Title

ELECTROCHEMICAL REDUCTION OF POTASSIUM FROM POTASSIUM CHLORIDE IN PROPYLENE CARBONATE ELECTROLYTE WITH ALUMINUM ANODES

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Publication Date

1978-12-01

To be submitted for publication

LBL-8505
Preprint

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December 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

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Electrochemical Reduction of Potassium from Potassium Chloride in Propylene Carbonate Electrolyte with Aluminum Anodes

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December 1978

Abstract

A process is proposed for the electrochemical reduction of potassium metal from $KAlCl_4$ dissolved in propylene carbonate, using aluminum as a sacrifical anode. The basic feasibility of this process scheme has been evaluated by measurements of the electrolyte composition and conductivity, and of the cell voltage and electrode potentials, as a function of charge passed. Results show that the overall cell reaction proceeds according to:

$$Al + 3\ KCl = 3K + AlCl_3 \ .$$

The aluminum chloride is expected to be continuously recovered by an electrolyte reprocessing step.

Preliminary estimates indicate that the electrical energy required for producing potassium by this method should be less than 2 kilowatt hours per kilogram potassium. This process scheme may also be applicable to production of other alkali metals from their chlorides.

1. Introduction

Potassium, an important metal because of its high reactivity and its low ionization energy, is one of the more abundant elements in the world. At present, potassium metal is mainly used in the manufacture of potassium superoxide as the source of oxygen in gas mask application and in the production of sodium-potassium alloy as a heat transfer fluid. One potential use of potassium would be as the seeding material in magnetohydrodynamic power plants for the conversion of heat directly to electricity.

Unlike lithium and sodium, potassium is not produced commercially by an electrochemical process. The present molten salt electrolytic process for making lithium and sodium cannot be used for potassium for the following reasons:

(1) Potassium has a high vapor pressure at normal cell-operating temperatures. The metal mist formed is undesirable.

(2) Corrosion is severe at the melting point of the potassium chloride. Eutectics at lower temperature have not been developed.

(3) The metal is highly reactive. It reacts more readily with oxygen than with sodium, and it can form potassium carbonyl, an explosive.

The current industrial method for potassium manufacture involves a thermochemical process at about 800°C. The process scheme shown in figure 1 involves an exchange reaction between sodium metal and the potassium chloride melt. The potassium metal is then recovered by distillation using the upper section of the column. Since the process is operated at high temperature, energy and material costs are high. The present selling price of potassium is five dollars per pound for technical grade (98.5% min.) in bulk quantity[15]. It is not certain how much the price could be lowered if the demand for the metal were to increase.

Major considerations for producing potassium more cheaply involve the reduction of the costs of the energy and of materials of containment. Such a process should be operated at a lower temperature. Any process utilizing a molten salt bath would be unlikely to be successful. Since potassium reacts with water, possible candidates would involve non-aqueous solvent media at room temperature.

The development of an electrochemical process for potassium production has been of interest in this laboratory since the initial electrochemical studies in propylene carbonate (PC) by Harris and Tobias[1] twenty years ago. The electrochemical behavior of the alkali metals in

