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CATHODIC REDUCTION OF POTASSIUM IN PROPYLENE CARBONATE ELECTROLYTES

Oscar Antonio Chacon
(M.S. thesis)

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# CATHODIC REDUCTION OF POTASSIUM IN PROPYLENE CARBONATE ELECTROLYTES

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Cathodic Reduction of Potassium in Propylene Carbonate Electrolytes

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Abstract

Metallic potassium was electrodeposited at room temperature from 0.5 - 1.0m KAlCl₄ and KPF₆ solutions in propylene carbonate (PC). Good quality deposits were obtained in electrolysis continued for up to 150 hours at current densities up to 30 mA/cm². Careful removal of impurities from the solutions was necessary to assure absence of discernable attack of potassium by the electrolyte. The effect of current density, temperature and deliberately added low level concentration of water, propylene glycol and propylene oxide on the appearance of the deposit were observed.

Overpotentials were determined by both transient and steady state techniques. Assuming simple charge transfer rate limitation, the exchange current, \( i^0 \), in these solutions appears to be in the range of \( 10^{-5} - 10^{-7} \) amp/cm². Deviation from Tafel behavior indicate, however, that other rate limiting steps may play a dominant role above 1 mA/cm².
I. INTRODUCTION

Potassium, one of the strongest reducing agents, is abundantly available in the outer layers of the earth crust. Unlike sodium, potassium is not produced in any significant quantities. Potassium metal is used in the manufacture of potassium superoxide (KO₂) and as a heat-transfer fluid in certain nuclear reactors. Reagents derived from potassium metal find many uses in organic syntheses. Finally, potassium may find application in magnetohydrodynamic power plants for the conversion of heat directly to electricity. The common method for recovery of active metals, electrolysis of the fused halides or hydroxides, does not work well for potassium because of the high solubility of the metal in its fused salts. Instead, the limited quantities currently used are obtained by exchange reaction in the molten state between potassium compounds (KCl, K₂CO₃) and sodium vapor. The produced potassium usually contains a considerable level of sodium impurity.

Electrodeposition of potassium from solutions of its salts in nonaqueous solvents appears as a feasible promising alternative. This subject was recently reviewed by Brenner. Earlier attempts (1895-1905) failed to yield metallic deposits from solutions of pyridine and acetone. More recent efforts by Mandell and co-workers (1955) involving these same solvents also failed. Solutions of alkali metal halides and aluminum halides in nitromethane and in nitrobenzene were also explored but the final conclusion was that these solvents were not suitable for economical electrodeposition of potassium. Ethylenediamine, phosphorous oxychloride, propylene
and ethylene carbonate and some lactones\textsuperscript{12} were also reported to be unsuitable solvents for the cathodic reduction of potassium. Harris\textsuperscript{12} however succeeded in obtaining the liquid NaK from solution of the iodides in propylene carbonate. Recently Jorne and Tobias\textsuperscript{13} proved the feasibility of depositing potassium from KAlCl$_4$ and KPF$_6$ solutions in propylene carbonate. However, until the present work was initiated no coherent deposits of potassium were obtained by electrodeposition using a practical range of current densities.

This study was designed to explore the feasibility of reducing potassium at practical rate from a suitable salt dissolved in propylene carbonate at ambient temperature. Particular attention was given to the procedures required for the preparation and purification of the solutions prior to the electrolysis.

II. EXPERIMENTAL

2.1 General

2.1.1 Solvent Purification

The "as received" Propylene Carbonate (Jefferson Chemical Company, Houston, Texas) contains a tenths of a percent of water, propylene glycol (PG), propylene oxide (PO) and 1,2 propanediol alcohol. Besides it develops a yellow color when stored in the factory container, possibly due to polymerization reactions.

