

## Investigations on an aqueous lithium secondary cell

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### Abstract

The deposition and stripping of lithium from different substrates has been investigated in saturated aqueous solutions of LiCl/LiOH to assess the possibility of developing a secondary lithium battery with high energy density and high power density, and based on water as a solvent. On mercury electrodes, a low catalytic activity for hydrogen evolution is observed, together with a positive shift in potential on amalgamation. This means that lithium deposition is the predominant electrode reaction at negative potentials. Indeed, the lithium charge recovery at a mercury anode is 98.5%. Other practical anode materials, however, fail to give a charge recovery anywhere close to this value. Anode materials investigated include metals that alloy with lithium and materials that form lithium insertion compounds. Manganese dioxide appears to be an effective cathode material for a battery using saturated LiCl/LiOH as the electrolyte. The positive electrode reaction at MnO<sub>2</sub> in this medium is shown to be lithium insertion rather than protonation, and acceptable rechargeability is observed.

**Keywords:** Secondary lithium cells; Aqueous secondary lithium cells; Lithium chloride; Manganese dioxide; Intercalation

### 1. Introduction

Interest in electric vehicles (EVs) is once again on the increase. It is being stimulated by legislation in California and other States of the USA that requires the introduction of 'zero emission' vehicles. Unfortunately, the source of motive power remains problematic even though a large research effort has been expended over many years. The lead/acid battery still retains its position at the forefront of candidate batteries despite the limited range engendered by the low energy density of this battery.

Lithium is an obvious choice as an active battery material for EV batteries because of its low atomic weight and high reactivity, and lithium battery systems are being developed that offer the prospect of high energy density. Nevertheless, lithium electrolytes in ambient-temperature systems are typically dissolved in organic solvents, or polymeric materials, and both options limit the power density that can be achieved in comparison with aqueous systems.

It has been noted in work on the solvent extraction of metals [1,2] that saturated lithium chloride has a high lithium activity and a low free-water activity. Indeed, such a solution is 13.5 M in LiCl but only 0.11 M in H<sub>2</sub>O; most of the water is strongly bound in

complexes of the type Li(H<sub>2</sub>O)<sub>n</sub><sup>+</sup>, where  $n \approx 4$ . Consequently, it is reasonable to conclude that saturated lithium chloride might form the basis of an aqueous lithium secondary battery. In principle, such a battery could have a high power density, as well as a high energy density, since it contains a very conductive solution. The specific conductivity of saturated lithium chloride is about 50 mS; this is an order of magnitude greater than that of organic electrolyte systems.

For a lithium electrode to operate efficiently in an aqueous solution, hydrogen evolution needs to be suppressed. The reversible potential of the lithium electrode in 13.5 M lithium ion solution is  $-3.2$  V versus the Ag/AgCl electrode in saturated LiCl, whereas the reversible potential of the hydrogen electrode (RHE) in saturated LiCl is  $-0.9$  V (i.e., 0.3 V more negative than in conventional, neutral solutions due to the reduced activity of water). Although the potential of the RHE can be shifted to  $-1.3$  V if the solution is also saturated with lithium hydroxide (about 3 M), a large gap remains.

Two possible approaches to overcome the potential gap can be suggested. First, a substrate might be found that has a high hydrogen overpotential so that the onset of hydrogen evolution is displaced to much more negative potentials. Second, a substrate might be selected that

interacts with lithium metal to lower its activity so that metal deposition occurs at less negative potentials. The objective of both approaches is to eliminate the gap without sacrificing energy density.

Recently, aqueous lithium secondary batteries have been described [3] in which the anode potential is less negative than that for hydrogen evolution; this is achieved by incorporating lithium in a suitable insertion compound. Such an approach results, however, in a substantially lower cell voltage and lower energy density than batteries based on lithium metal itself. For example, the open-circuit voltage of a cell in which lithium transfers between a  $\text{VO}_2$  anode and a  $\text{MnO}_2$  cathode is about 1.5 V in the fully charged state [3], whereas that for  $\text{Li/MnO}_2$  is about 3.5 V. The former 'rocking-chair' system has an energy density similar to that of nickel/cadmium or lead/acid [3]. The battery could compete with the conventional systems in a range of applications because it offers fundamentally safe and cost-effective technology, but would not appear to be the answer for EVs.