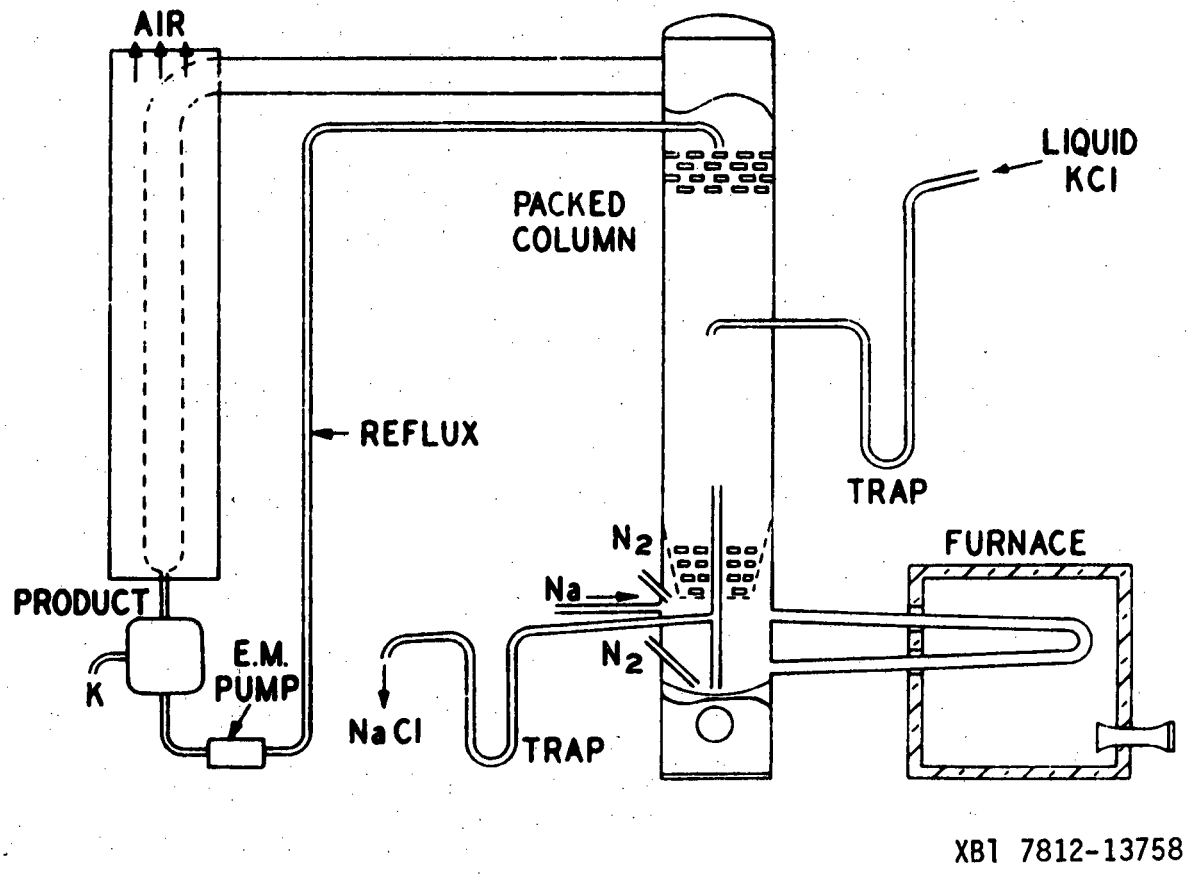

Figure 1. Continuous process for potassium production.[16]

PC, both from the thermodynamic and the kinetic points of view, was treated in a series of papers by Jorne and Tobias[5-8]. More recently Chacon[2] was able to obtain an adherent and high quality deposits of potassium from PC. Law[3] studied the optimal conditions for the deposition of potassium and explored the feasibility of scaling-up the potassium deposition in $KAlCl_4$/PC electrolyte. Electrolytic recovery of potassium in propylene carbonate will be possible when a suitable anodic reaction is found.

For any electrowinning process, the desirable characteristics of the anodic reactions are:

(1) The anode material and the material produced on the anode are chemically and electrochemically compatible with the solvent.

(2) The anodic reaction does not adversely influence the process at the cathode.

(3) The anodic process occurs at a potential as close as possible to that of the deposition of potassium to reduce the cell voltage.

(4) The material which reacts at the anode is cheap, readily available, and easily replaced or regenerated.

(5) The reaction allows a relatively simple cell design with a small gap between the electrodes, does not require the use of a diaphragm, and

permits easy operation and maintenance.

(6) The side products of the reaction are themselves useful.

For the electrowinning of potassium in $KAlCl_4$/PC electrolyte, we have considered the following three anodic reactions: the dissolution of potassium from potassium amalgam, the formation of chlorine, and the dissolution of a sacrificial metal.

Brenner[12] suggested the use of potassium amalgam. Jorne and Tobias[9] have patented a room temperature process for producing alkali metals by using the alkali metal amalgam obtained from aqueous electrolysis. However, since water at a ppm level is known to react with potassium deposit, trace amounts of water in the amalgam could interfere with the cathodic reaction. In his studies of the electrodeposition of alkali metals from non-aqueous solvents in a horizontal mercury cell, Pomp[10] has reported that the problem of water contamination limited the duration of the electrolysis to 30 minutes. However, the elimination of trace amounts of water from the potassium amalgam is not a simple problem.

If KCl is used as the source of potassium, the evolution of chlorine would be the logical choice for the anodic reaction. But the behavior of halogens in PC has not been studied, and in particular the stability of

PC with respect to chlorine has yet to be established.

Dissolving a sacrificial metal can be used as an anodic reaction. Since PC is stable over a wide potential range, most metals are expected to dissolve anodically in PC solution. The most difficult requirement is that the deposition of ions originating from the anodic reaction must be avoided. Even for the metals with very low solubility, the contamination of the potassium deposit with anode metal may not be negligible. The ideal sacrificial metal should not deposit before potassium. Chacon[2] and Law[3] have reported that the $AlCl_4$ ion cannot be cathodically reduced from $KAlCl_4$/PC electrolyte, and consequently potassium deposits contain no aluminum. Aluminum thus could be a useful sacrificial metal if it dissolves and forms the stable ionic species $AlCl_4^-$.

The purpose of this report is to examine the basic feasibility of a process to produce potassium by electrochemical reduction with a sacrificial aluminum anode from potassium chloride in propylene carbonate electrolyte.

2. Experimental

All experimental work, such as electrolyte preparation and electrolysis, was performed in a dry glove box with a helium atmosphere.[2] The water content of the helium gas was continuously monitored and maintained at about 2 ppm by recirculating the gas through a gas purifier (Kewaunee Scientific Engineering 2C1982) to remove water and oxygen.