The following purification process was used: 3.5 liter of PC were percolated through a glass column filled with 400 grams of aluminum oxide (aluminum oxide Woelm basic, activity I). The purpose
of this step was to dry PC and to eliminate the compounds producing yellow color. The colorless PC obtained is more stable in the distillation process and the distillate more pure. The percolate was then distilled at 0.5 mm Hg, in a modified vacuum distillation column (semi-cal series 3650, Podbielniak). The reflux ratio was 1:1 and the head temperature 68-70°C. The first 20% and the last 20% were discarded. The distillate contains a few parts per million of PO, no PG, and an unknown amount of water. The closed receiving vessel was detached from the distillation column and attached to a glass column filled with molecular sieves (Linde, 13X). At the bottom of the column there was a collection vessel with teflon needle valves. All the joints were made with vacuum ground glass joints. The column and the receiving flask had inlets for the purified helium admittance and for the pumping down of the system. The column was filled with 400 grams of molecular sieves dried in a stream of dried argon for 36 hours at 350°C. After evacuating the system up to 1 μHg, it was filled with purified helium and the PC was passed through the column and collected in the receiving vessel at 10 cc per minute. This drying method is known to produce a PC with less than 10 p.p.m. of water. The percolate still contains some p.p.m. of PO. Then, the receiving vessel was evacuated up to 5 μHg for 2 hours. This eliminates practically all of the PO. Every batch of PC was analyzed for PG and PO using gas chromatography and it was rejected if it showed more than 5 p.p.m. of PG. Pieces of K retained shiny surfaces for an indefinite time in PC purified by the above method.
The gas chromatograph employed was an Aerograph Hy-Fi model 600 coupled with a Variac Hydrogen generator and a 1mV full scale recorder (Sargent model SR)

The analysis conditions were:

- Argon Carrier: 25 cc/min.
- Hydrogen flow rate: 25 cc/min.
- Air flow rate: 300 cc/min.
- Column temperature: 140°C
- Injector port temperature: 110°C
- Size sample: 10-40 μl

With this equipment, the method had a sensitivity of 5 p.p.m. of PG and 10 p.p.m. of PO with a sample of 20 μ liters.

2.1.2 Glove Box

The vacuum glove box was basically the same used by Jorne with minor modifications. All the valves were changed to bellows vacuum valves and all of the copper tubing was replaced. All joints of the box were sealed with hard epoxy and every seam was leak tested with a helium detector. The box was filled with high purity helium (Liquid Gases Plant, University of California, Berkeley).

In the first part of this work, the helium was passed through a homemade gas purifier using two 4 x 12 inch stainless steel columns, one filled with molecular sieves and the other with B.T.S. catalyst. Both were regenerated periodically.
Beginning July 1974, a Kewaunee Scientific Engineering 2C1982 gas purifier was used.

The glove box operation was essentially the same as by Jorne but the box was evacuated and refilled every other day when it was used with the homemade gas purifier. Following installation of the Kewaunee purifier the helium was recirculated continuously around the clock.

2.2 Electrolytic Solutions

2.2.1 Salt Purification

The three solutes used in this work, KCl (Baker analyzed reagent), AlCl₃ (Mallinckrodt analytical reagent) and KPF₆ (alfa inorganic), were purified as follows:

KCl. The water and the HCl that this salt may contain were eliminated by melting KCl inside a quartz tube in a Pt boat under a flow of purified helium. The quartz tube had a "O" ring seal and two vacuum stopcocks. After the melting, the tube was evacuated to 1µHg in a vacuum line and transferred to the glove box. Only the amount necessary for the preparation of a single batch of solution was purified each time.

AlCl₃. The analytical reagent grade AlCl₃ contains FeCl₃ plus water absorbed in the handling of the factory bottle. In addition some HCl is produced by reaction of water with the AlCl₃. The FeCl₃ gives yellow colored solutions and the water and the HCl could decompose the solvent. The method of purification used was designed to get rid of these impurities. About 300 grams of AlCl₃
and 50 grams of Al metal pellets were placed in one of the bulbs of the sublimator shown in the figure 1a. The system was pumped down to 1 μHg for 24 hours and after that, the vacuum was broken allowing a small flow of purified He to go through the sublimator. Following, the AlCl₃ containing bulb was heated up to 300°C and the other was cooled with dry ice. The sublimation lasted for 10 hours. After this period of time the purified AlCl₃ was transferred to a glass container fitted with an "O" ring seal. This operation was made in a plastic glove bag filled with purified He. The plastic bag was preferred because the sublimated AlCl₃ rich in HCl fumes would contaminate the He atmosphere in the vacuum glove box. The AlCl₃ obtained by the above procedure was again sublimated in the glass tube shown in the figure 1b. The process was carried out at 1 μHg to eliminate the HCl vapor. The tube was pumped down for 48 hours and after that, the part containing AlCl₃, was heated at 100°C for 8 hours. The AlCl₃ condensed in the cold part. When the sublimation was completed, the tube was sealed off with a torch and stocked for future use.

