

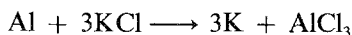
# *Electrochemical reduction of potassium from potassium chloride in propylene carbonate electrolyte with aluminium anodes*

R. T. ATANASOSKI\*, H. H. LAW†, C. W. TOBIAS

*Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of California, Berkeley, CA 94720, USA*

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Potassium has been cathodically deposited in a propylene carbonate electrolyte with concurrent dissolution of aluminium. Starting with an  $\text{AlCl}_3$ -free electrolyte, changes in the composition and conductivity of the electrolyte, as well as those of the electrode potentials, were measured as a function of charge passed. Anodic and cathodic current efficiencies were both close to 100%. The observed behaviour is consistent with the overall reaction stoichiometry



This reaction and its analogues for other alkali metals may conceivably form the basis of practical processes at ambient temperatures for the recovery of alkali metals from their chlorides with concurrent production of aluminium chloride.

## 1. Introduction

Potassium is one of the more abundant elements and is an important metal because of its high reactivity and its low ionization energy. At present, potassium metal is mainly used in the manufacture of potassium superoxide for use as the source of oxygen in gas mask applications, and in the production of sodium–potassium alloy for use as a heat transfer fluid. Because the present thermochemical process [1] for the reduction of potassium is difficult and costly to operate this metal is very expensive compared to sodium and lithium and consequently markets have not developed for potassium.

The development of an electrochemical process for potassium production has been a subject of interest to Harris and Tobias since their initial electrochemical studies of propylene carbonate (PC) [2]. The electrochemical behaviour of the alkali metals in PC, from both the thermodynamic and the kinetic points of view, was

treated in a series of papers by Jorné and Tobias [3–7]. Chacon [8] was able to obtain a high quality adherent potassium deposit from PC. Law [9] studied the optimal conditions for potassium deposition both in solid and liquid form and explored the feasibility of scaling-up the deposition process in  $\text{KAlCl}_4$ -PC electrolyte.

For a practical process, the major technical obstacle is the anodic reaction. For the electro-winning of potassium in  $\text{KAlCl}_4$ -PC electrolyte, three anodic reactions have been considered: the dissolution of potassium from its amalgam, the oxidation of chloride to chlorine and the dissolution of a sacrificial metal. Brenner [10] suggested the use of potassium amalgam as a source of potassium for a non-aqueous electrorefining process. Tobias and Jorné [11] examined the feasibility of a room-temperature process for producing alkali metals using the alkali metal amalgams obtained from aqueous electrolysis. In spite of the potential benefits offered, this

\* Present address: Institute of Electrochemistry, ICTM, Belgrade, Yugoslavia.

† Present address: AT & T Bell Laboratories, Murray Hill, NJ 07974, USA.

refining process from alkali amalgams has not been further advanced because mercury-chlorine cells are currently not in favour due to environmental pollution considerations. If KCl were used as the source of potassium, the evolution of chlorine would be the logical choice for the anodic reaction. Curiously, the behaviour of halogens in PC has not been a subject of thorough evaluation until recently. Hanson [12] found that PC reacts with purified and dried chlorine. Moreover, the evolution of chlorine in the presence of  $\text{AlCl}_3$  does not occur from free chloride ions but from the strong  $\text{AlCl}_4^-$  complex. Hence, the anodic discharge of  $\text{AlCl}_4^-$  requires high positive potential [13].

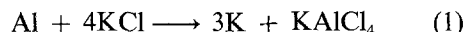
The ideal sacrificial metal should not deposit before potassium. Chacon [8] and Law [9] have reported that the  $\text{AlCl}_4^-$  ion cannot be cathodically reduced from  $\text{KAlCl}_4$ -PC electrolyte and consequently potassium deposits contain no aluminium. Thus, aluminium could be a useful sacrificial metal if it were to dissolve, forming the stable ionic species  $\text{AlCl}_4^-$ . The purpose of this work is to examine the basic feasibility of such a process.