Technical grade propylene carbonate (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 (aluminum 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 ppm of water and less than 5 ppm of propylene glycol. The details are given elsewhere[3].

The salts, potassium chloride and lithium chloride, were reagent grade. They were finely ground and then dried under vacuum (10^{-3} mm Hg) at 300°C for several days.

In the experiments for conductivity measurements, the cell was an H-type with one chamber used for electrolysis and the other chamber for conductance measurement. An aluminum rod (99.9995%) with 0.5 cm diameter was used as

the anode. The cathode, a cylindrical platinum screen electrode (2.5 cm diameter, 40 cm^2 surface area), was placed concentrically around the anode. The reference electrode was a potassium-filled capillary in the same solution. The electrolyte was made of 2 grams of powdered potassium chloride in 40 cc of propylene carbonate. The solution was stirred by a magnetic bar when the current was on. The conductivity was measured in quiescent solution by using an A.C. bridge method at 1 kHz. The conductance cell consisted of two parallel bright platinum plate electrodes with a cell constant of 0.0218 cm^{-1}, determined by using 10^{-3} M KCl at 25°C. The instruments used were an A.C. Generator Detector (Model 861A, Electro Scientific Industries), and Variable Decade Capacitors (Models CDA-2 and CDA-3, Cornell-Dubilier Electronic Division, Federal Pacific Electric Division).

The cell used in experiments for composition analysis and current efficiency is shown in figure 2. The anode was an aluminum cylinder (99.9995%). The cathode was the same platinum screen electrode mentioned earlier. A potassium-filled glass capillary tube served as the reference electrode. The electrolyte contained 1.392 grams of potassium chloride in 20 cc of PC. The solution was stirred during the entire experiment. The concentration of aluminum, potassium, and lithium was determined by