KPF₆. The main impurity in this salt is water. KPF₆ can not be melted because it decomposes. For this reason heating in vacuum was not a workable dehydration method. After heating at 150°C under atmospheric pressure for 3 days, the sample was enclosed in a glass tube fitted with an "O" ring seal and a vacuum stopcock. This tube was then attached to a vacuum line and pumped down to 1 μHg for 4 days.
Fig. 1 Apparatus for sublimation of the AlCl₃.
2.2.2 Solution Preparation

The methods for preparation of solutions of KA1Cl₄ and of KPF₆ were different:

**KA1Cl₄**: The heat of solution of AlCl₃ in PC is very large, enough to decompose the solvent, resulting in brown solution. The only way to minimize decomposition is to add the AlCl₃ slowly to the well cooled solvent. The device in figure 2 was designed to meet this requirement. Powdered AlCl₃ was put in the upper container and the PC and the powdered KCl in the lower one. The amount of salts necessary to prepare a solution were weighed in a small torsion balance inside the glove box. The device was closed and transferred out from the inert atmosphere. The solvent was cooled to the temperature of an acetone - dry ice bath. Then it was removed from the bath and a small amount of AlCl₃ added with the help of a vibrator. After the dissolution of this batch of AlCl₃ was completed, the lower container was cooled again and more AlCl₃ added. The procedure was repeated until all the AlCl₃ was dissolved. Following, the AlCl₃ solution was allowed to reach room temperature and it was stirred for 6-8 hours to dissolve the KCl. This method yields a colorless solution.

**KPF₆**: The preparation of this solution presents no problems. The salt dissolves quite fast in PC without heating. The appropriate amount of the salt was weighed and mixed with the solvent in a closed container inside the glove box. 15 minutes of stirring by hand was enough to prepare a 1M solution.
Fig. 2. Apparatus for the preparation of the KA1Cl₄ solutions.
2.2.3 Solution Purification

Even though the ingredients of the electrolyte were carefully dried as described above, following preparation of the solution, the latter required additional treatment to remove reaction products produced when AlCl₃ was mixed with PC. A cooled absorption column containing granular alumina (Woelm basic, activity I) was used for this purpose. Cooling was necessary because it was found, that upon addition of the solution to the column the exothermic adsorption reaction on the surface of alumina particles causes decomposition to occur. (Solution purified by passing through uncooled columns gave poor potassium deposits.) The apparatus used to purify the solutions is shown in figure 3. The procedure was as follows: The aluminum oxide was dried in the round bottom flask at 1 atm and 100°C for 36 hours. The teflon needle valve was closed and the flask transferred to the column. 60 cc of PC were put in one of the addition funnels and 50 or 60 cc of solution in the other. The column was closed and all the system was pumped down to 1 atm for several hours. The appropriate amount of Al₂O₃ was then introduced in the column and the system pressurized with purified He. The temperature in the jacket of the column was maintained by circulation of ice-water at about 5°C. After making sure that the column reached this temperature, 30 cc of PC were added very slowly and then the solution. The first 40 cc of percolate were discarded in one of the receiving flasks at the bottom of the column. When the solution level at the top of the column disappeared another 30 cc of PC were passed through. The
Fig. 3. Apparatus for the purification of the KA1Cl₄ solutions.
percolation lasted until 40 cc of the solution were collected. Then, the two teflon valves in the solution receiving flask were closed and the latter was transferred into the glove box. This method of purification consistently gave colorless and stable solutions and the K deposits obtained in them were always reproducible.

2.3 Deposition Studies

2.3.1 Cells and Electrodes

The cell used for deposition studies has two compartments connected by a porous glass plate. The cell is fitted with ball-socket joints. The caps have a tungsten lead, overlaid with uranium glass for a vacuum tight seal, to be used as electrode holder. The electrodes are contained in glass cups with a tungsten lead that projects into the cup to provide electrical contact with the K metal. The cups are attached to the electrode holder by a brass connector. The solution was stirred with a small magnetic stirrer covered with teflon. The complete set up is shown in the figure 4. The procedure for the preparation of the K electrodes was as follows: K sticks (Mallincrodt) were melted inside the glove box in a small glass melting pot heated by an electrical resistance. The melted K was poured into the cups and it was allowed to cool to room temperature. The spherical surface obtained was cut under dried cyclohexane with a clean knife to leave a flat surface. After washing it with purified PC, the electrode was transferred to the cell and this was closed and the clamps tightened. The reason for cutting the electrode surface under cyclohexane is discussed in section 3.1.
Fig. 4. Cell for electrodeposition studies.
The electrodes prepared by this method always kept shiny surfaces for many days and they dissolved evenly upon anodic polarization.

2.3.2 Effect of Current Density and Temperature

Almost all of these experiments were carried out in the cell described in 2.3.1. When the effect of stirring on the deposit structure was studied, the cell shown in figure 5 was used. The cell current was provided by a regulated DC power supply (Electric Measurements C621). The current and the applied voltage were monitored by a Keithley 160 and El Dorado 1820A multimeters.

