ELECTROCHEMICAL SCIENCE



Deposition Studies of Lithium and Bismuth at Tungsten Microelectrodes in LiCI:KCI Eutectic

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ABSTRACT

Tungsten microelectrodes (diam = 25μ m) have been used to study the deposition and stripping behavior of Li/Li⁺ and Bi/Bi³⁺ in the LiCl:KCl eutectic at 400°C. The Li deposition current can be simulated assuming the growth of a single hemisphere of liquid metal on the microelectrode. High stripping current densities were observed and quantitated using standard electrochemical equipment. An inverted microscope assembly was employed for *in situ* observation of the Li/Li⁺ deposition and stripping processes at the microelectrode. A precipitate appears to form in the melt surrounding the electrode during Li deposition.

The lithium/iron disulfide battery using a molten LiCl/ KCl electrolyte has been proposed for use as a high power, rapid discharge (pulse) battery (1). During discharge, current densities in excess of 100 A cm⁻² are expected. Because of these high current densities it is difficult to monitor and to analyze the electrochemical processes using conventional electrochemical equipment.

Microelectrodes with dimensions of only a few microns have properties which make them ideal for the study of high current density processes (2). Because of their small size, IR drops are minimized thus reducing errors in the measurement of potentials. In addition, low absolute currents are realized allowing use of conventional electrochemical equipment. We have demonstrated the effectiveness of these electrodes to study species of high concentration in the ambient-temperature chloroaluminate molten salt, AlCl₃:ImCl, (Im⁺ = 1-ethyl-3-methylimidazolium). A 25 μ m diam tungsten disk electrode was used to investigate the reduction of the 5.1M Im⁺ cation, the oxidation of the 1M Cl⁻ anion, and the oxidation of the 4.1M AlCl₄⁻⁻ anion (3).

The LiCl:KCl eutectic has a Li⁺ concentration of 17M and a Cl⁻ concentration of 30M at 450° C (4); such a media provides a test of the applicability of microelectrodes for the study of high faradaic current-density processes in an aggressive environment.

Experimental

Equipment.-Tungsten was chosen as the material for the microelectrodes. Tungsten does not alloy with Li as do a large number of other metals, including Pt (4, 5). Also, it appears that tungsten can be used to study the chloride/ chlorine couple; however, a W(O)/W(II) couple ($E^{\circ} = 0.142V$ vs. Ag/Ag⁺ reference electrode) in LiCl:KCl has been described in the literature (6). This couple may interfere with the use of tungsten at very anodic potentials. The tungsten microelectrode was constructed by sealing a length of 25 μ m diam tungsten wire (Alfa) in 1 mm id \times 1/4 in. od Pyrex capillary tubing under vacuum to avoid oxidation of the tungsten wire. Copper wire with a small winding of Al wire was then inserted into the glass capillary tubing; careful melting of the Al winding under vacuum resulted in good electrical contact between the tungsten and copper wires. The sealed end of the glass was ground to expose a tungsten microdisk of 25 µm diam. The microdisk was polished with alumina powder starting with 1 μ m and progressing to 0.05 μ m.

The counterelectrode consisted of a tungsten wire immersed directly in the LiCl:KCl eutectic melt. It was not placed in a separate compartment since, for each set of experiments, minimal currents were drawn; therefore, no changes occurred in the melt composition due to reactions at the counterelectrode. The reference electrode consisted of a Ag wire immersed in LiCl:KCl eutectic melt 0.08M in AgCl. This reference melt was contained in a 5 mm NMR tube which was dipped into the analyte melt; ion conductivity of the glass at the temperatures of the studies provided electrical contact between the reference electrode and the analyte solution. With this reference electrode assembly, the Li/Li+ couple varied somewhat from one cell assembly to the next probably due to large junction potentials. Initial Li deposition potentials ranged from -2.7 to -3.1V for different cell assemblies. These potentials are cathodic of the accepted value for the $\bar{\rm Li}/{\rm Li^+}$ couple of -2.59V vs. a Ag/Ag⁺ reference electrode (4). However, the potential of a given reference electrode remained constant for all experiments performed with each cell assembly as indicated by the reproducible Li deposition behavior. Efforts to measure the open-circuit potential after depositing Li onto the microelectrode were thwarted by attack of the insulating glass by the Li.

The Pyrex electrochemical cell was constructed as shown in Fig. 1. The cell was 1 in. in diam and approximately 8 in. in length. The lower portion of the cell was inserted into another glass tube of larger diameter. Adequate temperature control was obtained by wrapping this outer glass tubing with heating tape and insulation. A 1/16 in. K-type thermocouple was inserted between the heating tape and the outer glass tubing, and this thermocouple was connected to an Omega CN 5000 Series temperature controller. The temperature of the melt, however, was monitored by a 1/16 in. K-type thermocouple sheathed in glass and placed directly in the melt. This dual thermocouple arrangement prevented overheating of the melt which may have resulted due to a time lag for heat transfer from the heating tape to the melt. A gas sparging tube (1/4 in. Pyrex) and the microelectrode assembly were introduced through the top of the cell using a Teflon o-ring assembly inserted into a 14/20 ground glass joint. The counterelectrode, thermocouple, and Ag reference wire were introduced through side-arm tubes capped with a rubber septum.