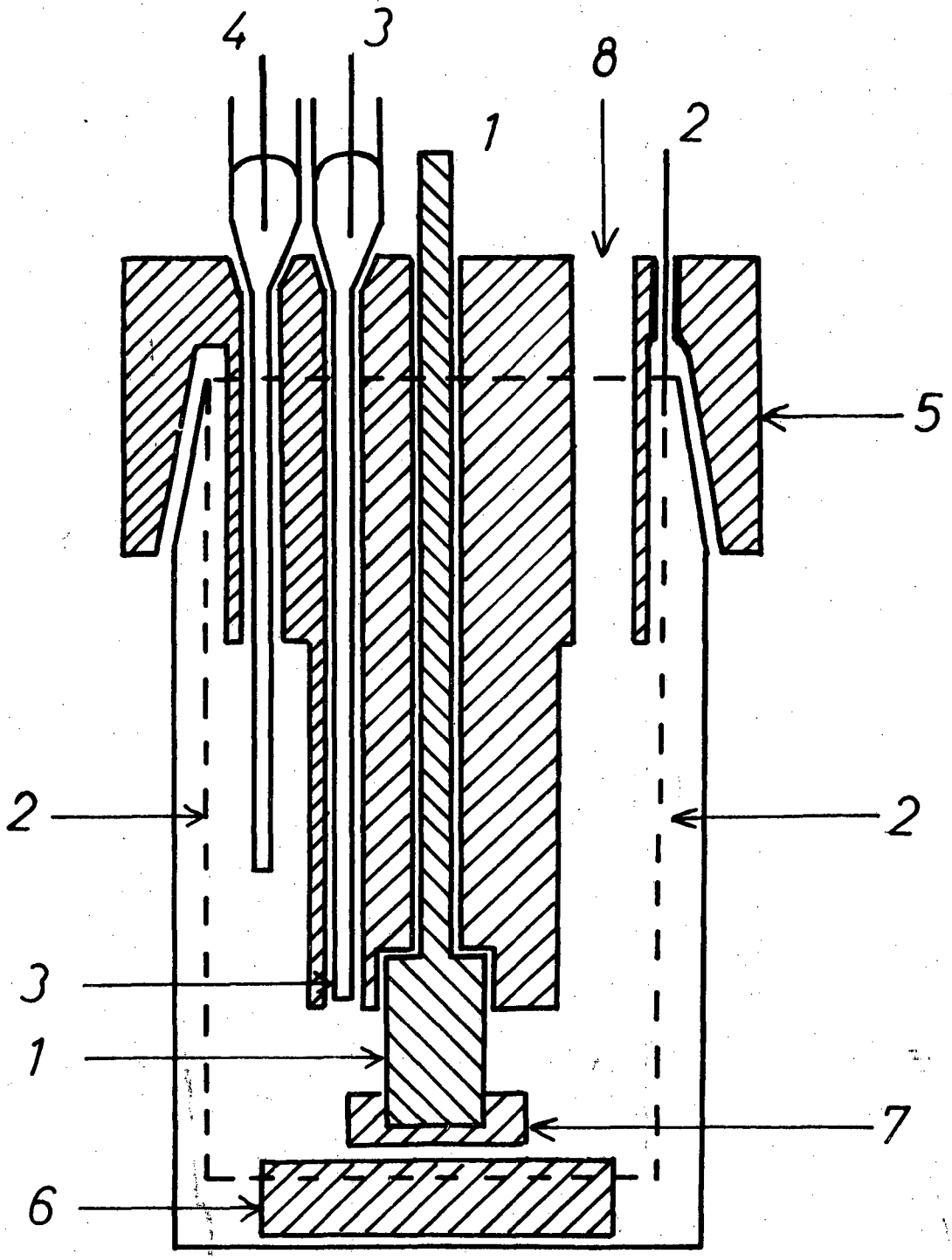

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Figure 2. Electrochemical cell with cylindrical geometry: (1) Aluminum Anode (0.635 cm diameter, 1 cm^2 surface area); (2) Platinum screen electrode (2.5 cm diameter, 40 cm^2 surface area); (3) and (4) Reference electrodes, potassium filled glass capillary pipet; (5) Teflon holder; (6) Teflon coated magnetic stirring bar; (7) Teflon cap for aluminum electrode; (8) Opening for thermometer or for taking samples of electrolyte.

using atomic absorption spectroscopy (Perkin-Elmer M 360). Samples of the electrolyte (two per analysis; 50 microliter each) were taken by a CENTAUR 50 microliter automatic pipet and diluted with distilled water outside the glove box. No residue or phase separation was noticed in the sample after dilution. The reproducibility of the results was $\pm$10%. A Princeton Applied Research Model 371 potentiostat and a Wenking Model 61 RD potentiostat were alternately employed as power sources. The digital voltmeters used (Digitech 266 DC Voltmeter and Weston Model 4444 digital multimeter) all have high input impedance, 1000 megohm or higher.

potassium manufacturing method, the price of potassium produced by the proposed method can possibly be reduced significantly.

4. Process Feasibility Studies

The basic feasibility of the proposed process is determined by studying the process at the electrodes and the changes of the electrolyte properties. Such changes would answer the crucial question of whether aluminum would behave as we expected. Would aluminum dissolve anodically? If so, would the aluminum ions combine with the chloride ions and form stable complexes so that the aluminum introduced from the anode would not incorporate with the potassium deposit?

The conductivity and the composition of the electrolyte, the cell voltage and the related electrode potentials are measured as a function of the charge passed in order to gather information on the time dependence of the process.

4.1. Conductivity Measurement

Because of the low solubility of KCl and the low conductivity of KCl/PC electrolyte, the detection of small changes of composition is possible by measurement of conductivity. The open circuit potential of the cell is -0.55 volt; the aluminum anode is more negative than platinum gauze cathode. The electrolysis is started at a current of 0.1 mA. As shown by the conductivity curve in

figure 3, there is no apparent change in the conductivity of the electrolyte even after a period of 50 hours. An increase of the current to 0.3 mA also does not effect any change. The conductivity of the electrolyte remains at 9.9×10^{-6} ohm^{-1} cm^{-1} until the current is increased to 1 mA. The current is further increased during the electrolysis to 1.5, 2 and 4 mA. The conductivity increases linearly with the amount of the charge passed. At the end of electrolysis, the conductivity is 1.88×10^{-4} ohm^{-1} cm^{-1} with a total charge of 250.2 coulombs (69.5 mA-hours) passed.

The conductivity reflects unequivocally the changes which take place in the composition of the electrolyte. In the ideal case, the material entering the solution during the anodic dissolution is directly proportional to the quantity of electricity passed, Q. The change of conductivity is independent of the current applied in any particular part of the experiment.

The initial part of the conductivity curve clearly shows that no aluminum dissolution occurs at currents below 0.3 mA. It is conceivable that in this low current density range instead of aluminum dissolution, an impurity of the solvent (e.g. glycols, propylene oxide, water), present at 1-10 ppm level, is oxidized at the aluminum/electrolyte interface.