The temperature was maintained ±0.5 degree at a preassigned value by a water bath fitted with electrical heaters and a cooler (Neslab Instruments, Burham N.H.).

The temperature in the batch was controlled by a Sargent Thermomonitor. The procedure followed in these experiments was as follows: Inside the glove box, the potassium electrodes were prepared. The cell was filled with about 35 cc of solution and the joints were lubricated. The electrodes surfaces were cut and the two electrodes holders were inserted into the cell. The cell then was taken out of the glove box and put into the controlled temperature bath. After waiting at least 30 minutes to allow the cell to reach the bath temperature, the current was turned on. Progress of the dissolution and deposition reaction was followed visually. After the appropriate number of coulombs were passed through the cell the current was turned off. The deposit was examined insitu with a low magnification microscope (X23) and photographs were taken. Alternately, the
dissolution-deposition period was immediately followed by passing current in the reverse direction, and the forward-reverse cycle repeated over extended periods (up to 100 hours) of time.

2.3.3 Effect of Impurities

The cell and other equipment used were the same as described in 2.3.2. The experimental procedure was modified in the following way. First, the cell was filled with pure solution and its purity was checked observing the quality of the deposit obtained at 1m A/cm². After this the cell was transferred into the dry box again, opened and the cathode replaced by a fresh one. 20μl of PC electrolyte containing an appropriate concentration of water and propylene glycol and oxide was added to each compartment using a 50μl Hamilton syringe. The cell was closed again, taken out of the glove box and an appropriate current was applied. When the desired number of coulombs were passed, the deposits were inspected.

2.4 Electrode Kinetic Measurements

2.4.1 Cell and Electrodes

The cell used had three compartments. All three were fitted with ball-socket joints. In the central compartment, a small glass cup with K was used as a reference electrode. The other electrodes and electrode holders were similar to 2.3.1. To minimize the concentration overpotential, a special welded cylindrical stainless steel stirrer was employed. Two rings were connected by two L cross-section straight members. To the bottom of the metallic frame
Fig. 5. Cell for electrode kinetic measurements.
was attached a teflon covered magnetic stirrer. The complete set up is shown in figure 5.

2.4.2 Simple Step Galvanostatic Method

This method was chosen because it permits to obtain the IR drop for each current setting. A block diagram of the electrical circuit is shown in figure 6. The current pulse was generated by an Pulse Generator (Lawrence Berkeley Laboratory) connected to a Wenking Potentiostat working in a galvanostatic mode. The potential was observed versus time in a Tektronic Oscilloscope and the traces were analyzed from Polaroid prints.

Also, the ohmic resistance of the cells was measured using a a.c. bridge. Sinusoinal signals at 20 kHz were generated by an a.c. Generator Detector, Model 861A, Electro Scientific Industries, Portland, Oregon. The cell resistance was balanced with an Impedance Bridge, Model 290A, Electro Scientific Industries, Portland, Oregon.

2.5 Analysis of the Deposits

The major constituents of the deposits were analyzed by powder X-ray diffraction for potassium and by spark emission spectra for aluminum.

The samples for the X-ray analysis were enclosed in 0.3-mm diameter quartz capillaries, both ends were sealed with fast setting epoxy. The X-ray patterns were obtained with Cu 22 radiation.

For the Al analysis the deposits were washed by soaking them in pure PC for 3 days. The 50 cc of PC was changed 6 times
Fig. 6. Apparatus for simple step galvanostatic measurements.

- g - pulse generator
- c - counter electrode
- o - oscilloscope
- p - potentiostat
- r - reference electrode
- vr - variable resistance
- w - working electrode
during the above period. This method was thought best to leach out the electrolyte from the porous deposits. After repetitions leaching the samples were sealed into a small glass container provided with a plastic cap, sealed with epoxy resin.

III. RESULTS AND DISCUSSION

3.1 Stability of Potassium in Pure PC and in Electrolytes

The first problem that had to be solved after obtaining pure solution was a partial passivity of the potassium electrodes. After passing an appropriate number of coulombs through the cell, the anodes surfaces appeared unevenly pitted but it was possible to see the original surface in the rest of it. The cathode surfaces were almost entirely covered by loose porous deposits. The original surface could be easily exposed by shaking.