The work presented here has been directed towards the goal of identifying materials that promise the development of an aqueous lithium secondary battery with a high voltage and a high energy density. The results of these studies were described briefly at the 8th Australian Electrochemical Conference [4].

## 2. Experimental

### 2.1. Chemicals

Lithium chloride was obtained from two sources: most experiments were conducted using May and Baker AR LiCl, but one batch of LiCl was prepared from  $\text{Li}_2\text{CO}_3$  (Merck extra pure) and HCl (BDH Aristar). All solutions were filtered and further purified as described below. The LiOH was BDH Sepramar. All other chemicals were AR grade.

### 2.2. Anode materials

Aluminium electrodes consisted of high purity (99.999 wt.%) blocks cast in epoxy resin. The working area of  $0.5 \text{ cm}^2$  was polished using  $5 \mu\text{m}$  alumina. Bismuth, indium, lead and tin electrodes were similarly constructed, but their surfaces were abraded with #1200 silicon carbide paper. Mercury electrodes (BDH Aristar grade) were single drops with surface areas of  $0.14 \text{ cm}^2$ .

Highly oriented pyrolytic graphite (Union Carbide, USA) and petroleum coke (Kaiser) were both cast in epoxy resin in the same manner as the metal electrodes. The pyrolytic graphite was oriented with either the basal plane or the edge plane exposed. Other electrodes,

i.e., spectrographic carbon rod (Union Carbide, USA) and carbon foil (Sigraflex F10, Germany), were simply immersed a few mm into the cell solution; fresh surfaces were used for each experiment. Graphite powder electrodes were prepared by pressing 0.17 g of powder (Lonza KS24) into a 1 cm diameter pellet.

Ferric oxide (BDH calcined  $\text{Fe}_2\text{O}_3$ ) was mixed thoroughly with 25% of its weight of graphite (Lonza KS24) by tumbling overnight in a small vial. Portions of this mixture were pressed in a 1 cm diameter die at 57 MPa to give a pellet of about 1 mm thick; the resistance between the faces was typically  $0.3 \Omega$ . Pellets were prepared in the same way from a mixture of 5 parts  $\text{MoO}_2$  (Johnson Mathey Alpha Products, Germany) and 1 part Teflon powder (Hoechst, Hostafion N LP92); the resistance between the faces was typically  $1 \Omega$ .

### 2.3. Cathode materials

Manganese dioxide electrodes were prepared from electrolytic manganese dioxide (EMD) (BHP-Utah) that had been mixed intimately with 25% natural graphite (Lonza KS24) and 0.5% acetylene black by tumbling for 48 h with several stainless-steel balls in a small glass vial. Pellets of 1 cm diameter were formed by pressing 0.2 g of the electrode mixture on to an expanded tantalum mesh spot-welded on to tantalum foil.

### 2.4. Electrochemical methods

Potentials were controlled with a PAR Model 173 potentiostat fitted with a Model 179 coulombmeter and an Amel Model 567 function generator. Reference electrodes were normally Ag/AgCl/saturated LiCl or Hg/Hg<sub>2</sub>Cl<sub>2</sub>/saturated LiCl, but Al wire in saturated LiCl was also used in some experiments to ensure solution contamination was avoided. All potentials are quoted versus Ag/AgCl in saturated LiCl. This reference electrode had a potential of  $-0.064 \text{ V}$  versus a saturated calomel electrode and, hence,  $0.18 \text{ V}$  on the standard hydrogen electrode scale.

Cycling of lithium on to metal substrates was carried out in a conventional three-compartment cell. For cycling on to compacted pellet substrates, a modified version of a cell designed for determining the rechargeability of manganese dioxide in alkaline media [5] was employed. The pelletized electrodes were subjected to constant pressures of  $27 \text{ N cm}^{-2}$  during cycling in order to inhibit mechanical degradation and maintain good electrical contact between the electrodes and the tantalum discs on which they were mounted.