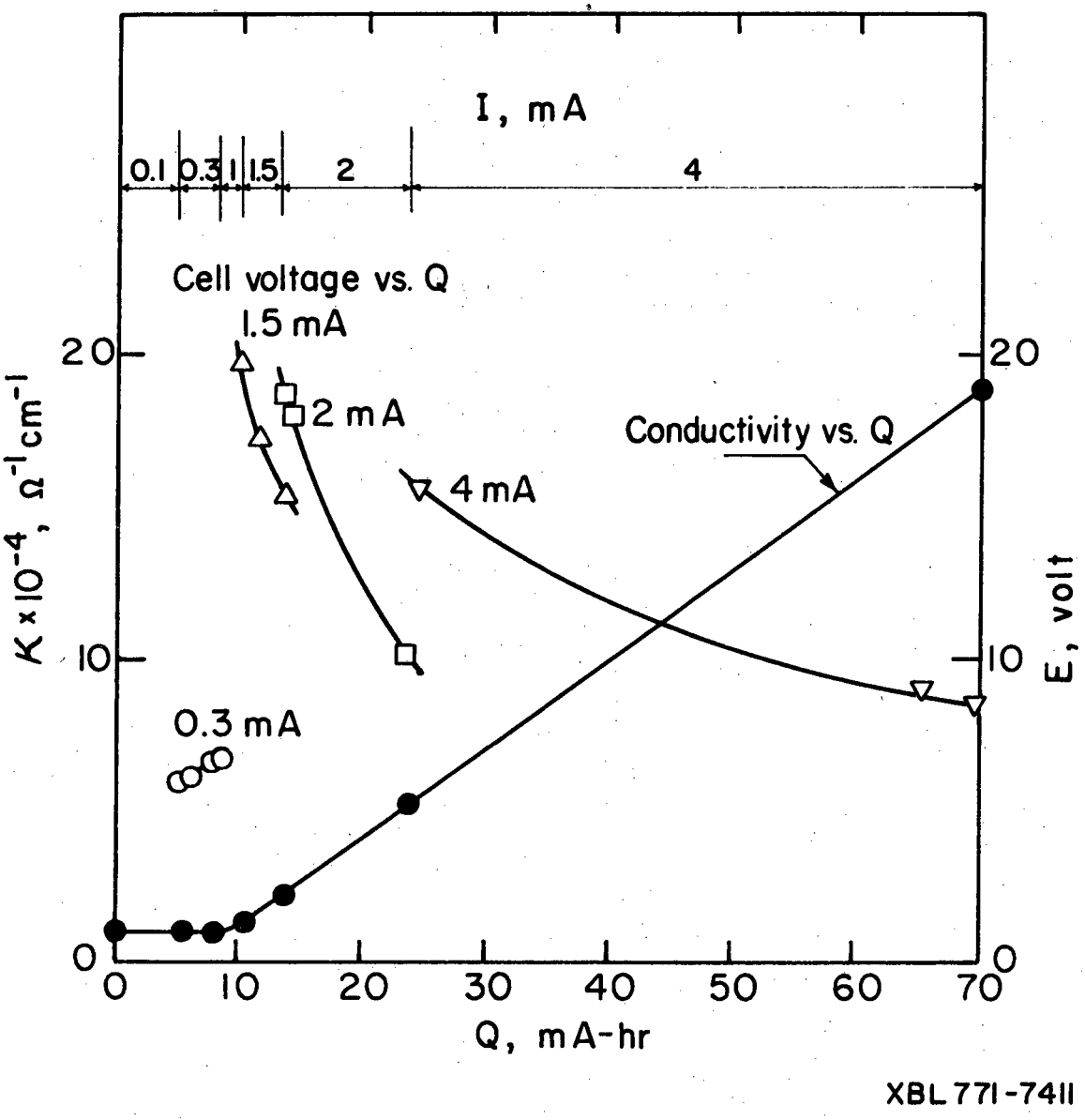

Figure 3. Changes of conductivity and cell voltage during the electrolyses of the system: (+) Al|KCl,KCl(s)/PC|Pt (-) . Working electrode: aluminum wire, 1.5 mm diameter, and 1.5 cm^2 surface area.

The part of the conductivity curve in figure 3 at current densities higher than 0.3 mA/cm^2 shows that the electrolyte conductivity is a linear function of charge passed. A linear function is expected as most electrolytes exhibit direct proportionality between specific conductance and concentration at low concentration. The overall reaction is

$$Al + 4\,KCl \rightarrow 3\,K + K^+ + AlCl_4^- \quad . \qquad (6)$$

For three faradays of charge passed, one mole of aluminum is dissolved, three moles of potassium are deposited, and one mole of $KAlCl_4$ is formed. Because of the formation of $AlCl_4^-$ complex ion, the dominant ionic species are K^+ and $AlCl_4^-$. Hence we expect the conductance of the electrolyte to behave as that of a binary salt and to depend linearly on the charge passed.

4.2. Composition Analyses

The concentrations of potassium and aluminum were monitored closely in order to obtain greater insight into the processes taking place in the electrolyte. The experiment was started at a constant current of 0.42 mA. The initial cell voltage was about 20 volts, the limit of the potentiostat used. The potentials of both electrodes drop rapidly, and as the potential drops, the current increases. The changes of the potential of the electrodes

as a function of time for several current densities are presented in figure 4. The concentrations of potassium and aluminum obtained by atomic absorption analyses are plotted against the quantity of electricity passed in figure 5.

The increase of the concentration of aluminum along the theoretical line drawn for a charge transfer number of 3 proves that the increase of the conductivity in the previous electrolysis is due to increasing electrolyte concentration resulting from aluminum dissolution.