Assuming that the solution was pure, the most obvious explanation for this behavior is that passivity could have been produced during the electrode preparation. As the cast potassium was cut in the glove box, the freshly exposed surfaces could have reacted with the water and oxygen impurities in the helium atmosphere. However, even when the electrode was cut under pure PC, a purple color developed on the new surface. Instead, cutting under dry cyclohexene was tried. The shiny metallic electrode surfaces obtained in this manner dissolved evenly and the cathodic deposits stuck more to the cathode surfaces. The development of the purple color may have been caused by heating the potassium in cutting process, activating thereby a reaction with the PC solvent. To gain a better understanding of
this problem, pieces of potassium in PC were heated to the melting point. When the potassium melted a purple film developed on the surface. The reaction is apparently very slow and is arrested when the surface is fully covered. However, by stirring the solvent the attack progressed further, resulting in a dilute gray-blue dispersion. A sample of the solids after filtering was analyzed by X-ray analysis. The pattern obtained is shown in figure 7, together with a pure potassium pattern for comparison. The extra lines do not correspond to KOH, K₂O or K₂CO₃. No further attempt was made to identify the reaction products or to establish the nature of the reaction responsible for the attack of potassium.

3.2 Stability of the Electrolytic Solutions

The stability during storage was established by observing the change in color of the solutions enclosed in sealed containers and by observing the appearance of electrodeposited potassium obtained following increasing time periods of storage.

The KPF₆ solutions with or without purification did not demonstrate any yellow discoloration after two weeks of standing. Potassium deposits obtained from fresh solutions were similar to those reduced from "aged" samples. On the other hand the KAlCl₄ solutions without purification developed a light yellow color after 10 days. The purified solutions did not show any discoloration after two weeks and the good quality deposits obtained indicated that the solutions did not deteriorate during storage.
Fig. 7a. Powder X-ray diffraction pattern of the mixture of solids produced by heating potassium at 65°C in PC.

Fig. 7b. Powder X-ray diffraction pattern of potassium.
Trying to explain the instability of the unpurified solutions, about 1000 ppm of water was added to a purified solution. A light yellow color developed after four days. Propylene glycol and propylene oxide did not produce any discoloration. This could mean that the yellow coloration was caused by absorption of moisture during solution preparation.

The stability of the solutions during electrolysis was studied by prolonged and cyclic electrolysis. The long term electrolysis was conducted for 160 hours at 1mA/cm². The solutions of both salts demonstrated excellent behavior during this period of time. Up to 120 hours, the deposits looked similar to those obtained after 10 hours of deposition. After 120 hours a change in the structure of the deposited potassium was noted. Some metallic needles started to grow and they increased in size and number in the final 40 hours. The growing of needles is discussed in section 3.3.1. Deposits obtained after 65 and 160 hours are shown in figure 8 a,b.

The cyclic electrolysis were carried out reversing the current (1mA/cm²) every 12 hours. After 10 cycles the deposit looked similar to that obtained with fresh solutions.

Purified electrolytic solutions demonstrated excellent behavior (i.e., yielded good potassium deposits) even after 10 hours storage at 50°C, followed by electrolysis at 25°C.

3.3 Electrodeposition of Potassium

To extend Jorne's micropolarization studies into a more practical region of process variables further work was done to explore the effect
Fig. 8a. Potassium deposit from KAlCl₄ (0.5m) solution in PC. Current density: 1mA/cm². Temperature: 25°C. Duration of electrolysis: 65 hours. Magnification: X20.

Fig. 8b. Potassium deposit from KAlCl₄ (0.5m) solution in PC. Current density: 1mA/cm². Temperature: 25°C. Duration of electrolysis: 160 hours. Magnification: X20.
of current density, temperature and impurity concentration on the nature of the potassium deposits.

3.3.1 Effect of the Current Density

The effect of the current density was studied in the range of 0.4 m A/cm² to 30 m A/cm². The results were similar for the two solutes employed (i.e., KAlCl₄ and KPF₆). The morphology of the potassium obtained can be divided into two types: With currents from 5 m A/cm² to 30 m A/cm² the deposits appeared as a fine blue-black powder. This powder became finer as the current increased. Another characteristic of these deposits is that apparently after reaching an equilibrium thickness they start to separate from the electrode. Currents up to 5 m A/cm² produce a deposit of metallic spheres. Three representative deposits are shown in figures 9a, b and 10. The number of coulombs passed through the cell (36 coulombs, 14.5 × 10⁻³ g) was the same for all three cases. It is interesting to note that the size of the spheres decreases with increasing the applied current density.