## 2. Process description

One of the process schemes we have chosen to evaluate involves potassium chloride as a potassium source and aluminium metal as the sacrificial anode in  $\text{KAlCl}_4$ -PC electrolyte. High purity potassium chloride is cheap, abundant and readily available. Aluminium metal is also relatively inexpensive per gram equivalent\*.

The process consists of anodically dissolving aluminium and depositing potassium at the cathode, consuming aluminium and potassium chloride and yielding  $\text{AlCl}_3$  or  $\text{KAlCl}_4$  as side products. The process involves the following reactions. Aluminium is anodically dissolved to form the trivalent aluminium ion which would immediately solvate by PC according to Keller *et al.* [14]. Simultaneously, three potassium atoms deposit at the cathode. In the presence of chloride ions the dominant aluminium species is  $\text{AlCl}_4^-$  [14]. The complexing ability of  $\text{AlCl}_3$

makes the use of KCl as a source of potassium ions in the PC system possible. In spite of its low solubility when dissolved alone ( $3.52 \times 10^{-4} \text{ mol kg}^{-1}$  at  $20^\circ \text{C}$  [15]), KCl can form the complex  $\text{KAlCl}_4$  with  $\text{AlCl}_3$ , providing a concentration of more than  $1 \text{ mol kg}^{-1}$  potassium cations for reduction [3]. In summary, the net reaction for the cell process is



For every three moles of potassium produced, one mole of  $\text{KAlCl}_4$  is formed which may be removed, for example, by crystallization. Alternatively, aluminium chloride may be recovered as the side product by continuing the process without excess KCl. The electrode reactions remain the same as before and the net cell reaction is



## 3. Experimental details†

All experimental work such as electrolyte preparation and electrolysis was performed in a dry glove box with a helium atmosphere. The water content of the helium gas was continuously monitored and maintained at about 2 p.p.m. Technical grade PC (Jefferson Chemical Company, Houston, Texas) was purified by vacuum distillation at 3 mm Hg after passing it through a column of dried molecular sieve (Linde, 13X) and alumina (aluminium oxide, Woelm basic, ICN, Cleveland, Ohio). The first 10% of the distillate was discarded. The middle 60% was transferred to the glove box for use without further purification. The distillate obtained had less than 1 p.p.m. water and less than 5 p.p.m. propylene glycol. Reagent grade potassium chloride or lithium chloride were finely ground and then dried at  $300^\circ \text{C}$  under vacuum ( $10^{-3} \text{ mm Hg}$ ) for at least 48 h.

In the experiments for conductivity measurements an H-type glass vessel was used with one chamber serving as the electrolysis compartment and the other for conductance measurements. An aluminium rod (99.9995%, 0.5 cm in diameter) served as the anode. The cathode, a cylindrical platinum screen (2.5 cm in diameter,

\* One gram equivalent of aluminium at the current market price, \$1.80 per kg, cost 1.6 cents.

† For greater detail, see [9].

40 cm<sup>2</sup> surface area), was placed concentrically around the anode. The reference electrode was a potassium-filled capillary in the same solution. Initially 2 g powdered potassium chloride were added to 40 cm<sup>3</sup> PC. The suspension was stirred by a magnetic bar before and during electrolysis. The changing conductivity was measured in the quiescent solution using an a.c. bridge at 1 kHz. The conductance cell contained two parallel bright platinum plate electrodes with a cell constant of 0.0218 cm<sup>-1</sup>, determined using 10<sup>-3</sup> M KCl aqueous solution at 25°C.

A separate, single compartment cell used in experiments for composition analysis and for the determination of current efficiency is shown in Fig. 1. The anode was a cylindrical aluminium rod (99.9995%) while the cathode was the same platinum screen electrode mentioned earlier. A potassium-filled glass capillary served as the reference electrode. The electrolyte containing 1.392 g KCl suspended in 20 cm<sup>3</sup> PC was magnetically stirred. The concentrations of aluminium and potassium were determined by atomic absorption spectroscopy with a reproducibility of  $\pm 10\%$ .