According to reaction (6), the concentration of potassium should be increasing in proportion to that of aluminum. However, the concentration of potassium (figure 5) does not show such behavior; it decreases instead with the quantity of electricity passed. The explanation is that the fine powder of potassium chloride salt is dispersed uniformly in the electrolyte due to strong stirring, and the analysis does not distinguish whether the potassium was present originally in the dissolved or crystalline state. The solubility of KCl in PC is 4×10^{-4} M[11]. We expect to have only 0.3 mg of potassium in the system. The initial potassium concentration observed so far corresponds to the value calculated if all the potassium salt had been dissolved. Therefore the curve for potassium in figure 5 represents only the total potassium

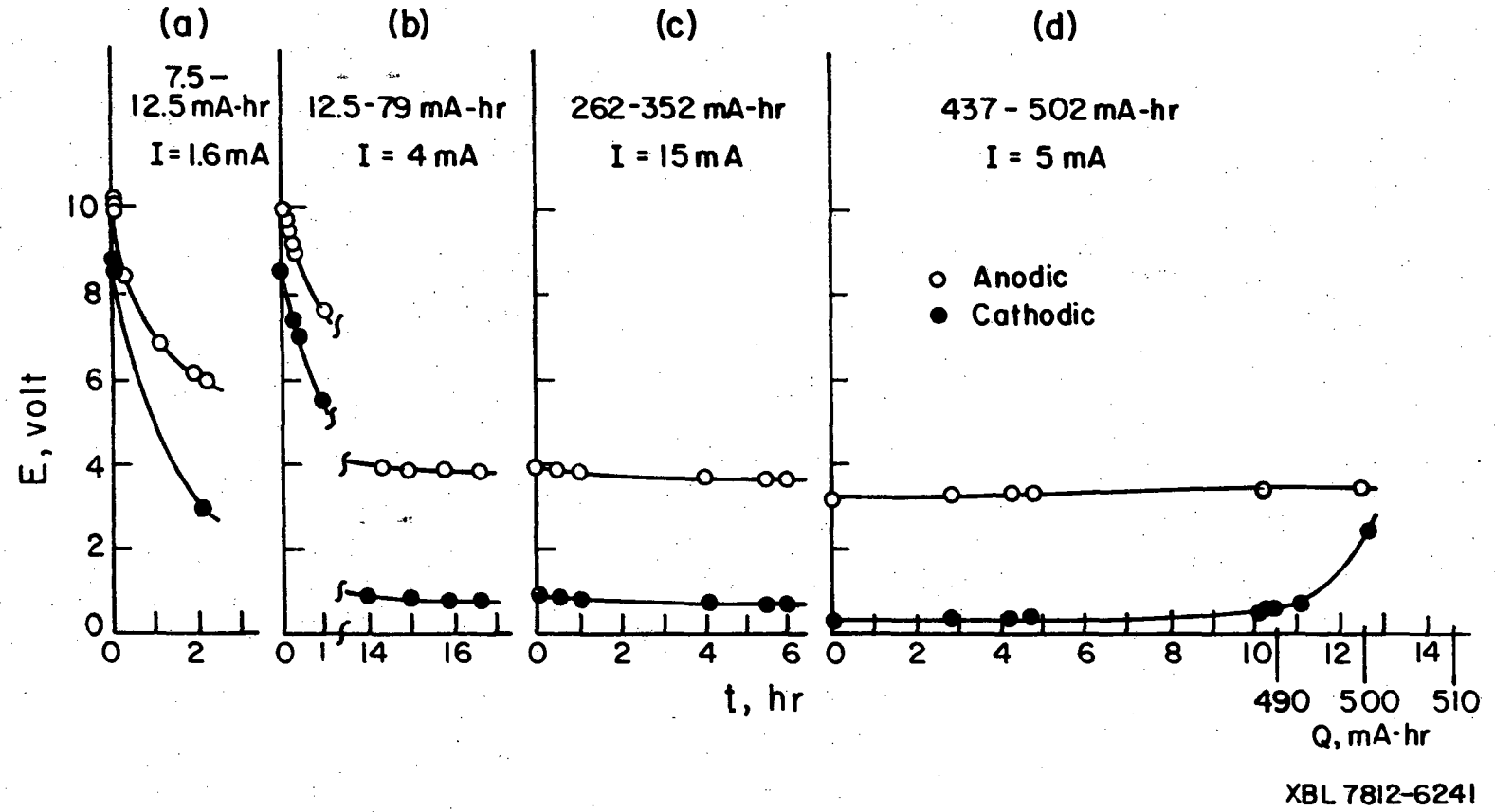

Figure 4. Changes of electrode potentials during the electrolysis of the system: (+) Al|KCl,KCl(s)/PC|Pt (-) . Working electrode: Aluminum cylinder, 1 cm^2 surface area. Part a: 1.6 mA, Q from 7.5 to 12.5 mA-hr. Part b: 4 mA, Q from 12.5 to 79 mA-hr. Part c: 15 mA, Q from 262 to 352 mA-hr. Part d: 5 mA, Q from 437 to 502 mA-hr.