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Fig. 1. High-temperature cell: (a) Pyrex glass cell; (b) 0.08M Ag⁺/Ag reference electrode; (c) 25 μ m diam W microelectrode; (d) W counterelectrode; (e) K-type thermocouple sheathed in Pyrex glass; (f) W microdisk sealed in Pyrex glass; (g) Cu lead wire with Al wire solder; (h) 25 mm o-ring joint; (i) Teflon valve.

Cyclic staircase voltammetry and normal pulse voltammetry were performed with a PAR Model 273 potentiostat/ galvanostat which was controlled by a computer system similar to that described elsewhere (7).

The microscope used was a Leitz Diavert inverted microscope placed on a Micro-G (Technical Manufacture Corporation) vibration isolation table.

Melt preparation.—Melt charges (ca. 10g) were prepared by grinding together 59 mole percent (m/o) LiCl (anhydrous, Alfa) and 41 m/o KCl (J. T. Baker) under helium. The electrochemical cell, with the melt charge added, was then assembled. The melt purification method was similar to that reported in the literature (8). The melt was heated to 200°C under vacuum for several hours. A flow of anhydrous HCl was introduced into the melt charge, and the temperature was raised to 400°C (eutectic mp = 352°C) to melt the charge. This HCl purge was maintained for 1h before finally purging the molten eutectic with argon for *ca.* 1h.

Results and Discussion

Cyclic voltammetry.—Lithium, rather than potassium, is the alkali metal initially deposited from the melt (9). Before Li deposition was examined at the tungsten microelectrode, it was necessary to cycle the potential of the microelectrode several hundred millivolts beyond that required for Li deposition to observe the initial appearance of a small Li deposition current. Following this, repeated scans to less cathodic potentials resulted in rapid growth of the Li deposition current until reproducible Li deposition behavior was observed. This pretreatment appears to clean the electrode, possibly removing an oxide layer from the tungsten surface.

Cyclic staircase voltammograms for Li deposition at a 25 μ m tungsten electrode are shown in Fig. 2 and 3. The quantity of Li stripped upon scan reversal in Fig. 2 is obviously less than that deposited. Reaction of Li with the Pyrex glass is probably the main cause of this discrepancy (5). Scanning to a more cathodic potential, Fig. 3, results in an $E_{\rm p}^{\rm c}$ at ca. -3.4V for Li deposition and a rapid rise in the current occurs beyond -3.7V. Scan reversal shows two stripping peaks at -3.4 and -2.9V. Although the exact fea-



Fig. 2. Reduction of Li⁺ to Li(liq) at 25 μ m W in LiCl:KCl eutectic at 405°C. Staircase cyclic voltammogram, scan rate = 2 V s⁻¹.

tures of the cathodic scans beyond -3.7V were variable, the peak at -3.4V followed by the rapid rise was qualitatively reproducible for different electrodes. Extended use of an electrode resulted in severe corrosion of the insulating glass leading to increased deposition currents and to the inability to distinguish the two deposition processes. The less cathodic reduction and stripping peaks are due to deposition of liquid Li, while the more cathodic reduction may be due to reduction of K⁺ from the melt. It is unlikely that a Li/K alloy forms since Li is reported to not form alloys with other alkali metals (5). At this stage, we can only speculate at the process giving rise to the more cathodic deposition process.

A staircase cyclic voltammogram for oxidation of Cl⁻ to Cl₂ is shown in Fig. 4. The curve was reproducible. The linearity of the curve indicates ohmic behavior. Assuming the current is strictly controlled by IR drop, the slope of the Cl⁻ oxidation voltammogram can be used to estimate a cell resistance of 700 Ω . For a planar microdisk electrode, the cell resistance was calculated from Eq. [1]

$$R = \rho/4r$$
 [1]

where ρ is the melt resistivity and *r* is the radius of the electrode (10). Taking the resistivity of LiCl:KCl eutectic to be 0.64 Ω cm (4), the cell resistance is calculated to be 127 Ω . While not identical, the same order of magnitude resistance values obtained in both calculations indicate that the IR drop may be the dominant parameter controlling the shape of the Cl⁻ oxidation curve. For Cl⁻ oxidation, the low IR drop advantage of the microelectrode is not realized; however, the Cl⁻ concentration is at an extreme of 30*M*! Smaller microelectrodes would be required to examine the Cl⁻ oxidation in any detail.

