The effect of ultrasound on lithium surfaces in propylene carbonate

Peter R. Birkin *, Emmanuel Eweka, John R. Owen

University of Southampton, Chemistry Department, Highfield, Southampton, SO17 1BJ, UK

Abstract

Ultrasonic irradiation of lithium metal electrodes is demonstrated to erode surface layers and subsequently reduce the interfacial resistance. Dynamic impedance measurements were employed to monitor the erosion and reformation of surface layers formed on lithium electrodes placed in a propylene carbonate electrolyte in the presence and absence of ultrasound, respectively. In the presence of ultrasound a marked decrease in the resistance (ca. 310 Ω cm^2 to 225 Ω cm^2) was observed over a 400 s period. Other experiments employing a 50 μm diameter Cu microelectrode showed that ultrasound had a marked effect on both lithium plating and stripping. It was found that the stripping efficiency was reduced from ca. 60% under silent conditions to only ca. 18% in the presence of ultrasound. Subsequent experiments demonstrated that ultrasound efficiently removes lithium from a lithium coated copper microelectrode in the absence of any stripping or plating processes. The results demonstrate that ultrasound, under the conditions reported here, removes lithium from the surface of the microelectrode, increases the voltage required for lithium plating, reduces the interfacial resistance of films formed on lithium within a propylene carbonate electrolyte and decreases the efficiency of the stripping/plating process. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ultrasound; Lithium; Interfacial resistance; Erosion; Cavitation; Propylene carbonate

1. Introduction

Lithium batteries promise the highest possible specific energy of all known electrochemical energy storage systems because of the extreme reactivity and low molar mass of the metal [1]. However, the major problem with lithium is that all the available electrolytes with sufficient conductivity for high power at room temperature are thermodynamically unstable against this metal.

The success of lithium metal cells depends on the kinetic stability provided by a passivating layer of a solid corrosion product formed at the interface [2,3]. This forms by reaction of lithium with the electrolyte, but subsequently acts as a physical barrier between the reactants and thus gives lithium batteries an impressive storage life.

The benefits of a passivating layer are offset by a substantial ohmic loss due to its resistance to ion transport and a consequent lowering of the specific power. The power loss is particularly significant during the first stage of discharge, when a 'voltage delay' is experienced during

the breakdown of the layer [4]. Another detrimental effect of the passivating layer occurs during cell charging; a non-uniform current density at the surface leads to the formation of highly reactive lithium dendrites. The presence of finely divided lithium causes a fire hazard as well as a slow loss of charge and electrolyte decomposition.

Ultrasonic generation of transient cavitation is well known to result in surface damage and erosion [5–8].[1] The proposed mechanisms are shock wave generation and microjet impact on the surface. These processes are associated with the asymmetric collapse of cavitation bubbles near a solid/liquid interface. Evidence of the effect of microjets on an electrochemical reaction at a microelectrode has recently been found in the form of well-resolved current pulses corresponding to the hydrodynamic disturbances caused by individual cavitation events at or near the interface [9,10].

The application of ultrasound to heterogeneous processes, for example the Barbier reaction, has been shown to result in beneficial 'activation' phenomena [11,12]. It

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* Corresponding author. Tel: +44-0-1703-594172; Fax: +44-0-1703-676960; E-mail: prb2@soton.ac.uk

[1] Characterisation and Determination of Erosion Resistance, ASTM, 1969, Philadelphia.

would seem timely that a study be performed on the effect of ultrasound on the lithium/electrolyte interface as this is both of relevance to synthetic applications, to the deployment of ultrasound in heterogeneous reactions, and to the possible advantages if any of applying ultrasonic irradiation to a lithium battery at some stage of the charge or discharge cycle. In this work, irradiation with ultrasound was investigated as a means of eroding the passivating layer prior to, or during the initial stage of discharge of a lithium electrode. A second objective of the work is to study the effect of ultrasound on the lithium plating reaction during cell charge. Dispersion of the passivating layer during charging may therefore be expected to lead to smooth plating without the formation of lithium dendrites.