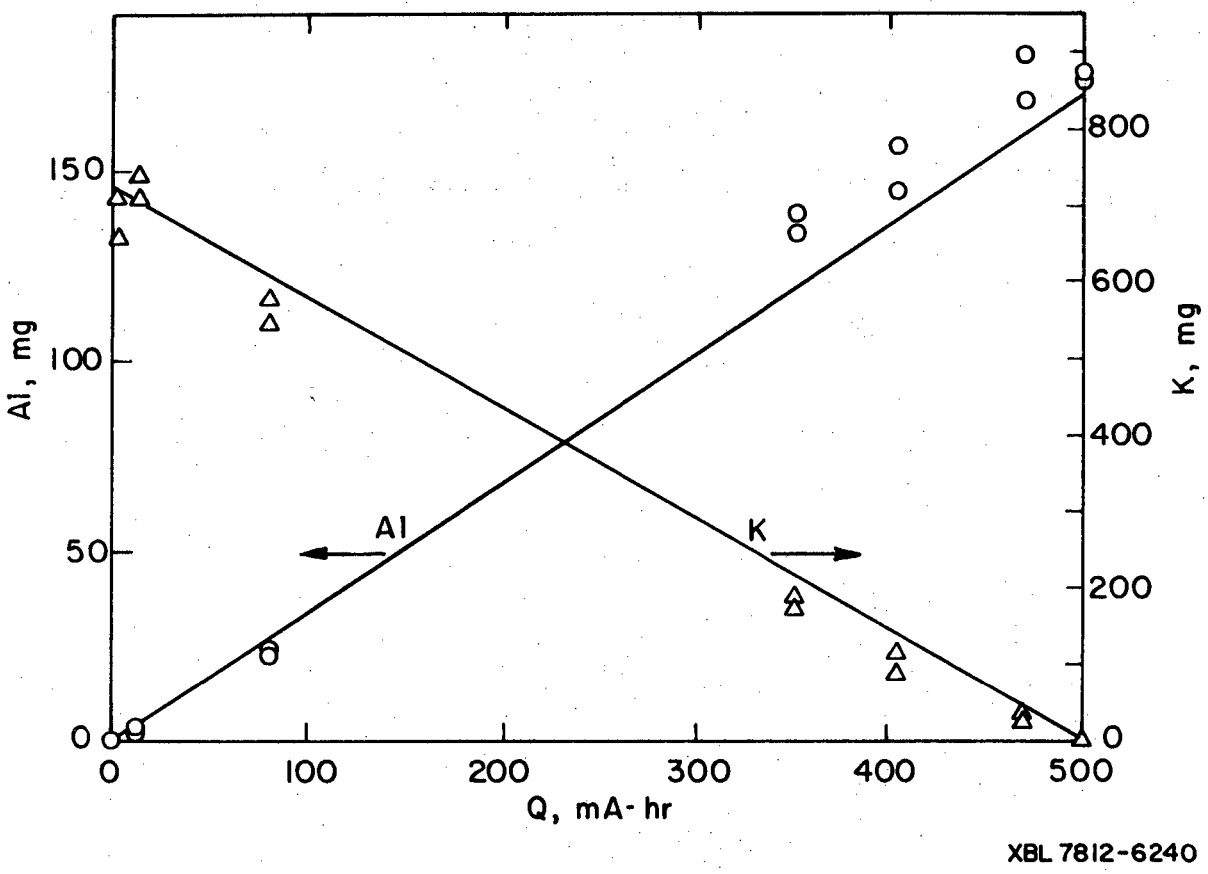

Figure 5. Concentration of potassium and aluminum vs. Q, the quantity of charge passed; same system as in figure 3.

5. Conclusions

The measurement of conductivity, composition, cell voltage, and electrode potential establishes the elementary feasibility of the proposed scheme to reduce potassium metal from potassium chloride in $KAlCl_4$/PC electrolyte with the equivalent dissolution of an aluminum anode. The conductivity and the cathodic limiting current show the progress of the overall reaction according to:

$$Al + 4\,KCl \rightarrow 3\,K + K^+ + AlCl_4^- \quad . \qquad (6)$$

Aluminum dissolves anodically with a 110% current efficiency. The aluminum complex, $AlCl_4^-$, is not reduced at the cathode and potassium chloride is depleted with a 100% current efficiency.

The energy requirement for the proposed electrolysis process can now be estimated. The rest potential of an active aluminum electrode with respect to potassium in $KAlCl_4$/PC solution is considered to be 2 volts. Operating at a current density of 10 mA/cm^2 with a total overpotential of 0.5 volt and assuming a cell gap of 5 mm and an electrolyte conductivity of 0.005 $ohm^{-1}\ cm^{-1}$, it takes 1.09 kw-hr to produce one pound of potassium and to dissolve an equivalent amount of aluminum in a parallel plate cell. Based on a pessimistic estimate of 5 cents per kw-hr, the cost of electricity for electrolysis would be only one percent of the current selling price of technical

grade potassium.

The proposed process should not be limited to potassium since the aluminum ion complexes with all the alkali chlorides as well. An electrolysis run with lithium chloride was also carried out. Figure 6 shows the change of the concentration of both lithium and aluminum in the solution during the electrolysis. Behavior similar to that described in the KCl/PC system is observed and therefore the same conclusions can be drawn by analogy. We expect that all alkali metals can be produced by electrolysis in PC solutions using aluminum as a sacrificial anode.