Pellets of  $\text{MnO}_2$  were charged at a constant current of 10 mA in saturated LiCl to a potential of 1.2 V. The pellets were washed with water, dissolved in  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ , and then analysed for lithium and manganese.  $\text{MnO}_2$  electrodes were cycled at a constant current or

in a current-limited, constant-potential, charging mode. In the former, the cell was discharged at 10 mA to  $-0.3$  V and then charged to 1.2 V. In the latter, the discharge procedure was the same, but the electrode was held at 1.2 V for 3 h as the final stage of the charging regime.

To ensure that solutions were saturated, experiments were usually conducted with solid LiCl present in the cell.

### 2.5. Purification of electrolyte solutions

Lithium chloride solutions were purified by passing them through a column packed with Chelex 100 (Bio-Rad AR grade) to extract the ions of any impurity metals that may be present. The Chelex was first converted from the sodium to the lithium form in situ by flushing with nearly saturated LiCl solution until no sodium was detected in the eluate by a flame test. The first lithium chloride solutions obtaining after completing this procedure were rejected; the subsequent purified solution was collected and concentrated by evaporation under vacuum.

Following passage through the Chelex column, some solutions were further treated by pre-electrolysis for periods of up to 11 days using a working electrode of reticulated vitreous carbon (RVC, the Electrolysis Co., USA). In a number of cases, solutions were also purified by pre-electrolysis using a mercury pool electrode. The progress of purification was monitored using anodic stripping voltammetry (ASV) on a glassy-carbon electrode.

## 3. Results and discussion

### 3.1. Mercury anodes

Although mercury is not a practical anode substrate, it is a useful material to assess the feasibility of a lithium aqueous secondary battery based on saturated LiCl/LiOH. Mercury is a very poor catalyst for hydrogen evolution [6] and amalgamates with lithium to reduce its activity and hence shift the deposition potential to less negative values. Cyclic voltammograms for lithium deposition on a  $0.14$  cm<sup>2</sup> mercury drop from saturated LiCl/LiOH are shown in Fig. 1. The performance of the lithium electrode on various substrates was considered in terms of charge recovery. This is defined as the modulus of the positive charge passed in stripping lithium as a percentage of the negative charge passed during the deposition of lithium. The charge recovery on mercury was 98.5%, which is of the order required for a functioning battery electrode.

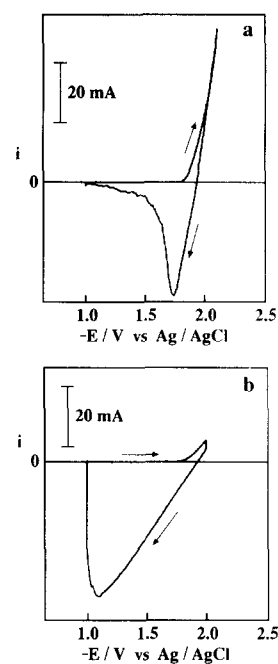


Fig. 1. Cyclic voltammograms for Li deposition/stripping on a  $0.14$  cm<sup>2</sup> mercury drop in saturated LiCl/LiOH: (a) potential scanned at  $50$  mV s<sup>-1</sup> from  $-1.0$  to  $-2.1$  V and back, and (b) potential scanned at  $50$  mV s<sup>-1</sup> from  $-1.0$  to  $-2.0$  V, held at  $-2.0$  V for  $120$  s, and scanned back to  $-1.0$  V.

### 3.2. Aluminium anodes

Lithium interacts with aluminium to form alloys with high lithium activity. This property has led to aluminium being considered as an anode substrate in lithium organic electrolyte batteries [7]. The charge recovery of lithium from saturated LiCl/LiOH solutions was studied using a test regime that involved scanning the potential from  $-1.0$  to  $-3.0$  V at  $50$  mV s<sup>-1</sup>, holding the potential at the lower value for  $120$  s to deposit lithium, and then scanning back to  $-1.0$  V to strip the lithium.