2. Experimental

2.1. Electrodes and equipment

A Schlumberger Solartron 1250 frequency analyser and a Hitech DT2101 potentiostat were employed to record impedance data. The data were transferred to a PC through a RS 232 cable and in-house written software. A Cu microelectrode (50 μm diameter) was constructed in-house and sealed in glass as described in the literature [13]. An Oxford electrodes galvanostat, modified to accommodate low currents expected at microelectrodes, was used for lithium plating experiments on the Cu microelectrode. Potentiometric data were recorded on a PC interfaced through an ADC card (Talisman Electronics, Computer Boards CIO-DAS08/16) using software written in-house.

The Cu microelectrode, after polishing was rinsed with water, buffed on a clean polishing cloth and washed with dry isopropanol (BDH GLC Grade, 99%). All other electrodes, whether the experimental set up was a conventional three electrode arrangement or a 2 electrode arrangement, were lithium. Ultrasound was generated using a Semat ultrasonic bath (operating at a measured frequency of 50 kHz). The ultrasonic bath had dimensions of 24 cm long by 13.5 cm wide and 10 cm deep. Measurement of the ultrasonic sound field was performed using a 8103 Brüel and Kjaer hydrophone and Brüel and Kjaer Charge amplifier Type 2635. The resultant output was recorded on a Gould 465 digital oscilloscope. The peak to peak voltage was measured from this device and converted into the appropriate pressure measurement.

2.2. Chemicals

Lithium metal (Lithco, 0.1 mm thick sheet) was used as received and stored in a glove box at all times. Propylene carbonate (Aldrich 99% purity) was used as received. Lithium hexafluoroasenate, $LiAsF_6$, (Lithco, Electrochemical Grade) was dried under vacuum at 120–140°C for 48 h.

2.3. Cell and solution preparation

All solutions were made up in a dry box (ca. 5 ppm H_2O). Cells and electrodes were also assembled within the dry atmosphere. Two different cell designs where employed in this study. In the first, employed for impedance measurements, a lithium foil electrode of defined area was employed in a 3 electrode arrangement in an adapted 3 necked round bottomed flask. Lithium working macroelectrodes were constructed from lithium foil (0.1 mm thickness). The lithium working electrode was constructed with a defined area by masking an area of foil supported on a glass slide with polyimide tape (RS). An approximately square area of 0.05 cm^2 was left exposed to the solution. Counter and reference electrode consisted of relatively large pieces of lithium foil (ca. 2 cm^2). All three electrodes were held in solution using crocodile clips. The electrodes were placed through the central neck while the two remaining connections were sealed with subaseal plugs. Before removal from the dry box ca. 25 cm^3 of electrolyte was added to the cell. The cell, once sealed, was then removed from the dry box for electrochemical/ultrasound investigation. The electrolyte was observed to remain reasonably water free during the course of the experiment. This observation was made from the state of the lithium metal. The lithium foil remained pristine and shiny throughout the experiment and for a period of several months outside the glove box. These observations indicate that the water content of the electrolyte remained low and the seals of the cell were reasonably tight.

The second cell, employed for lithium plating stripping studies on a 50 μm Cu microelectrode under galvanostatic control, was constructed from a modified boiling tube. In this case a large piece of lithium metal (ca. 3 cm^2) was used as a reference/counter. Again the cell was assembled in the dry box and then removed for electrochemical/ultrasound experiments.

Both cells were exposed to ultrasound by partial immersion into a ultrasonic cleaning bath filled with tap water. The temperature of the water bath was measured during a set of experiments and was found to be in the range 22–26°C. It was also noted that the temperature of the bath rose slowly during irradiation of the cell with ultrasound but never exceeded the range of 25–27°C. This increase in temperature (ca. +2–3°C) was expected and is the result of the sound energy input during irradiation of the liquid.

All solutions consisted of 1 mol dm^{-3} lithium hexafluoroasenate, $LiAsF_6$, in propylene carbonate.