Although it is likely that the Li deposition curve is also influenced by IR drop, it is not dominated by this effect. This is probably a result of the increasing effective radius of the working electrode as the liquid Li is deposited.



at 405°C. Staircase cyclic voltammogram, scan rate = 4 V s^{-1} .



Fig. 4. Oxidation of Cl⁻ to Cl₂ at 25 μ m W in LiCl:KCl eutectic at 405°C. Staircase cyclic voltammogram, scan rate = 4V s⁻¹.

Double potential step chronoamperometry (DPSC).— Since it was desired to examine very high current densities at the microelectrodes, double potential step chronoamperometry (DPSC) was used to monitor Li deposition and stripping. The DPSC experiments were performed after treating the tungsten electrode using cyclic staircase voltammetry as described above. A DPSC experiment is shown in Fig. 5 in which the first step was from a conditioning potential of -1.0V to a Li deposition potential of -3.3V. After 1s of Li deposition, the potential was stepped to -1.0V resulting in rapid stripping of the Li. The time and data aquisition parameters were chosen such that data points were taken at 4 ms intervals; therefore, during the stripping process, the first data point was taken 4 ms after stepping back to -1.0V.

The current density during stripping of Li is extremely high. Using the area of the tungsten disk $(4.9 \times 10^{-6} \text{ cm}^2)$, a current density of 1300 A cm⁻² is calculated from the stripping current of 6.4 mA. This high current density is maintained for several milliseconds before a rapid decay in current is observed. There appears to be an upper limit to the stripping current as can be seen by the grouping of data points immediately following the step to -1.0V; this limitation is not due to instrumental constraints. As will be discussed later, this limitation may be due to precipitation of KCl from the resulting K⁺-rich melt in the vicinity of the microelectrode.

The current density can also be calculated using the area of the Li hemisphere resulting from the 1s deposition at -3.3V. For a 1s deposition at 1 mA, as in Fig. 5, a Li hemisphere of 40 µm should be deposited, giving a stripping current density of 64 A cm⁻². This lower current density is based on the maximum quantity of Li deposited and should be taken as a minimum current density value. The



Fig. 5. Current-time behavior for DPSC of Li on 25 μ m W electrode. Maximum current on deposition at -3.3V is 200 A cm⁻² (curve A), and on stripping at -1.0V is 1300 A cm⁻² (curve B). Current densities are calculated based on area of disk, 4.9×10^{-6} cm². (1 mA = 200 A cm⁻².)

true current density will vary as the Li is stripped. Also, integration of the deposition and stripping curves, indicates that only 30-50% of the deposition charge is recovered during stripping. This is a result of Li corrosion of the insulating glass and of physical loss of liquid Li from the electrode surface.

The Li deposition current vs. time behavior is better seen in Fig. 6 where the depositions were performed at increasing overpotentials, η . For high overpotentials, the deposition current initially drops and reaches a minimum before gradually increasing. This initially decreasing current is difficult to analyze; the current transient at these short times may include charging currents as well as nucleation phenomena (11). Following this initial decrease, the current gradually increases indicating growth of the Li deposit. The current density during Li deposition at high overpotentials increases from 100 to 200 A cm⁻² based on the area of the tungsten microdisk.

To analyze the current behavior at the microelectrode during Li deposition, it is important to remember that at the temperature of this study Li (mp = 179° C) is liquid. The Li deposition behavior observed here is very similar to that seen for other deposition studies such as Hg deposition from aqueous solution on Pt (12, 13) and carbon microelectrodes (12), and Hg deposition from aqueous solution on small Ir electrodes (14). These prior studies successfully analyzed the deposition process assuming a nucleation phenomenon followed by hemispherical diffusion-controlled growth of the deposition in a similar manner.

One important difference between this and previous studies is the extremely high concentration of Li⁺ vs. the low concentrations (1-100 mM) of electroactive species in the previous studies. With the high Li⁺ concentration and assuming instantaneous nucleation, enough liquid Li is deposited within the first milliseconds to fully coat the tungsten electrode. At the minima in the high-overpotential curves in Fig. 6, the radius of the Li hemisphere, calculated from the charge passed, is ca. 10 μ m. Therefore, the radius of the growing Li hemisphere is approximated by the radius of the microdisk at t = 0 s, *i.e.*, $r_0 = 12.5 \,\mu$ m. In previous studies, the growth of the hemisphere was slow, so r_0 was taken as zero. Using an r_0 of 12.5 μ m is physically analogous to assuming the initial Li nucleus is 12.5 μ m in radius.