Fig. 2 shows charge/discharge voltammograms for an aluminium electrode in saturated LiCl/LiOH for the third and tenth cycles. The charge recovery on the initial cycle was quite low, but reached a constant value of 21% by the third cycle. In many electrodeposition systems, hydrogen generation arises from the influence of co-deposition of impurity metals rather than the metal under deposition or the substrate. Since saturated LiCl is  $13.5$  M, even very low levels of impurities in the solid electrolyte would result in significant concentrations in the solution. To determine whether the poor charge recovery found at aluminium was due to impurity deposition, a study was made of the effect of extensive purification procedures involving passage through Chelex 100 and extended pre-electrolysis at reticulated carbon and mercury pool electrodes. Purification was continued until no strippable metals could be detected by anodic stripping voltammetry. Despite this procedure, no improvement in charge recovery was

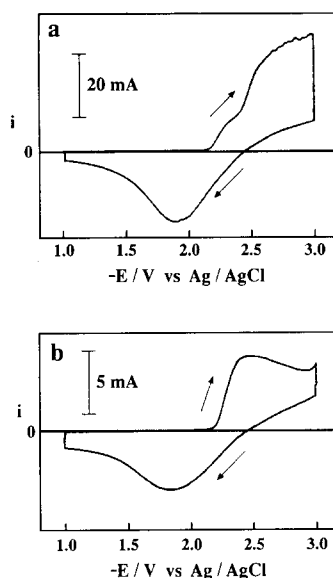


Fig. 2. Cyclic voltammograms for Li deposition/stripping on Al in saturated LiCl/LiOH. Potential scanned at  $50 \text{ mV s}^{-1}$  from  $-1.0$  to  $-3.0$  V, held for 120 s, and scanned back. Electrode area =  $0.5 \text{ cm}^2$ . (a) Third cycle, and (b) tenth cycle.

obtained and this indicates that the low value was an intrinsic property of the aluminium.

The effect of a number of organic additives on charge recovery was investigated. No effect was observed from the addition of quaternary ammonium ions, which would be expected to adsorb on the negatively charged Li/Al alloy, or of methylene blue that has been reported [8] to enhance the efficiency of lithium electrodes cycling in organic electrolytes. A Nafion membrane, formed on the surface of an aluminium electrode by evaporation from solution, decreased both deposition and stripping charges but did not increase charge recovery. Presumably, water of solvation was transported through the membrane with the lithium ions.

A number of inorganic chemicals are known [9] to inhibit the hydrogen-evolution reaction. No effect on charge recovery was observed, however, on the addition of  $\text{As}_2\text{O}_3$ ,  $\text{Na}_2\text{S}$  or  $\text{CS}_2$  at concentrations of  $10^{-4}$  or  $10^{-3}$  M. When lead was present at high concentrations ( $> 10^{-3}$  M), the recovery was increased to a maximum of 30%, but both deposition and stripping charges were decreased by nearly an order of magnitude.

Mercury did not decrease the rate of hydrogen evolution on aluminium, although small peaks were observed for the deposition and stripping of lithium into co-deposited mercury. The mercury also caused the aluminium to dissolve at potentials more positive than  $-1.7$  V.

### 3.3. Other metal anodes

Voltammetric determinations of charge recovery were carried out on other metals with low catalytic activity

for hydrogen evolution, viz., lead, tin, bismuth and indium [6]. Of these, only bismuth showed a measurable charge recovery, but the value of 20% was even lower than that for aluminium.

### 3.4. Insertion anodes

Recent developments in lithium organic electrolyte batteries have involved the use of anode as well as cathode substrates into which lithium is inserted (or intercalated) on charge. The stored energy is derived from the difference in activity of lithium in the two materials. A lithium-ion battery based on this principle is reported [10] to overcome safety concerns related to the use of pure-lithium metal electrodes in conventional lithium batteries.