It is quite surprising to obtain spheres because usually metals deposited from nonaqueous solvents present structures involving powders, sponge, wiskers or dendrites. In view of the low melting point of potassium, 63.4°C, one possible explanation may be that the surface overpotential is sufficiently high to produce enough heat to melt the surface of small crystals. High surface tension would then cause a spherical shape to grow.
Fig. 9a. Potassium deposit from KA1Cl₄ (0.5m) solution in PC. Current density: 0.8 mA/cm². Temperature: 25°C. Duration of electrolysis: 10 hours. Magnification: X20.

Fig. 9b. Potassium deposit from KA1Cl₄ (0.5m) solution in PC. Current density: 0.4 mA/cm². Temperature: 25°C. Duration of electrolysis: 20 hours. Magnification: X20.
Fig. 10. Potassium deposit from KAlCl₄ (0.5m) solution in PC. Current density: 4 mA/cm². Temperature: 25°C. Duration of electrolysis: 2 heures. Magnification: X20.
In the early part of this work, besides the sphere type deposit, another type of structure was obtained at $1 \text{mA/cm}^2$ on three separate occasions. Metallic needles, about two mm long, covered the entire surface of the electrode. Later, despite extensive efforts, the needle type deposit could not be reproduced. However, during the study of the solution stability by long term electrolysis at $1 \text{mA/cm}^2$ needles growing out of spheres (fig. 8b) were again observed. No systematic effort was possible to undertake within the scope of this project to clarify the conditions conducive for the formation of the beautiful needle type deposits. Because these were obtained in all cases at low current densities, hence at low overpotential, it is likely that the melting point of the potassium was not reached on the surface. On the other hand it is well known that extremely low levels of impurities, in the range of a few parts per million can profoundly affect the crystal morphology in electrodeposition. Our inability to consistently reproduce this type of deposit indicates that the presence or lack of a readily adsorbed impurity may have been responsible for the preponderance of needles in the three specific cases described above. There remains also a remote possibility to explore: it is conceivable that the metallic looking needles were not pure potassium, but some organo-metallic phase, or even possibly a potassium-aluminum alloy. Regrettably all attempts to isolate one of the needles, and transfer them into a glass capillary for X-ray diffraction analysis, failed.
3.3.2 Effect of Temperature

Deposits were also obtained at 7°C and 50°C with a current density of 0.8 mA/cm² over 10 hours. Results are shown in figures 11a and 12.

The potassium deposited at 7°C had a powder structure with purple color at the edges and dark gray in the center of the electrode. It was not possible to see spheres even under microscope. The same electrode was allowed to reach 25°C and the cell was powered again at 0.8 mA/cm². In the figure 11b it can be seen that spheres were produced in the initial deposit.

In figure 12, the deposit obtained at 50°C looks completely metallic without porous structure.

The mechanism of formation of spheres by melting of the surface appears to receive support by the above results. At 7°C the dissipation of heat may be enough to avoid the softening of the deposited potassium. On the other hand, at 50°C not only the melting point of potassium is closer but the rate of heat transfer to the solution is also lower. This may be responsible for the smoother nodular appearance of the deposit shown in figure 12.

3.3.3 Effect of Impurities

The effect of propylene glycol, propylene oxide and water was studied by examining the deposits obtained at 25°C with current density of 1 mA/cm².

**Propylene Glycol:** 200 ppm to 400 ppm of PG was added to the solutions. Some of the results are shown in figure 13 a,b. The
Fig. 11a. Potassium deposit from KAlCl₄ (0.5 m) solution in PC. Current density: 0.8 mA/cm². Temperature: 7°C. Duration of electrolysis 10 hours. Magnification: X20.

Fig. 11b. Potassium deposit on the above electrode. Current density: 0.8 mA/cm². Temperature: 25°C. Duration of electrolysis: 10 hours. Magnification: X20.
Fig. 12. Potassium deposit from KAlCl$_4$ (0.5m) solution in PC. Current density: 0.8 mA/cm$^2$. Temperature 50°C. Duration of electrolysis: 10 hours. Magnification: X20.
sphere growing is partially inhibited and the effect is more pronounced as the PG concentration is increased. The inhibition and the dark deposit may be produced by the reaction of the PG with the deposited potassium. When the PG is depleted to a low level by the reaction, the deposited potassium starts to grow in small spheres. This is shown in figure 14.

The results are similar for the two salts studied.

Water: This effect was studied in solutions with 150 ppm of water. The behavior of the solutions depends on the type of salt used.

The results in KPF$_6$ solutions were similar to those found in PG solutions. After the added water is depleted during the initial period of electrolysis (30 hours) the "normal" potassium spheres start to grow again. However, this was not observed in KA1Cl$_4$ solutions, even after 30 hours of electrolysis. This is shown in figure 15 a,b. The different behavior of the two solutions has not been resolved. The effect of the water may be amplified by hydrolysis of the solvent catalyzed by HCl. A set of possible hydrolysis mechanisms producing glycols and alcohols is given by Silvester.