2.4. Impedance monitoring

The effect of ultrasound was investigated by measuring the impedance spectrum before, during and after a period of continuous ultrasonic irradiation. The electrode was held at 0 V vs. Li/Li^+ at all times. In each case the impedance was monitored between 5 kHz and 10 Hz as a

function of time. Each impedance spectrum took ca. 23 s to record and the process was repeated every 60 s. The data recorded in this way were transferred to a PC for analysis after the experiment was performed. In order to analyse the data Boukamp software was employed to perform batch curve fitting of the impedance data recorded. These data were then used to calculate the interfacial resistance at the surface of the electrode.

3. Results and discussion

3.1. Dynamic impedance studies

Fig. 1 shows the impedance spectra of a lithium electrode exposed to the electrolyte solution for ca. 3.5 h (○) and then the same film after exposure to 400 s continuous ultrasound (●). The spectra indicate that the surface of the lithium interface has been covered with a partially blocking film the resistance of which is subsequently reduced by the application of ultrasound. Such film formation is known to be heavily dependent on the solvent, electrolyte, electrolyte impurities and length of exposure of the lithium surface to the electrolyte [14–17].

Fig. 2 shows the variation in the film resistance measured as a function of time during the experiment. The shaded region indicates the time period during which ultrasound was applied to the system. Prior to the application of the sound field, the resistance of the film was fairly stable over the time scale investigated in this experiment. On exposure of the cell to ultrasonic irradiation there is a clear decrease in the interfacial resistance indicating ero-

Fig. 2. Plot showing the film resistance determined from the Boukamp Data analysis software. The experiment was performed under the same conditions as shown in Fig. 1. The shaded region shows the time period during which the cell was irradiated with ultrasound.

sion of the passivating film on the lithium electrode. This reduction continued until the application of ultrasound was terminated at ca. 500 s. Over the 400 s exposure to ultrasound the film resistance fell by ca. 25% (ca. 310 Ω cm^2 to 225 Ω cm^2). After the ultrasonic irradiation of the liquid was terminated the resistance of the film increased indicating film reformation occurs over the surface of the electrode.

It was noted that during the exposure to ultrasound bubbles formed within the cell and small pieces of lithium were eroded from the surface of the lithium counter and reference electrodes. These observations, along with the film resistance decline during ultrasonic irradiation of the cell, are consistent with the removal of surface layers from the lithium metal as the result of cavitation.

3.2. Lithium plating / stripping study

The effect of ultrasound on lithium plating and stripping on a 50 μm diameter copper microelectrode was also investigated. These experiments were performed under constant current conditions. Fig. 3 shows the lithium plating and stripping region of the potential time curve in the absence (. . . . . .) and presence (————) of ultrasound. The figure shows that, in the absence of ultrasound, the potential rises, after a nucleation overpotential peak, to a steady value and remains there until the current was reversed. After ca. 90 s plating the current polarity was reversed, stripping lithium metal from the surface of the electrode. At ca. 150 s the potential of the electrode rises sharply indicating that all the lithium metal has been removed from the electrode surface. This experiment indicated that ca. 60% of the charge employed to deposit the lithium metal was regained. The deviation from 100% efficiency maybe due to the combination of parasitic Faradaic processes and electrical isolation of material from the electrode surface.
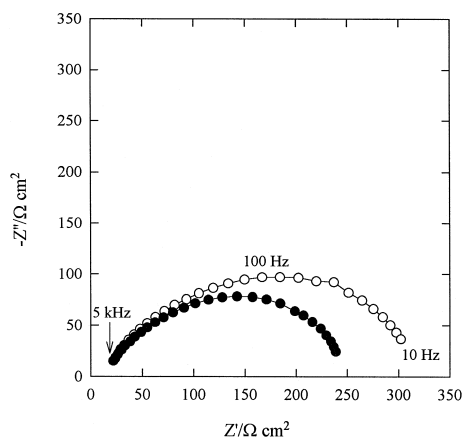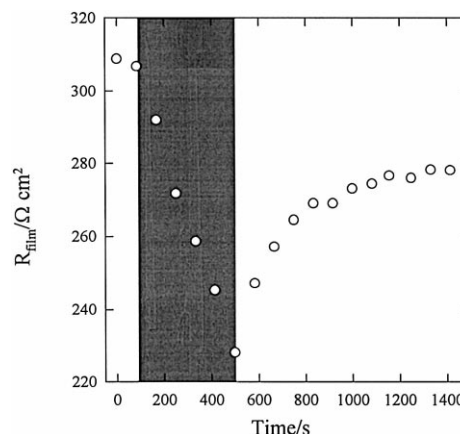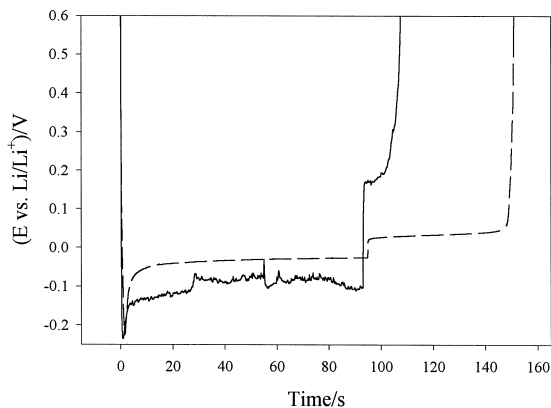