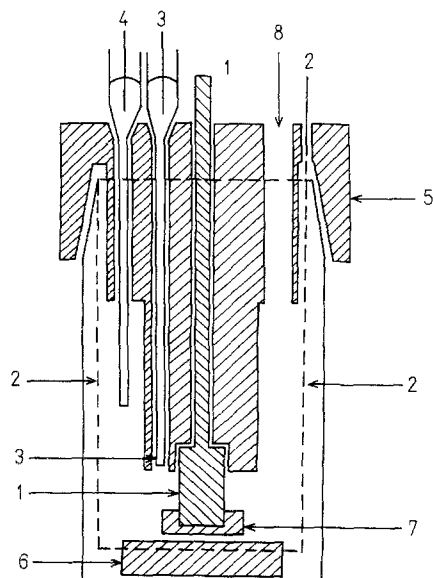


Fig. 1. Electrolysis cell with cylindrical geometry: (1) centre electrode; (2) platinum screen electrode (2.5 cm diameter, 40 cm<sup>2</sup> surface area); (3) and (4) potassium reference electrodes; (5) Teflon holder; (6) Teflon coated magnetic stirring bar; (7) Teflon cap for the centre electrode; (8) opening for thermometer or for taking samples of electrolyte.

#### 4. Results and discussion

Because of the low solubility of KCl and the consequent low conductivity of the KCl-PC electrolyte, small changes of composition due to the formation of AlCl<sub>3</sub> were detected by conductivity measurement. The electrolysis was started at a current of 1 mA and the current was increased during the dissolution of aluminium to 1.5, 2 and 4 mA. As shown in Fig. 2, the conductivity increases linearly with the amount of charge passed, reflecting changes which take place in the electrolyte composition. In the ideal case, the material entering the solution during anodic dissolution is directly proportional to the quantity of electricity (*Q*) passed. A linear dependence is expected since at low concentrations most electrolytes exhibit close to direct proportionality between specific conductance and concentration. Note that the change of conductivity is independent of the current applied in any particular part of the experiment. Because of the formation of AlCl<sub>4</sub><sup>-</sup> complex ion the dominant ionic species are K<sup>+</sup> and AlCl<sub>4</sub><sup>-</sup>. Hence we expect the conductance of the electrolyte to behave like a binary salt and to depend linearly on the charge passed.

The concentrations of potassium and alumi-

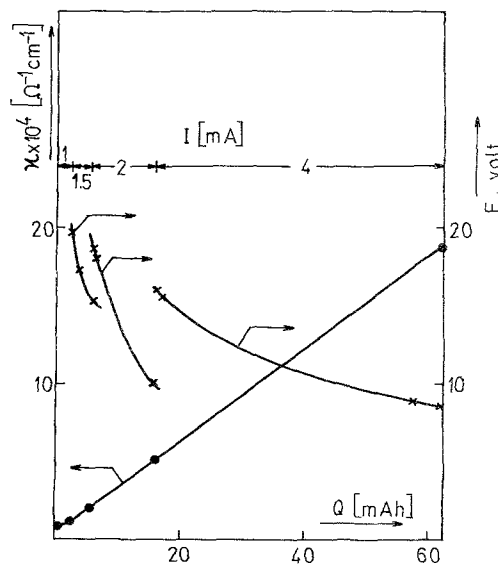


Fig. 2. Changes of conductivity and cell voltage during the electrolysis of the system: anode, Al/KCl, KCl(s), PC/Pt, cathode. Working electrode: aluminium wire, 1.5 mm diameter, 1.5 cm<sup>2</sup> surface area.