In the present work, a number of different carbons were investigated since carbon is known [11–13] to intercalate lithium from organic electrolytes. Unfortunately, however, copious quantities of hydrogen were evolved from carbon electrodes in saturated LiCl/LiOH at potentials more negative than about  $-1.5$  V. Significant charge recoveries were only obtained with graphite pellets when the potential was restricted to  $-1.3$  V, see Table 1. This potential is close to the reversible value for hydrogen at unit fugacity in saturated LiCl/LiOH and hence the application of carbon anodes is restricted by the catalytic activity of this material. The addition of quaternary ammonium compounds or lead to inhibit hydrogen evolution had no effect on charge recovery.

Conceptually, a thin mercury film on a lithium insertion compound would appear to be an ideal anode substrate. The charge recovery should be that of mercury, while the insertion compound would act as the energy storage medium. The deposition of mercury on carbon was investigated from this viewpoint. Unfortunately, mercury does not significantly reduce hydrogen evolution on carbon although, as with aluminium, small

Table 1  
Carbon electrodes tested for lithium charge recovery

Carbon electrode	Intercalation potential (V)	Time (s)	Recovery (%)
Graphite foil	-2.5	120	0
Spectrographic C rod	-2.5	120	0
Petroleum coke	-2.5	120	0
Highly oriented pyrolytic graphite:			
Cleavage plane	-2.3	120	2
Edge planes	-2.3	120	17
Graphite pellets	-1.3	120	80
	-1.3	360	56
	-2.5	120	0*

\* Pellet disintegrated.

peaks could be seen for lithium deposition into, and stripping from, co-deposited mercury (Fig. 3). The failure to suppress hydrogen on carbon appears to result from the discrete morphology of the deposited mercury. Microscopic examination showed that mercury did not completely wet the carbon surface, but instead formed droplets.

Molybdenum dioxide [14] and ferric oxide [15,16] have also been proposed as insertion anodes for lithium organic electrolyte batteries. The molybdenum oxide electrodes tested in the present work consisted of pellets of molybdenum oxide with 10% Teflon as a binder. These electrodes could be employed only between  $-0.2$  and  $-1.3$  V since they appeared to be oxidized at potentials above the former value and copious amounts of hydrogen were evolved at potentials more negative than the latter value. The charge recovery for scans to  $-0.9$  V are shown in Table 2. Values up to 85% were obtained, but this is not good enough for a viable cathode. It is apparent that, as with carbon, the catalytic activity for hydrogen evolution is too high. With ferric oxide anodes in saturated LiCl/LiOH electrolyte, copious amounts of hydrogen were evolved at potentials more negative than  $-1.3$  V and caused the pellet to disintegrate. When the potential was restricted to  $-1.0$  V, charge recoveries were not negligible, particularly

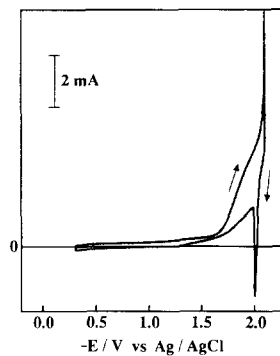


Fig. 3. Cyclic voltammogram for Li deposition/stripping on spectrographic carbon in saturated LiCl/LiOH with  $2 \times 10^{-4}$  M HgCl<sub>2</sub>. Scan rate  $20 \text{ mV s}^{-1}$ . Electrode area  $\sim 1 \text{ cm}^2$ .

Table 2  
Other intercalation electrodes tested for lithium charge recovery

Carbon electrode	Intercalation potential (V)	Time (s)	Recovery (%)	
Molybdenum dioxide	$-0.9$	120	85	
	$-0.9$	2100	44	
Iron oxide	Before cycling	$-1.0$	120	68
		$-1.0$	1500	35
	After cycling	$-1.0$	120	85
		$-1.0$	360	83
		$-1.2$	120	38 <sup>a</sup>

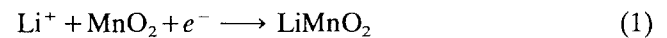
<sup>a</sup> Pellet disintegrated.

after cycling, but, again, the high catalytic activity for hydrogen evolution renders the material inappropriate in the aqueous electrolyte.

