growth during the electrodeposition process. Generally, we have satisfied this condition for the other alloy systems by keeping the deposition times short so that electrodeposits are <1 μ m thick.

Finally, the chronoamperometric current transients recorded at -0.2 V for both Cu(I) and Ag(I) reduction to their respective metals were used to obtain diffusion coefficients for the metal ions. Nonlinear curve fitting analysis, employing Eq. 1 and 3, was applied to the data from 0 to 50 s to give $D_{\rm Cu(l)}=8.3 imes 10^{-7}~{
m cm}^2~{
m s}^{-1}$ and $D_{\rm Ag(l)}=6.4 imes$ $10^{-7} \text{ cm}^2 \text{ s}^{-1}$

Conclusions

Near-steady-state analysis of chrononamperometric data collected at a microelectrode is an effective means for analyzing the electrodeposition of MAl_x from room tempera-

Table IV. Near-steady-state analysis for the chronoamperometric electrodeposition of CuAl, at a 250 µm tungsten microelectrode.

E _{deposit} [V vs. Cu/Cu(I)]	x in CuAl _x from $I_{\rm NSS}$ at 120 s	E _{deposit} [V vs. Cu/Cu(I)]	x in CuAl _x from I _{NSS} at 120 s
-0.40	0.00	-0.65	0.62
-0.50	0.02	-0.70	0.76
-0.55	0.25	-0.75	0.89
-0.60	0.38	-0.775	0.90

ture chloroaluminate ionic liquids. The analytical approach forwarded here is generally applicable to alloys formed via an underpotential deposition (UPD) mechanism, is easy to implement, and provides a continuous monitor of the electrodeposition process. In addition, proper application of the general equations describing the chronoamperometric current response provides a means for determining the diffusion coefficient for the current-limiting metal ion in the electrodeposition process.

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Amorphous Nb/Fe-Oxide Ion-Storage Films for Counter **Electrode Applications in Electrochromic Devices**

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ABSTRACT

The electrochromic properties of mixed Nb/Fe-oxide films with amorphous structure which were prepared via the sol-gel route were determined. Films with Nb/Fe molar concentration ratios 0.2:1, 0.4:1, and 1:1 exhibit ion-storage capacities up to 18 mC/cm² depending on Nb/Fe molar ratio. Electrochromically films behave as optically passive electrodes with a coloration efficiency of nearly zero at $\lambda > 480$ nm, while at shorter wavelengths a relatively strong anodic coloring was observed, yielding negative coloration efficiencies up to -20 cm²/C. Coloring/bleaching changes of films are correlated with the ex situ IR spectroscopic measurements of charged/discharged films showing distortions of the film structure with Li⁺ ion insertion/extraction reactions. Electrochemical stability of Nb/Fe (0.4:1)-oxide films was tested up to 2000 cycles in a sol-gel electrochromic device consisting of sol-gel-derived WO_3 films and hybrid organic/inorganic ionic conductor with ionic conduc-tivity of about 10^{-4} S/cm serving for lamination of the electrodes.

Introduction

Electrochromic (EC) devices have attracted interest for automotive applications and "smart" windows for buildings.^{1,2} Most EC devices rely upon the layers and films which are produced by vacuum deposition methods and semisolid Li⁺-doped organic polymeric ion conductors. The sol-gel route, however, in combination with the dipcoating technique,⁴ is a unique way of making electrochromic films, ion-storage counter electrodes,5 and hybrid organic/inorganic materials with ionic conductivity (ormolytes).^{6,7} Flexibility of the sol-gel processing for forming novel materials and films with multicomponent structure represents the main advantage of the sol-gel processing, making the preparation of laminated EC devices assembled entirely from films and layers obtained via the sol-gel route possible, i.e., all sol-gel EC devices.8

WO₃ films are the most frequently used materials for EC devices irrespective of how they are produced. Their electrochemical and electrochromic properties are decisive for the development of other cathodically colored active electrochromic films (like Nb_2O_5 for example⁹) and for ion-storage counter electrode films.¹⁰ The counter electrode films should provide the balance of charges which are exchanged during coloring/bleaching of an EC device. Their ion-storage capacity and cycling stability must be comparable to that of the active coloring film to compensate for the Li⁺ insertion/extraction reactions occurring at the active electrochromic film.

Despite the indispensability of counter electrodes for the functioning of EC devices, their development has been slow compared to WO₃ films. Many are incompatible with WO₃, their cycling stability is only a few hundred cycles or their ion-storage capacity is below 10 mC/cm², which is too low to be acceptable for devices with WO₃ active films.⁵

Counter electrodes can be optically passive, i.e., their transmittance should remain unchanged during the $\rm Li^+$ ion insertion/extraction reactions (like $\rm CeO_2^{-8,10-12}$ and SnO₂^{13–15}), or may color in a complementary way (like Niand Co-oxides¹⁶⁻¹⁸) with respect to the coloration of WO_3 films. The last category refers to counter electrodes which are classified with mixed cathodic/anodic electrochromism.¹⁹ V₂O₅, a typical example, is ranked among the most promising ion-storage films known. This is because films with ion-storage capacity up to 35 mC/cm² can be easily produced either by vacuum or wet deposition (solgel techniques).20 The main drawback is the pronounced mixed anodic/cathodic electrochromism, which brings about a decrease in film transmittance with Li⁺ insertion in the visible spectral range while producing an increase in transmittance at shorter wavelengths (λ < 400 nm). This increase is caused by bandgap widening.²¹ As a result, the color of the films changes from yellow to green, giving rise to an unacceptable coloration of the device employing V_2O_5 and WO_3 films.

Cogan et al.²² attempted to decrease the relatively strong mixed anodic/cathodic electrochromism of V2O5 films by depositing mixed Nb/V-oxide films. Accordingly, because of the cathodic coloring, sputtered $Nb_{0.6}V_{1.04}O_2$ films exhibit a coloration efficiency of approximately $5 \text{ cm}^2/\text{C}$ in the visible spectral range, while at $\lambda < 400$ nm strong anodic coloration gives a negative coloration efficiency value $-40 \text{ cm}^2/\text{C}$). The results show that the cathodic coloring in the visible spectral range cannot be completely eliminated, signifying that Nb/V oxide films are still unsuitable for practical EC device applications. In addition, the films exhibit slow oxidation (noted during cyclic voltammetry measurements), which indicates a relatively sluggish Li* insertion/extraction reaction in this type of mixed oxide