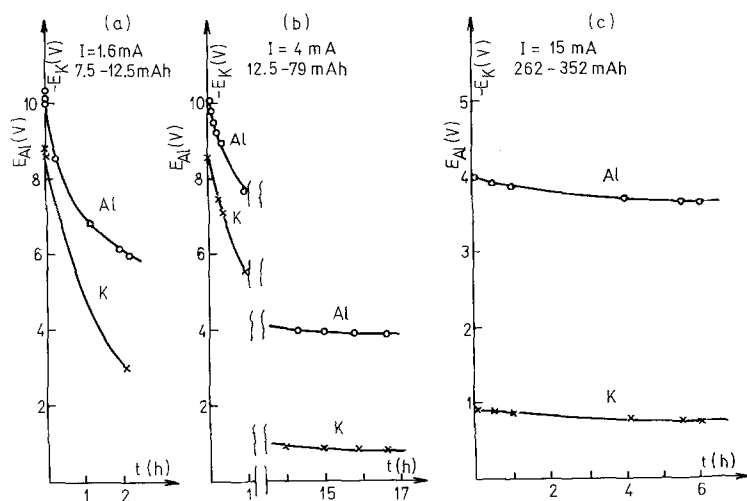


Fig. 3. Changes of electrode potentials during the electrolysis of the system: anode, Al/KCl, KCl(s), PC/Pt, cathode. Working electrode: aluminium cylinder, 1 cm<sup>2</sup> surface area; 1.392 g KCl. (a) 1.6 mA;  $Q$ , 7.5–12.5 mA h. (b) 4 mA;  $Q$ , 12.5–79 mA h. (c) 15 mA;  $Q$ , 262–352 mA h.

mium were closely monitored in order to obtain information about the processes taking place. The experiment was started with 1.329 g KCl (corresponding to 0.0187 mol) which would require an equivalent of 500 mA h charge to reduce all the potassium.

At a constant current of 0.42 mA the initial cell voltage was about 20 V, the limit of the potentiostat used. The potentials of both electrodes dropped rapidly and as the potential declined, the current increased. The changes in the potential of the electrodes (not corrected for  $IR$  drop) as a function of time for several current densities are presented in Fig. 3. Fig. 4 depicts the cathodic potential versus  $Q$  near the end of electrolysis. The sudden jump of cathodic potential at about 490 mA h indicates that the concentration of potassium decreases to the point where a current of 5 mA is equal to or greater than the cathodic limiting current. The transition time of the cathodic potential versus  $Q$  curve in Fig. 4 provides a basis for estimating the current efficiency of the cathodic process. As previously mentioned the total amount of potassium present in the electrolyte requires 500 mA h of charge to be passed. Since the transition was observed to start after 490 mA h the cathodic current efficiency is thus very close to 100%. This is further supported by the absence of aluminium in the potassium deposit.

The increase in aluminium concentration during dissolution is plotted against the quantity of electricity passed in Fig. 5. The increase in the

aluminium concentration along the theoretical line drawn for a charge number of 3 indicates that the increase in conductivity is caused by the increasing electrolyte concentration resulting from aluminium dissolution. From the weight loss of the aluminium anode the current efficiency is 100%.

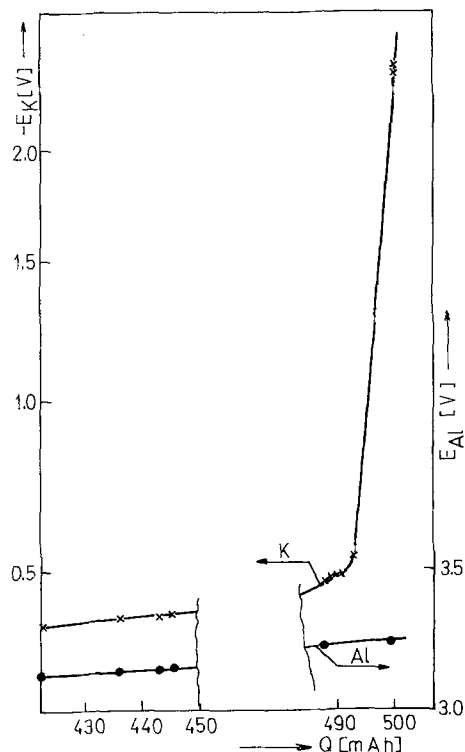


Fig. 4. Changes of the electrode potentials by the end of the electrolysis defined in Fig. 3.  $I = 5$  mA.