The diffusion-controlled current to a growing hemisphere of liquid Li has both a linear and a hemispherical diffusion component. This current can be described by Eq. [2] and [3] (11)

$$dr(t)/dt = I(t) \{ M/[2\pi n \mathbf{F} \rho) r(t)^2] \}$$
[2]

$$I(t) = n\mathbf{F}ADC[(\pi Dt)^{-1/2} + r(t)^{-1}] [1 - \exp(n\mathbf{F}\eta/RT)]$$
[3]

where r(t) is the radius in cm of the Li hemisphere at time t; ρ is the density of Li (0.52 g/cm³); M is the molecular



Fig. 6. Reduction of Li⁺ at 25 μ m W in LiCl:KCl eutectic at 405°C. Potential step from -1.0V to: (a) -3.00; (b) -3.05; (c) -3.10; (d) -3.15; (e) -3.20; (f) -3.225; (g) -3.25; (h) -3.27; (i) -3.30; (j) -3.325; (k) -3.35; (l) -3.375V.



Fig. 7. Simulation of Li(liq) deposition current on 12.5 μ m W microelectrode as a function of overpotential and time. Overpotential: (A) 10; (B) 30; (C) 60; (D) 110; (E) >200 mV. $D = 3.5 \times 10^{-5}$ cm² s⁻¹; [Li⁺] = 17M.

weight of Li (6.9g); D is the diffusion coefficient for Li⁺; C is the concentration of Li⁺ in LiCl/KCl (17 × 10⁻³ mol/cm³); η is the overpotential; and A is the area in cm² of the growing hemisphere given by $2\pi r(t)^2$. The two terms contained in the first bracket of Eq. [3] are the linear and hemispherical diffusion components, respectively. Substitution of Eq. [3] into Eq. [2] yields a nonlinear differential equation which is evaluated numerically using the Euler approximation, *i.e.*, substitution of $\Delta r(t)$ and Δt for dr(t) and dt, respectively. Deposition curves generated employing this method are shown in Fig. 7. The overpotential was increased from 10 mV to infinity (>200 mV), and D for Li⁺ was estimated from earlier experiments to be 3.5×10^{-5} cm² s⁻¹. Qualitatively, the experimental and calculated curves are in agreement.

It is instructive to solve separately the linear and hemispherical diffusion equations even though such a separation will not give a strictly correct solution to the problem. This approach results in analytical solutions which are described in Appendixes A and B. The equation describing hemispherical diffusion to a growing nucleus has been previously reported and discussed (15, 16). Deposition curves showing the contribution each diffusional component makes to the total current at infinite overpotential are shown in Fig. 8. The linear diffusion component decreases initially but does not go to zero because of the increasing area of the hemisphere. The hemispherical component continually increases and gives rise to the observed large increase in current with time of deposition. The sum of the two components is also shown; qualitatively, it also has the same shape as the experimental curves. The numerical solution calculated using Eq. [2] and [3] is also shown. The model based on separation of the diffusion components results in a total current well below



Fig. 8. (A) Linear diffusion, (B) hemispherical diffusion, (C) linear + hemispherical diffusion, and (D) Euler solution for diffusion to a growing Li(liq) hemisphere at a 25 μ m W electrode; [Li⁺] = 17M; $D = 3.5 \times 10^{-5}$ cm² s⁻¹.

that obtained from the numerical solution of Eq. [2] and [3]. Separation of the component does, however, provide a clear picture of how the linear and hemispherical components contribute to the deposition current.

Although the experimental and calculated curves agree qualitatively, the minima are sharper and the current values lower for the experimental curves. Using a *D* value of 1.8×10^{-5} cm² s⁻¹ for Li⁺, the calculated currents are in better agreement with the experimental currents in Fig. 6. However, from several runs, it was found that deposition and stripping currents were often approximately twice those in Fig. 6. In fact, the curves in Fig. 6 are the lowest currents observed for several experiments and should be used as a lower limit for Li⁺ diffusion. The Li⁺ diffusion coefficient can only be placed in a range of 1.8×10^{-5} cm² s⁻¹. This range is similar to the value of 2.93×10^{-5} cm² s⁻¹ determined for Li⁺ in LiNO₃ at 350°C (17).

To help elucidate the problem of variable Li currents, electrodes were removed from the melt after use, washed with water, and examined under a microscope. For the electrode used to obtain the data in Fig. 6, the tungsten microdisk was clearly visible even though the glass surrounding the microdisk had been badly etched. There were no apparent cracks in the glass encasing the electrode; therefore, it can be assumed that the electrode retained its disk configuration during the experiments. The area of etched Pyrex glass was circular with a radius of ca. 200 µm, and the tungsten microelectrode was in the center of this etched area. This indicates that the Li grew radially from the tungsten microelectrode in all directions, consistent with the proposed model for deposition. For some electrodes, the glass surrounding the tungsten disk was cracked resulting in larger effective electrode areas. For these cracked electrodes, higher currents were observed, and the minima were broadened as expected for larger area electrodes. Finally, one electrode gave nearly twice the currents in Fig. 6 with sharper minima. This electrode showed no glass cracking and etching occurred in a radial fashion for a distance of ca. 50 µm from the tungsten disk. The observed currents may be a function of electrode activation as well as of effective electrode area.

