ELECTROCHEMISTRY OF LITHIUM IN ROOM TEMPERATURE MOLTEN SALT ELECTROLYTES

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ABSTRACT

The demonstration of a stable reversible lithium anode is an important step in the development of practical secondary batteries using room temperature chloroaluminate melts as electrolytes. Riechel and Wilkes found that proton added to a sodium chloride buffered melt as ethylmethylimidazolium hydrogen dichloride provides a more negative voltage window and nearly reversible deposition-stripping behavior for sodium when proper proton concentration is maintained. While EMIHCl₂ is a proven proton source and is also effective for lithium deposition-stripping behavior, its stability in the melt is limited with HCl being lost relatively rapidly into the vapor phase. We have explored many possible alternatives and have found triethanolamine·hydrogen chloride to be an effective proton source with good stability in the melt. This paper presents our studies of lithium deposited on tungsten in proton rich lithium chloride buffered neutral melts.

INTRODUCTION

Room temperature molten salts formed by mixing 1—ethyl—3—methylimidazolium chloride (EMIC) with aluminum chloride have been intensively studied, particularly by Wilkes and coworkers at FJSRL, for more than a decade with the goal of developing high energy density batteries. Alkali metals have high oxidation-reduction potentials and relatively low atomic masses making them very attractive candidates as battery anodes. Lithium is of particular interest because it has the highest electricity storage density of the active metals.

The Lewis acid-base behavior of these melts has a substantial influence on their physical and electrochemical properties. Melt acidity is easily ascertained electrochemically since Al deposition only occurs from acidic melts and the melt window is significantly greater in neutral melts than in either basic or acidic melts. Because of the wide electrochemical window it is desirable to work with a melt which is exactly neutral but, as with most acid-base systems, maintaining neutrality is not easily achieved unless the system is buffered. The use of sodium chloride to buffer the melt to neutral composition has been demonstrated by Wilkes, et al. (1) More recently it was found that proton added to the melt as 1—ethyl—3—methylimidazolium hydrogen dichloride

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EMIHCl₂ provides a more negative voltage window and nearly reversible deposition-stripping behavior of sodium when proper proton concentration is maintained. We initially studied lithium chloride-buffered neutral melts by first removing protonic impurity (resulting from contamination by H₂O during synthesis and purification of EMIC) with ethylaluminum dichloride. By adding proper amounts of EMIHCl₂ nearly reversible deposition-stripping behavior of lithium could be observed at tungsten electrodes.

While EMIHCl₂ is a proven proton source, its stability in the melt is limited with HCl being lost into the vapor phase relatively rapidly in an open system. We investigated many possible alternative proton sources and found triethanolamine • hydrogen chloride (TEOA • HCl) to be an effective source. TEOA • HCl is electrochemically stable within the melt window, except for proton reduction which is expected, and maintains a stable proton concentration in the neutral melt for times two orders of magnitude greater than that obtained with EMIHCl₂. Proton enrichment of the melt with TEOA • HCl has been very successful in bringing a lithium chloride buffered melt to exactly neutral acidity which prevents aluminum deposition and stripping and in extending the cathodic limit of the melt but has not provided the desired stability of deposited Li in the melt. We have made some attempts to understand the role of added protons (or HCl) in the observed electrochemistry of lithium in the melt. In addition we have initiated a study of LiAl alloys in these melts and this is being continued.

EXPERIMENTAL

All experimental work was performed with materials and electrochemical cell contained a Vacuum Atmospheres dry box system with a helium atmosphere. Electrochemical measurements were accomplished with an EG & G Princeton Applied Research (PAR) Model 263 Potentiostat/Galvanostat interfaced with an IBM 486 personal computer using EG & G PAR 270 software and a Hewlett Packard plotter model HP 7475A. A three-electrode arrangement in a single compartment cell used a molybdenum foil counter electrode and Bioanalytical System (BAS) working electrodes of platinum, tungsten, or glassy carbon. Most of the work reported here was obtained with tungsten working electrodes. The reference electrode was an Al wire in 0.60 EMIC/AlCl₃ melt contained in a pyrex glass tube constructed with an asbestos tip to provide solution contact.

Components for the melt were synthesized and purified following the procedures developed by Wilkes and coworkers at FISRL. LiCl was dried for a minimum of 10 days in a vacuum oven at 130°C. The many compounds tested for improving proton stability in the melts were used as obtained from Johnson-Matthey or Aldrich. These included in addition to the triethanolamine • hydrogen chloride, a number of mono —, di — and tri — substituted amine • hydrogen chlorides, LiH and LiAlH₄. In general the
purity of melt components and additives were tested by preparing exactly neutral melts and observing the melt window using cyclic voltammetry.