Propylene Oxide: This compound did not show any effect on the deposits of potassium even at a concentration of 1000 ppm. This is rather surprising because the oxide structure is not expected to be stable against the alkali metals.

3.4 Electrode Kinetic Measurements

Polarization measurements were carried out in 0.5m and 1m solutions of KPF$_6$ and KA1Cl$_4$ by the method described in section 2.4
Fig. 13a. Potassium deposit from KAlCl₄ (0.5m) and Propylene glycol (200 ppm) in PC. Current density: 1 mA/cm². Temperature: 25°C. Duration of electrolysis: 10 hours. Magnification: X20.

Fig. 13b. Potassium deposit from KAlCl₄ (0.5m) and Propylene glycol (400 ppm) in PC. Current density: 1mA/cm². Temperature: 25°C. Duration of electrolysis: 10 hours. Magnification: X20.
Fig. 14. Potassium deposit from KAlCl₄ (0.5m) and Propylene glycol (400 ppm) in PC. Current density: 1 mA/cm². Temperature: 25°C. Duration of electrolysis: 30 hours. Magnification: X20.
Fig. 15a. Potassium deposit from KAlCl₄ (0.5m) and water (150 ppm) in PC. Current density: 1mA/cm². Temperature: 25°C. Duration of electrolysis: 10 hours. Magnification: X20.

Fig. 15b. Potassium deposit from KAlCl₄ (0.5m) and water (150 ppm) in PC. Current density: 1mA/cm². Temperature: 25°C. Duration of electrolysis: 30 hours. Magnification: X20.
using constant current pulses of 100 ms duration.

The values obtained for the exchange current and the transfer
coefficient are given in table I. Anodic and cathodic overpotential
behavior for 1 molal solutions of both salts are shown in the usual
semi-logarithmic plot of $\eta$ vs. $\log i$ in figures 16 and 17.
According to the Erdey-Volmer theory of simple charge transfer
process, in the Tafel region, i.e., when $|\eta| > 0.1$ volt

$$\ln |i| = \ln i^0 - \alpha_c n f \eta$$ \hspace{1cm} \text{cathodic process}

$$\ln i = \ln i^0 + \alpha_a n f \eta$$ \hspace{1cm} \text{anodic process}

with

$i$ = current density
$\eta$ = surface overpotential
$\alpha_c, \alpha_a$ = cathodic and anodic transfer coefficient, respectively.
$n$ = number of electrons
$i^0$ = exchange current
$f = F/RT$

The polarization values were obtained from photographic records
of oscilloscope traces. Typical traces are shown in figure 18. The
values obtained were corrected for the ohmic drop determined from
photographs similar to those shown in figure 19. The ohmic drop was
linear with current in the range studied. However, the values of
the IR drop determined in this manner were always about 20% smaller
Fig. 16. Tafel plot for potassium electrodes in KALCl\(_4\) (1m) in PC. Electrode area: 0.93 cm\(^2\). Temperature: 25°C.
**Figure 17.** Tafel plot for potassium electrodes in KPF$_6$ (1m) in PC. Electrode area: 0.93 cm$^2$. Temperature: 25°C.

- $i'_0 = 0.023$ mA/cm$^2$
- $\alpha_c = 0.27$
- $\alpha_a = 0.27$
Table I. Kinetic parameters of the potassium salt - FC solutions at 25°C

<table>
<thead>
<tr>
<th></th>
<th>KAlCl₄</th>
<th></th>
<th>KPF₆</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5m</td>
<td>1.0m</td>
<td>0.5m</td>
<td>1.0m</td>
</tr>
<tr>
<td>i₀ (mA/cm²)</td>
<td>0.021</td>
<td>0.033</td>
<td>0.018</td>
<td>0.023</td>
</tr>
<tr>
<td>αₐ</td>
<td>0.23</td>
<td>0.20</td>
<td>0.25</td>
<td>0.27</td>
</tr>
<tr>
<td>αₐ</td>
<td>0.23</td>
<td>0.21</td>
<td>0.24</td>
<td>0.27</td>
</tr>
</tbody>
</table>
than these measured by the a.c. bridge method described in section 2.4.2. This difference may possibly be explained by the effect of the nonuniform current distribution on the IR drop values determined by transient method. No effort was made to establish the validity of this tentative explanation.