### 3.5. Cathodes

In addition to a suitable anode, an appropriate cathode material must be identified if an aqueous lithium secondary battery is to be a reality. The ideal cathode involves incorporation of lithium since the electrolyte with such a material simply acts as a transport medium for lithium ions. In this case, only a small quantity of electrolyte is required. Manganese dioxide was investigated since this low-cost material would be an economic proposition for an EV battery.

The cell reaction for charging manganese dioxide electrodes in organic media is the incorporation of lithium:



and the overall reaction of an Li/MnO<sub>2</sub> battery is:



On the other hand, MnO<sub>2</sub> would not be useful if the positive electrode reaction was the insertion of protons as occurs in the alkaline Zn/MnO<sub>2</sub> battery, i.e.:



In this case, the overall process would be:



If Eq. (4) accounted for the total cell reaction, large quantities of electrolyte would need to be included and unacceptable changes in electrolyte composition would occur. Some proton insertion could easily be accommodated, however, provided solid LiCl is present in the battery to maintain saturation as the water content changes.

Analysis of a manganese dioxide electrode after discharge at 10 mA until the potential reached  $-0.3$  V gave a Li:Mn ratio of 1:3 compared with a ratio of 1:2 if all the charge had arisen from lithium insertion. The observed ratio could be low due to rinsing the electrode to remove LiCl from the pores of the cathode pellet. Nevertheless, the result does indicate that Eq. (1) was the predominant process in saturated LiCl. This result is in agreement with a previous report [3] of the action of MnO<sub>2</sub> in an aqueous lithium electrolyte.

Fig. 4 shows the capacity of the manganese dioxide electrode in saturated LiCl on applying 60 consecutive charge/discharge cycles under the current-limited constant-potential charging mode. It can be seen that there is a rapid loss in capacity over the first few cycles but the capacity levels off to a constant value after 25 to 30 cycles. The cumulative capacity over 60 cycles was similar to that found in 9 M KOH [5].

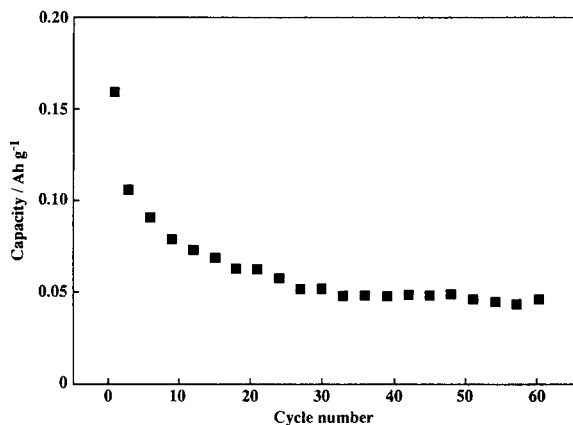


Fig. 4. Discharge capacity vs. cycle number for  $\text{MnO}_2$  pellet using current-limited, constant-potential charging in saturated  $\text{LiCl}$ .

#### 4. Conclusions

Investigations have been carried out that establish the feasibility of a lithium secondary battery with a saturated  $\text{LiCl/LiOH}$  aqueous electrolyte. By shifting the lithium deposition potential to less negative values, and inhibiting hydrogen evolution, it is possible to cycle a lithium electrode with a charge recovery close to a practical value of 99%. Unfortunately, the only anode material identified that achieves this objective is mercury. Less environmentally sensitive anode materials tested fell short of the required performance.

Manganese dioxide could act as a suitable cathode material for a lithium secondary battery with the saturated  $\text{LiCl/LiOH}$  aqueous electrolyte. It was found that the reaction at the  $\text{MnO}_2$  electrode was the insertion and removal of lithium and that rechargeability was acceptable.

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