Fig. 1. Plot showing impedance spectra recorded between 5 kHz and 10 Hz of a lithium electrode prior to (○) and after exposure (●) to ca. 400 s ultrasound. The cell contained a 1 mol dm^{-3} LiAsF$_6$/propylene carbonate electrolyte and the experiment was performed under anaerobic conditions as described in the text. The data was recorded between 5 kHz and 10 Hz. In this experiment the depth of water in the bath was approximately 7–8 cm.

Fig. 3. Plot showing the electrode potential recorded as a function of time for a 50 μm diameter copper microelectrode under galvanostatic control. The cell contained a 1 mol dm^{-3} LiAsF$_6$/propylene carbonate electrolyte and the experiment was performed under anaerobic conditions. The electrode was held at 0 nA prior to time t = ca. 0 and -50 nA after this point until time t = ca. 90 after which the cell current was reversed to $+50$ nA. The figure shows voltage potential curve in the presence (————) and absence (— —) of ultrasound. The ultrasonic bath contained ca. 5 cm depth of water.

In the presence of ultrasound the plating process requires a higher overpotential to maintain the constant -50 nA employed in the experiment. This is indicative of the removal of nucleation sites from the surface of the microelectrode. Consequently a higher overpotential is required to maintain the -50 nA constant current. In this case the plateau voltage, which is less stable, remains more negative at ca. -100 mV vs. Li/Li$^+$. Similarly when the current polarity was reversed, indicating lithium stripping at time t = 90 s, it is apparent that the time required to remove lithium from the surface decreases. Subsequently the stripping/plating efficiency falls to 18% in the presence of ultrasound. These results indicate that the efficiency of the plating/stripping process was reduced dramatically in the presence of ultrasound. This is attributed to the cavitation erosion of the lithium metal as it is deposited and stripped off the copper surface.

Fig. 4 shows the effect of ultrasound on a lithium coated microelectrode. Initially, -4.5 μC of charge was used to deposit lithium onto the surface of the 50 μm diameter copper microelectrode. This was performed at a -50 nA current in the absence of ultrasound. Assuming that the efficiency of the deposition process was 60% (as determined previously) this corresponds to an average thickness of lithium of ca. 0.19 μm. Fig. 4 shows the potential of the lithium coated microelectrode in the absence of a Faradaic current. In the absence of ultrasound the potential of the microelectrode remains approximately constant at 0.01 V vs. Li/Li$^+$. In theory the voltage should be 0 V vs. Li/Li$^+$. However, the positive voltage is an indication of a mixed potential set up by the oxidation of the lithium surface and the reduction of solution species to form the passive layer [18]. On exposure of the cell to ultrasound the potential immediately rises to ca.