In situ microscopic examinations.—A high-temperature cell, Fig. 9, was constructed to examine the surface of the 12.5 µm radius tungsten electrode during Li deposition and stripping. The cell consisted of a quartz cuvette with optical glass on all sides, including the bottom. The electrode assembly consisted of a tungsten microelectrode sealed in Pyrex, a tungsten wire counterelectrode (0.5 mm diam), and a Ag wire reference electrode immersed in LiCl:KCl contained in a separate fritted compartment. The cuvette and electrode assembly were designed to allow assembly in a dry box and subsequent transfer to the heater and microscope. An Al block heater was used to heat the cell to 420°C. A hole in the bottom of the Al block allowed examination of the tungsten microelectrode through the bottom of the cuvette using an inverted microscope. All observations were performed using a magnification of 100 times since lighting of the cell was insufficient to allow clear observations at higher magnifications. Several important observations were made.

During rapid deposition of Li, the melt became cloudy in the region surrounding the electrode indicating precipitation of salt from the Li⁺ depleted melt. This cloudiness obscured the electrode. The cloudiness is most likely a result of precipitation of KCl (mp = 772° C) from the now K⁺-rich melt. Similar concentration changes near the cathode have been observed for Ag deposition from KNO₃:LiNO₃ melts and have been related to problems expected for Li deposition from LiCl:KCl melts (18). Despite this precipitate, it was still possible to discern a bright, growing layer of Li during deposition. Because it was necessary to press the electrode against the bottom of the cell to achieve sufficient lighting, the Li appeared to grow in a flat layer along the surface of the insulating glass encasing the tungsten electrode. It was possible to obtain curves with the same features as Fig. 6 by raising the electrode slightly so that it was not in contact with the bottom of the cuvette.



Fig. 9. High-temperature cell for *in situ* observations: (a) Al block; (b) quartz cuvette; (c) cartridge heaters; (d) Pyrex shaft; (e) J-type thermocouple; (f) W counterelectrode; (g) 25 μ m diam W microelectrode assembly; (h) Ag/Ag⁺ reference electrode (i) Teflon electrode holder; (j) inverted microscope.

The insulating glass encasing the electrode was badly etched during the deposition processes. Reaction of the glass often resulted in the electrode being covered by an insoluble grainy material. Since it was necessary to press the tungsten electrode against the bottom of the cuvette to get proper lighting, etching of the bottom of the cuvette was observed during Li deposition.

Gas bubbles were also observed during Li deposition. This is probably H_2 evolution resulting from water impurities present in the melt. Because of difficulties encountered during cell assembly, the melt was exposed for short periods to ambient air.

After several hours of observations, the growth of metallic, dendritic Ag crystals was observed on the tungsten microelectrode at potentials cathodic of -0.2V as a result of leakage of the Ag/Ag⁺ reference electrode. Although the dendritic growths flaked off the electrode, it was possible to observe a stripping current.

At anodic potentials, Cl_2 evolution was observed at the electrode surface. No clouding of the melt occurred during this gas evolution.

Bismuth deposition.—To test the applicability of microelectrodes to the study of other deposition processes, a 0.12M solution of Bi³⁺ in the LiCl:KCl eutectic was prepared by addition of BiCl₃ to a purified melt.

A staircase cyclic voltammogram is shown in Fig. 10 for liquid Bi (mp = 271°C) deposition at 400°C. Excellent deposition and stripping behavior were observed for scan rates from 0.25 to 50V s⁻¹. Integration of the voltammograms showed that Bi stripping resulted in nearly quantitative recovery of the charge passed during deposition, unlike the case for Li.

Normal pulse voltammograms were also run on the $0.12M \text{ Bi}^{3+}$ melt. At a microelectrode, the concentration of the electroactive active species returns to its initial concentration following an analysis pulse, t_p , if the time between the pulses, t_w , is approximately ten times t_p (19). This eliminates the need to wait excessively long times be-



Fig. 10. Reduction of Bi^{3+} to Bi'(Iiq) at 25 μ m W in LiCl:KCl eutectic at 400°C. Staircase cyclic voltammogram, scan rate = 50V s⁻¹.

tween pulses or to physically stir the melt, thus greatly simplifying the construction of the high-temperature electrochemical cell. Normal pulse voltammograms at a 25 μ m diam tungsten microelectrode are shown in Fig. 11 for relatively short pulse widths. Well-defined limiting plateaus were obtained for pulse widths from 1 to 500 ms with a waiting time of 2s for $t_p = 1 - 250$ ms and 5s for $t_p = 500$ ms.