An acidic melt (0.55 mole fraction of AlCl₃) was prepared by adding the amount of AlCl₃ calculated to give the desired composition to an exactly neutral melt which had been treated with ethylaluminum dichloride. Then LiCl was added (with a calculated 25% excess) to buffer the melt back to neutral. LiCl was found to dissolve much more slowly than NaCl, requiring several days with occasional heating to 50°C for attainment of a neutral melt. Neutrality of this melt was demonstrated by the absence of Al deposition and stripping during a cyclic voltammetric scan. In a slightly acidic melt Al deposition could be observed at a cathodic potential approximately one volt more negative than in 0.55 melt. This Al deposition and stripping could be observed in buffered melts even after several days (up to 5 days) of stirring with LiCl in the melt. As with NaCl, LiCl was found to be insoluble in basic melt and all attempts to buffer a melt to neutral from the basic side with LiCl were unsuccessful.

RESULTS AND DISCUSSION

The buffered melt remained slightly acidic even after seven days of stirring with excess LiCl, similar to the observed behavior of NaCl buffered melts reported by Riechel and Wilkes. The cyclic voltammograms presented in this report were recorded at a sweep rate of 100 mV/sec using a W working electrode. Al deposition occurs at about -0.90 V and stripping at about -0.191 V (depending on melt acidity). The potential for Al deposition in this melt is more cathodic than the potential for the same process in more acidic melts by almost one volt. The Al stripping in this melt occurred at a potential that was reported for a corresponding NaCl buffered melt having an AlCl₃ mole fraction of 0.5002, suggesting that the LiCl buffered melt has a composition between 0.501 and exactly neutral. The deposition of Li at -1.6 V, significantly changes the Al stripping behavior.

In the search for a stable proton source three criteria were used:

1) the electrochemical stability of the proton source, no redox reaction within the electrochemical window of the melt, except for the desired proton reduction.
2) essentially reversible deposition-stripping behavior of lithium (nearly 100% cycling efficiency) which is reproducible without cleaning the electrode.
3) relatively constant proton content of the melt over a period of several days.

Of the ten compounds selected and tested as potential proton sources, only triethanolamine·hydrogen chloride satisfied our three criteria.
As background for our discussion, Fig. 1a shows CV behavior, at a W working electrode, for an exactly neutral melt and Fig. 1b for LiCl-buffered melt, representing typical CV behavior and showing the melt limits with a window of about 4.0 volts. Behavior in a LiCl-buffered melt which is near to but not exactly neutral is further seen in Fig. 2 with cathodic sweep limits of -1.80 V (Fig. 2a) and -2.7 V (Fig. 2b). Al deposition is clearly evident at about -1.0 V but the stripping, clearly seen in curve b at about 0.0V is significantly altered by Li deposition which occurs at about -1.7 V.

Figure 3 presents representative CV data for the addition of triethanolamine • hydrogen chloride to LiCl-buffered melt. Fig. 3a is for 0.10 M TEOA • HCl showing the deposition of Li but very little stripping. The cathodic sweep limit is -2.5 V. Figs. 3 b-d are for 0.20 M TEOA • HCl added to LiCl buffered melt showing essentially reversible deposition-stripping behavior for Li as a function of cathodic sweep limit, which are respectively (Fig. 3b), -2.20 V, (Fig. 3c) -2.50 V, and (Fig. 3d) -2.80 V. This series of CV curves shows clearly that when the proton concentration is maintained at the proper level (in this case 0.20 M) the Li deposition-stripping behavior or cycle efficiency is not dependent on the cathodic sweep limit. We also note that no Al deposition is observed indicating that the melt composition is exactly neutral.

The following summarizes the important cyclic voltammetric characteristics for 0.2 M TEOA • HCl in LiCl buffered melt:

For sweep rates from 10 mV/sec to 1 V/sec and cathodic sweep limits from 2.40 V to -2.90 V:
- Li deposition begins at -2.15 ± 0.02 V
- Li deposition peak at -2.40 ± 0.15 V
- Li stripping peak at -1.85 ± 0.15 V
- Cycle efficiency 0.74 ± 0.10

These results are comparable with those obtained using EMIHCl₂ as a proton source in LiCl-buffered neutral melt.

CONCLUSIONS

1. We have found that triethanolamine • hydrogen chloride provides a better proton source than ethylmethylimidazolium hydrogen dichloride with stability in the melts studied measured in weeks rather than hours.

2. Nearly reversible deposition-stripping of lithium is obtained in LiCl-buffered melts when the TEOA • HCl concentration is between about 0.20 and 0.225 M. It does not appear however, that the Li deposit on W is stable in this system.
3. The protective film which has been reported to form on Li does not form on the Li deposits under conditions in our melts where reversible deposition-stripping behavior is observed. The brown films which we observe with proton concentrations below the minimum concentration of 0.20 M may possibly be identified with the lithium oxide or lithium hydroxide films reported by other groups. The increased proton concentration appears to be related to the lack of this film formation and to the reversible deposition-stripping behavior.

4. The white precipitate formed when sufficient EMIHCl$_2$ or TEOA·HCl is added to provide reversible deposition-stripping behavior has been identified as LiAlCl$_4$.

REFERENCES

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Fig. 1b LiCl-buffered melt, sweep to -1.8 V

Fig. 2b LiCl-buffered melt, sweep to -2.7 V

Fig. 1a Neutral Melt

Fig. 2a LiCl-buffered melt, sweep to -1.8 V