0.08 V vs. Li/Li$^+$. This is consistent with first, improved mass transfer of material to the electrode and second, surface cleaning effects. These are both as the result of cavitation within the liquid. After ca. 40 s the potential of the microelectrode rises rapidly towards the open circuit potential of the copper electrode within the propylene carbonate/LiAsF$_6$ electrolyte. This experiment indicates that the application of ultrasound enhances the corrosion of the lithium metal plated onto the microelectrode in the previous silent experiment.

It should be noted that cavitation is an extremely localised and chaotic phenomenon and the associated sound field produced within the cells is particularly complex. This results in a difficulty in predicting the sound field within the cells and at the surface of the electrodes. However, the acoustic pressure within the bath was measured using a hydrophone and found to range between ca. 0.6–1.35 atm. It should also be noted that the observed effect of ultrasound on the electrochemistry, particularly in the microelectrode experiments, was dependent on the volume of liquid within the ultrasonic bath. In the impedance experiments the ultrasonic bath was filled to a depth of ca. 7–8 cm. and a relatively large working electrode employed. The reduction in the interfacial resistance was found to be repeatable and reproducible. However, in the microelectrode studies the depth of the liquid within the ultrasonic bath was reduced (ca. 5 cm). This depth reduction was found accelerate the erosion of the lithium layer on the surface of the microelectrode and was accompanied by an increased rate of erosion of the lithium counter/reference electrode employed in this particular cell. This resulted in lithium fragments suspended within the solution. This observation indicates that the sound field within the cell is, as expected, dependent on the volume of liquid. This will effect the observed results particularly
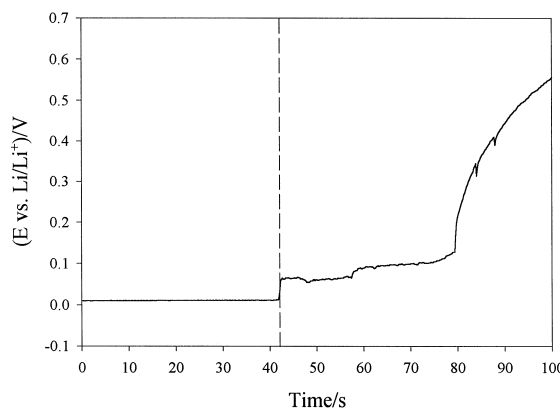

Fig. 4. Plot showing the electrode potential (————) recorded as a function of time for a 50 μm diameter copper microelectrode held at 0 nA. The experiment was performed under the same conditions as shown in Fig. 3. The lithium layer was deposited for 90 s at -50 nA. The microelectrode was exposed to ultrasound at time t = 42 s denoted by (— —).

considering the small volume of liquid probed by the 50 μm microelectrode. Nevertheless, the results presented here where found to be broadly reproducible with the erosion of the lithium interface on exposure to ultrasound always observed.

4. Conclusions

It has been demonstrated that the influence of ultrasound on the surface of a lithium electrode is to reduce the resistance associated with passive film formation. The reduction in film resistance, which coincided with the application of ultrasound to the system, was repeatable and extended up to a 25% reduction in the film resistance over a 400 s time period.

The application of ultrasound to the galvanostatic plating and stripping of lithium metal on a copper microelectrode indicated that the cavitation process had only a small influence on the nucleation overpotential required to initiate lithium plating. However, ultrasound was shown to dramatically increase the plateau voltage required after the initial nucleation step. This demonstrates the ability of cavitation to remove nucleation sites from the surface of the microelectrode as indicated by the continual more negative overpotential observed. The presence of ultrasound has been shown to decrease the efficiency of the plating/stripping process. The application of ultrasound was shown to increase the rate of corrosion of the surface and consequently remove lithium metal from the surface of a copper microelectrode.

These observations are consistent with the cavitation erosion of the surface of the lithium electrodes employed.

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