The current to a microdisk as a function of time is described by Eq. [4] through [6] below (20)

$$i = 4n\mathbf{F}DCr\{f[P(t)]\}$$
[4]

$$P = 4Dt/r^2$$
 [5]

For P < 1.44

$$f(P) = (\pi/4P)^{1/2} + \pi/4 + 0.094 P^{1/2}$$
 [6]

and for P > 0.88

$$f(P) = 1 + 0.71835 P^{-1/2} + 0.05626 P^{2/3}$$
[7]

For short times, *i.e.*, P < 1.44, appropriate substitutions can be made giving the diffusion-controlled limiting current, i_{lim} , for a normal pulse experiment of pulse width t_p , Eq. [8]

$$i_{\rm lim} = n \mathbf{F} C(\pi D)^{1/2} r^2 / t_{\rm p}^{1/2} + \pi n \mathbf{F} D C r$$
 [8]

The first term in Eq. [8] is simply the Cottrell equation (11). The second term differs by only a factor of $4/\pi$ from the diffusion-controlled limiting current, i_{ss} , to a microelectrode at long times as given by Eq. [9] (20)

$$_{\rm ss} = 4n \mathbf{F} D C r$$
[9]

At long times, the current to a microelectrode is independent of pulse widths.

Applying Eq. [8], a plot of i_{\lim} vs. $t_p^{-1/2}$ at short times should yield a straight line with a slope and intercept from



Fig. 11. Reduction of Bi³⁺ to Bi(liq) at 25 μ m W in LiCl:KCl eutectic at 400°C. Normal pulse voltammetry, pulse width: (A) 1; (B) 2; (C) 5; (D) 10 ms¹.

which the diffusion coefficient can be calculated. For pulse widths less than 50 ms and an estimated diffusion coefficient for Bi^{3+} of 10^{-5} , the parameter *P* is less than 1.44. Therefore, using pulse widths from 1 to 25 ms, the slope of a $i_{\rm lim}$ vs. $t_{\rm p}^{-1/2}$ plot gives a D value of $(2.2 \pm 0.2) \times 10^{-5}$ cm² s⁻¹ for Bi³⁺ in LiCl:KCl at 400°C. The intercept of the plot, however, has a negative value indicating a certain amount of error. Even so, this value agrees well with D values determined for Pb^{2+} and Cd^{2+} of 1.7×10^{-5} cm² s⁻¹ and $1.8\times 10^{-5}\ \text{cm}^2\ \text{s}^{-1},$ respectively, at a dropping Bi electrode in LiCl:KCl eutectic at 450°C (21). The currents at the longer pulse widths were considerably lower than expected from Eq. [7]. Examination of the electrode following the normal pulse experiments showed that the glass was not attacked, but the tungsten disk was recessed ca. 20 μm below the surface of the glass. The current to this "shielded" microelectrode would not have a contribution from hemispherical diffusion but would exhibit only linear diffusion characteristic. This also explains the negative intercept seen for the $i_{
m lim}$ vs. $t_{
m p}^{-1/2}$ plot.

The rising portion of the normal pulse voltammograms, particularly those with short, pulse widths, were not smooth but exhibited one or more discernible plateaus. This may be an artifact of the microelectrode, or it may be a result of the formation of subvalent Bi species such as Bi^+ or $Bi_5{}^{3+}$. These two species have been identified in molten NaCl:AlCl₃ (22, 23), and Bi^+ has been proposed to be formed in LiCl:KCl by reaction of liquid Bi with Bi^{3+} (24).

Deposition and stripping experiments for Bi were performed using DPSC to see if high stripping currents could be achieved. Deposition currents of only a few μ A's were observed; however, by depositing Bi at -0.5V for 10s, stripping the Bi at 0.5V gave a current density of 600 A cm⁻² calculated from the area of the microelectrode. Also, with long deposition times (>10s) the deposition curve showed a minimum followed by a slow rise in the current. Finally, it was observed that if Bi were deposited on the tungsten microelectrode for several seconds at -0.5V, the potential for Li deposition was shifted considerably anodic to <-2.0V. This is consistent with results reported at a dropping Bi cathode, for which Li deposition began near -0.8V vs. Bi/Bi³⁺ (21); this was attributed to the low activity coefficient of Li in Bi.

Conclusions

Lithium stripping at a tungsten microelectrode has been shown to give high current densities, 1300 A cm⁻², using the area of the tungsten microdisk ($r = 12.5 \,\mu$ m) in the current density calculation. The calculated current densities decrease with increasing amounts of Li deposited as expected for a growing hemisphere. The Li deposition at a tungsten microelectrode can be simulated using a model based on hemispherical and linear diffusion to a growing liquid Li hemisphere. In situ observations of the Li deposition/stripping process indicate precipitation of K⁺-rich melt in the melt region surrounding the electrode. Deposition of other metals can also be examined successfully as demonstrated for Bi.