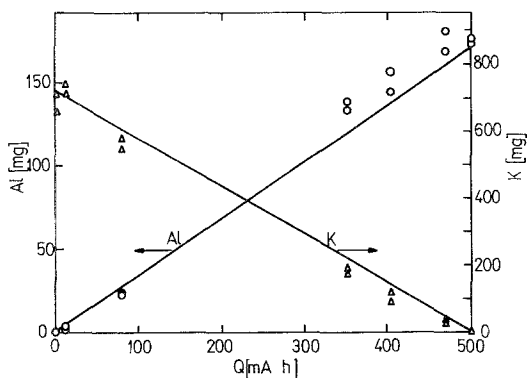


Fig. 5. Concentration of potassium and aluminium versus  $Q$ . Same system as in Fig. 3.

## 5. Conclusions

The foregoing measurements of conductivity, electrolyte composition, cell voltage and electrode potential demonstrate that potassium metal may be reduced from potassium chloride in  $\text{KAlCl}_4$ -PC electrolyte with simultaneous dissolution of an aluminium anode. The conductivity and the cathodic limiting current behaviour are consistent with an overall reaction according to Equation 2. Aluminium dissolves anodically with a  $100 \pm 5\%$  current efficiency. The aluminium complex,  $\text{AlCl}_4^-$ , is not reduced at the cathode and potassium chloride is depleted with a  $100 \pm 5\%$  current efficiency.

The energy requirement for the proposed electrolytic process can now be estimated. The measured potential of the aluminium electrode with respect to potassium in  $\text{KAlCl}_4$ -PC solution is typically 2.2 V. Operating at a current density of  $10 \text{ mA cm}^{-2}$  with a total polarization of 0.5 V and assuming a 5 mm cell gap and an electrolyte conductivity of  $0.005 \Omega^{-1} \text{ cm}^{-1}$  it takes 2.5 kWh to produce 1 kg potassium and to dissolve an equivalent amount of aluminium in a parallel plate cell. Based on an estimate of 10 cents per kWh, the cost of electricity for electrolysis would be in the order of 1% of the current selling price of technical grade potassium.

The proposed process should not be limited to potassium since the aluminium ion complexes with all the alkali chlorides as well. An electrolysis run with lithium chloride was also

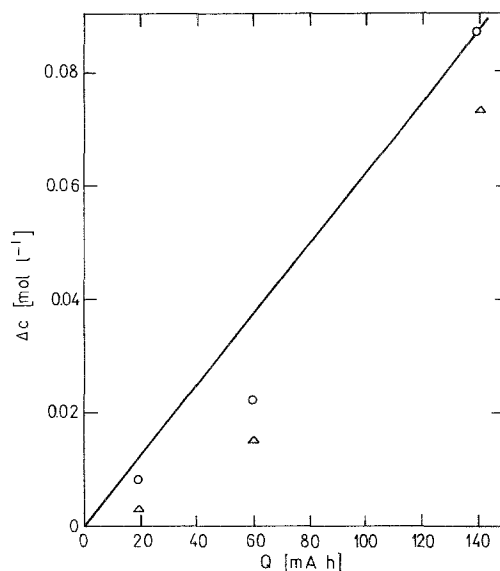


Fig. 6. Concentration of lithium and aluminium versus  $Q$ . Anode,  $\text{Al/LiCl}(\text{sat})$ , PC/Pt cathode.  $\circ$ , aluminium (average of two samples);  $\Delta$ , lithium (average of two samples).

carried out. Fig. 6 shows the change of the concentration of both lithium and aluminium in the solution during the electrolysis. Behaviour similar to that described in the  $\text{KCl}$ -PC system is observed and therefore by analogy the same conclusions can be drawn.

However, further studies are needed before one could securely evaluate the potential of the proposed system. The long-term stability of PC electrolyte with respect to anodically dissolving aluminium and cathodically depositing potassium has yet to be established. How impurities such as water influence the anodic and cathodic reactions is not yet known. Parasitic reactions could make the process impractical. Scale-up problems such as the collection of the potassium deposit and the recovery of aluminium chloride from the electrolyte will have to be addressed. We hope that this exploratory study will stimulate further interest in evaluating the possibility of electrowinning active metals in non-aqueous solvents and, in particular, in developing a process to produce potassium from potassium chloride dissolved in PC in the presence of aluminium chloride.

## Acknowledgement

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