Further studies , however, are needed before one could securely evaluate the potential of the proposed scheme. The stability of PC electrolyte to the dissolution of aluminum and the deposition of potassium has to be established. How the impurities, such as water, influence the electrochemical reactions is not known as yet. Scale-up problems, such as the collection of potassium deposit and the recovery of aluminum chloride from the electrolyte, will have to be addressed. Parasitic reactions could make the process impractical. We hope that this exploratory study will stimulate more interest in evaluating the possibility of electrowinning active metals in non-aqueous solvents, and, in particular, in developing

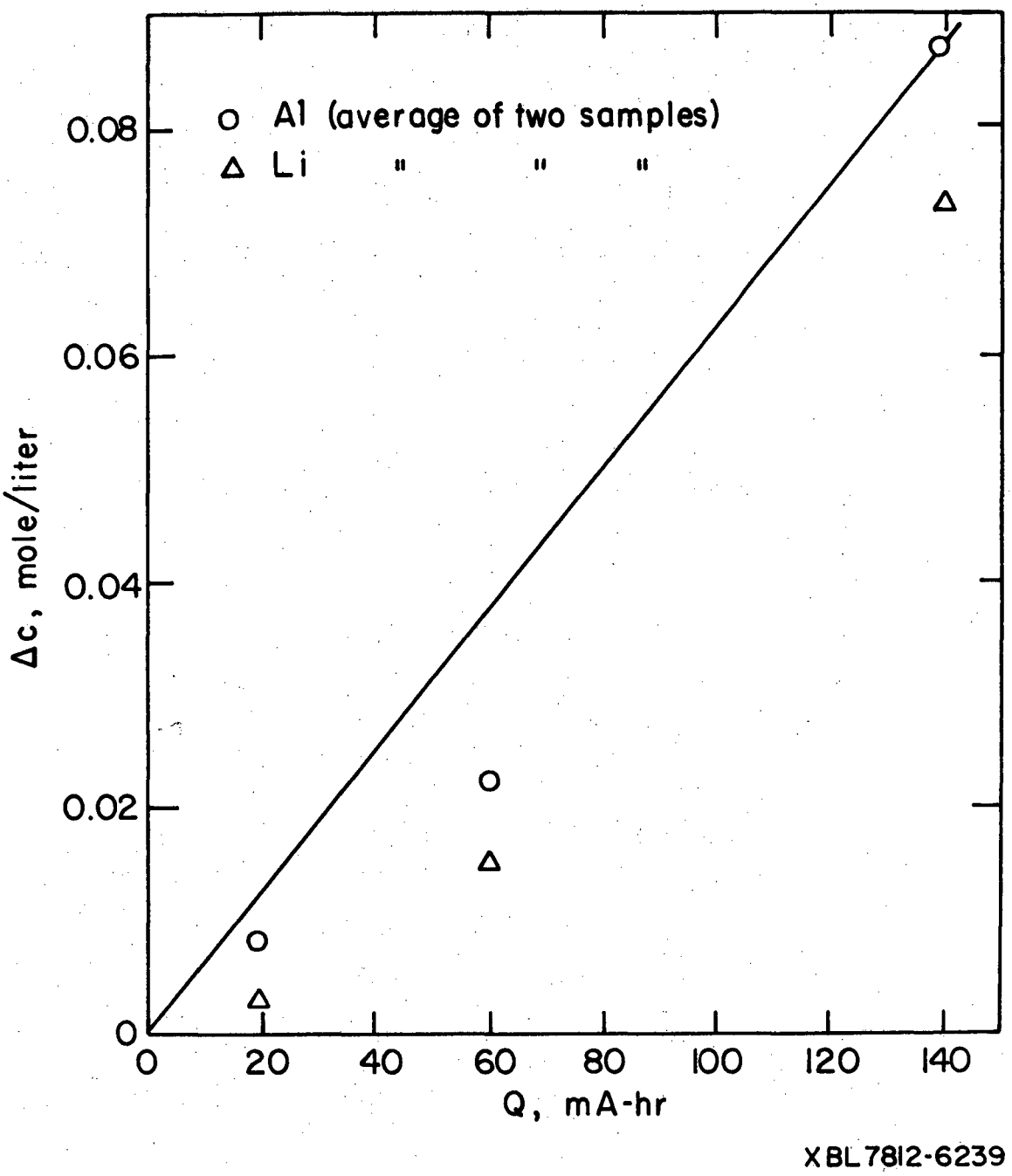

Figure 6. Concentration of lithium and aluminum vs. Q, the quantity of charge passed: (+) Al|LiCl(sat),PC|Pt (-) .

a process to produce potassium from potassium chloride in propylene carbonate solution.

Acknowledgement

This work was supported by the Division of Materials Sciences, Office of Basic Energy Science, U.S. Department of Energy.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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