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APPENDIX A

Calculation of the current to a growing hemisphere assuming the current is under hemispherical diffusion control

For hemisphere where Q(t) is the total charged passed at time t

Therefore

$$V(t) = (2/3) \pi r(t)^3 = [Q(t)/n\mathbf{F}](M/\rho)$$
 [A-1]

$$Q(t) = JI(t) at \qquad [A-2]$$

$$(2/3) \pi r(t)^3 = (M/n\mathbf{F}\rho)[\int I(t) dt]$$
 [A-3]

Differentiating with respect to t

$$(2/3) \pi 3[r(t)]^2 [dr(t)/dt] = (M/n\mathbf{F}\rho) [I(t)]$$
 [A-4]

The equation for hemispherical diffusion controlled current is

$$I(t) = 2\pi n \mathbf{F} DCr(t) \left[1 - \exp(n \mathbf{F} \eta / RT)\right]$$
 [A-5]

Therefore

 $(2/3) \pi 3 [r(t)]^2 [dr(t)/dt]$

$$= (M/n\mathbf{F}_0) \left\{ 2\pi n\mathbf{F} DCr(t) \left[1 - \exp(n\mathbf{F}_n/RT) \right] \right\} \quad [A-6]$$

Simplifying and rearranging

$$r(t) dr(t) = (MDC/\rho)[1 - \exp(n\mathbf{F}\eta/RT)] dt \qquad [A-7]$$

Integrating both sides and evaluating the left side from r(o) to r(t) and the right side from t = 0 to t gives

$$\int r(t) dr(t) = (MDC/\rho) \left[1 - \exp(nFn/RT)\right] \int dt \quad [A-8]$$

$$(1/2) \{ [r(t)]^2 - [r(o)]^2 \} = (MDC/\rho) [1 - \exp(n\mathbf{F}\eta/RT)] (t - o)$$
[A-9]

$$[r(t)]^{2} = r_{o}^{2} + (2MDCt/\rho) [1 - \exp(n\mathbf{F}\eta/RT)] \quad [A-10]$$

Substituting this value for $[r(t)]^2$ into the square of the equation describing hemispherical diffusion controlled current given by Eq. [A-5]

$$[I(t)]^{2} = (2\pi n \mathbf{F} DC)^{2} [r_{o}^{2} + (2MDCt/\rho)] [1 - \exp(n \mathbf{F} \eta/RT)]^{2}$$
[A-11]

Finally

 $[I(t)]^{2} = \{2\pi n \mathbf{F} CDr_{o}[1 - \exp(n \mathbf{F} \eta/RT)]\}^{2}$

+ $(\pi n \mathbf{F})^2 (M/\rho) (2CD)^3 t [1 - \exp(n \mathbf{F} \eta/RT)]^3 [A-12]$

In Eq. [A-12], the first term is the square of the hemispherical diffusion controlled current to a nongrowing hemisphere of radius r_0 , Eq. [A-5]. The second term is the square of the hemispherical diffusion controlled current to a growing hemisphere with a radius of zero at t = 0.

APPENDIX B

Calculation of the current to a growing hemisphere assuming the current is under planar diffusion control

For this case the derivation is the same except that

$$I(t) = (n\mathbf{F}AD^{1/2}C) \left[1 - \exp(n\mathbf{F}\eta/RT)\right] / (\pi t)^{1/2} \quad [A-13]$$

Since $A = 2\pi r^2$ for a hemisphere

$$I(t) = \{n\mathbf{F}2\pi[r(t)]^2 D^{1/2}C\} [1 - \exp(n\mathbf{F}\eta/RT)] (\pi t)^{-1/2}$$
 [A-14]

An abbreviated derivation is given below

$$V(t) = (2/3) \pi r(t)^3 = (M/n\mathbf{F}\rho) [\int I(t) dt]$$
 [A-15]

Differentiating with respect to t

(2/3)
$$\pi 3[r(t)]^2 [dr(t)/dt] = (M/n\mathbf{F}\rho) [I(t)]$$
 [A-16]

 $(2/3) \ \pi 3[r(t)]^2 \left[dr(t)/dt \right] = (M/n\mathbf{F}\rho) \left\{ n\mathbf{F}2\pi[r(t)]^2 \ D^{1/2}C \right\}$

$$[1 - \exp(n\mathbf{F}\eta/RT)](\pi t)^{-1/2}$$
 [A-17]

$$dr(t) = (M/\rho) (D^{1/2}C) [1 - \exp(n\mathbf{F}\eta/RT)] (\pi t)^{-1/2} dt [A-18]$$

Integrating and evaluating

$$\int dr(t) = \int (M/\rho) (D^{1/2}C) \left[1 - \exp(n\mathbf{F}\eta/RT)\right] (\pi t)^{-1/2} dt$$
[A-19]

 $r(t) = r_{o} + 2(M/\rho) (D^{1/2}C) [1 - \exp(n\mathbf{F}\eta/RT)] \pi^{-1/2} t^{1/2}$ [A-20] Combining Eq. [A-2] and [A-8]

$$I(t) = 2\pi \{r_0^2 + 2(M/\rho) (D^{1/2}C) [1 - \exp(n\mathbf{F}\eta/RT)] \pi^{-1/2} t^{1/2} \}^2$$

$$\times n \mathbf{F} D^{1/2} C [1 - \exp(n \mathbf{F} \eta / RT)] (\pi t)^{-1/2}$$
 [A-21]

Defining
$$X = [1 - \exp(nF\eta/RT)]$$
 and expanding Eq. [A-9]
 $I(t) = 2\pi^{1/2}r_0^2 nFD^{1/2}CX(t^{-1/2}) + 4r_0(M/\rho) nFDC^2X^2$

$$+ 8n\pi^{-1/2}\mathbf{F}(M/
ho)^2 D^{3/2} C^3 X^3(t^{1/2})$$
 [A-22]

The first term which has a $t^{-1/2}$ dependence is the planar diffusion controlled current to a nongrowing hemisphere of radius $r_{\rm o}$. The third term which has a $t^{1/2}$ dependence, but is independent of $r_{\rm o}$, is the planar diffusion controlled

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current to a growing hemisphere with a radius of zero at t = 0. The second term is a time-independent current. It is apparent that the planar diffusion current is a complex function of time when $r_{\rm o} \neq 0$.

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Carbon Microfibers with Conically Oriented Carbon Layers as Cathode Materials of Rechargeable Lithium Cells

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ABSTRACT

Carbon microfibers, in which carbon layers conically oriented to the fiber axis, were used as cathode materials of rechargeable nonaqueous lithium batteries. The effective charge storage capacity of the cell was about three times as large as those for various graphite materials reported so far, probably due to a unique structure of the carbon microfibers used in this study. The discharged coulombs did not decrease with the repetition of the charge-discharge cycles up to the 550th cycle.

Lamellar structure compounds such as titanium disulfide have been extensively investigated as cathode materials of rechargeable lithium batteries. Graphite also has a lamellar structure of hexagonal lattice plane of carbon and hence is one of the candidates for a cathode material to realize a high storage capacity. It is well-known that graphite intercalation compounds (GICs) are formed when molecules, ions, or atoms are intercalated into the gaps of the carbon layers. Dunning et al. (1) reported that GICs were formed by anodic oxidation of graphitic materials such as pyrolytic graphite carbon paper (Union Carbide), GRA-FOIL (Union Carbide), and reinforced pyrolytic graphite (Super Temp Company) in a nonaqueous solution of LiClO₄ dissolved in dimethyl sulfite as expressed by Eq. [1]. Then rechargeable batteries could be made by combination of both reactions on the graphite cathode and on the lithium anode (see Eq. [1] and [2])

charge
Cathode:
$$nC + ClO_4^- \rightleftharpoons C_nClO_4 + e^-$$
 [1]
discharge

charge
Anode:
$$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$$
 [2]
discharge

The batteries thus prepared had some advantages including high open-circuit voltage (>4V) and high coulombic efficiency (>80%). However, they revealed that the maximum charge storage capacity of these batteries were about 90C per unit gram of carbon (C g^{-1}). Ohzuku et al. (2) reported that GICs also could be formed in a propylene carbonate (PC) solution of LiClO₄ by anodic oxidation of graphite materials, and that the maximum charge storage was $85 \pm 5 \text{ Cg}^{-1}$, irrespective of the materials such as EG-1, EG-50, and G-40, produced by Nihon Carbon. Theoretical energy density of these batteries was calculated to be about 100 Wh kg^{-1} from the maximum charge storage of 90 C g^{-1} . However, this value is still smaller than that of lead-acid batteries (about 175 Wh kg⁻¹). Therefore, it is of urgent necessity to develop a new cathode material as well as to find an adequate electrolyte.

On the other hand, Matsuda et al. (3) studied the effects of electrolytes in PC solution on the performance of the battery employing a graphite fiber GF-25A (Nihon Carbon) as a cathode material, and reported that the coulombic efficiency of the charge-discharge cycle increased in the order of LiClO₄ < LiBF₄ < LiPF₆. However, the maximum charge storage was only 18 C g^{-1} , even for the best electrolyte $LiPF_6$. In contrast to the above, Nawa *et al.* (4) have succeeded in making an extremely large charge storage capacity (about 300 C g^{-1}) by employing a special kind of activated carbon fiber (specific surface area 1500-2500 $m^2 g^{-1}$) as a cathode material in a γ -butyrolactone solution of LiClO₄. This result offers the potential that the charge storage capacity could be enhanced by controlling the microstructure of the cathode material.