The values presented in the figures 16 and 17 were obtained by increasing the current in the cathodic or anodic direction. The data obtained in opposite direction i.e., by decreasing from the maximum value of current used, did not reproduce the former values. With fresh surfaces the data was reproduced within a 2% in the linear part and within a 5% in the nonlinear region.

Examination of the Tafel plots immediately reveals certain important features:

1. The anodic and cathodic quadrants are symmetrical, indicating that the transfer coefficient \( \alpha \) should be 0.5.

2. Between the lowest current density applied (0.1 m A/cm\(^2\)) and approximately 1.0 m A/cm\(^2\), the overpotential appears to increase linearly with the logarithm of the current density. This apparent behavior invites the assumption that we are facing here a Tafel region. Extrapolation of this line to the current axis yields an intercept corresponding to the approximate value of \( i^0 = 0.03 \text{m} A/\text{cm}^2 \). This value agrees reasonably with the one derived by Jorne\(^\text{13} \) (0.006 m A/cm\(^2\)) from the linear overpotential region.

3. The slope of the assumed Tafel region, however, leads to the absurd situation of \( \alpha_a = \alpha_c = 0.2 \). Inasmuch as the simple Erdey-Volmer
Fig. 18a. Overpotential determination using simple step galvanostatic method. KAlCl₄ (1m) - PC at 50°C. Cathodic current: 15.58 mA/cm². Vertical scale: 500 mV/div. Horizontal scale: 10 ms/div.

Fig. 18b. Overpotential determination using simple step galvanostatic method. KAlCl₄ (1m) - PC at 50°C. Anodic current: 3.57 mA/cm². Vertical scale: 200 mV/div. Horizontal scale: 10 ms/div.
**Fig. 19a.** IR drop determination using simple step galvanostatic method. KAlCl₄ (1m) - PC. At 50°C. Cathodic current: 2.62 mA/cm². Vertical scale: 200 mv/div. Horizontal scale: 2 ms/div.

**Fig. 19b.** IR drop determination using simple step galvanostatic method. KAlCl₄ (1m) - PC at 50°C. Anodic current: 3.57 mA/cm². Vertical scale: 200 mv/div. Horizontal scale: 2 ms/div.
kinetic expression assumes that there is only one charge transfer step responsible for the overpotential behavior, hence $\alpha_a = 1 - \alpha_c$, the interpretation of the linear region in our semilogarithmic plot may not be valid, i.e., the straight line would begin to curve downward upon further decrease of the current density, leading to a much lower $i^0$ value. Simple substitution of experimental overpotential and current density values in the Tafel equation shows that $\alpha_a = \alpha_c = 0.5$ would require $i^0 = 1 \times 10^{-7}$ amp/cm$^2$.

The only other way in which we could explain the large apparent Tafel slope would involve assumption of a transfer valency (n) of approximately 1/2. There is no obvious reaction mechanism which could yield this fractional value.

The downward curvature of the Tafel line above 1mA/cm$^2$ is equally puzzling. This type of behavior can usually be shown to be caused by concentration overpotential; the curve eventually becomes parallel to the overpotential axis, demonstrating a limiting current behavior. However, stirring had no effect on the overpotential in the current densities investigated.

Experiments were also carried out to learn more about the reproducibility of the results. The effect of anodizing the electrode before cathodic electrolysis is shown in figure 20. The electrode was anodizing for 45 minutes at 0.1mA/cm$^2$. It can be seen that the transfer coefficient does not change but the exchange current is smaller, about 27% less than the value obtained with the fresh surface. The effect of cathodic deposition is shown in figure 21 by
Fig. 20. Effect of anodizing the electrode on the kinetic behavior of potassium in KAlCl₄ (0.5m) in PC. Temperature: 25°C.
Fig. 21. Effect of cathodizing the electrode on the kinetic behavior of potassium in KAlCl₄ (1m) in PC. Temperature: 50°C.
the difference between two transient responses at 0.2m A/cm². After 165 constant current pulses with values ranging between 0.1m A/cm² and 30m A/cm², the overpotential obtained is larger than the value obtained on the fresh surface. This higher overpotential may correspond to a smaller exchange current. The above results indicate that there may be some kind of modification on the electrode surface by passing current in any direction.

In order to check the kinetic results obtained with the transient method, steady cell overpotential measurement were also performed. After imposing an appropriate current, the voltage was read until a steady value was obtained. This value was corrected for the ohmic drop determined by the a.c. method described in section 2.4.2. Results are presented in the figure 22 and are plotted according to the following relationship:

\[ V_{\text{cell}} = \left(\frac{1}{\alpha_a n_f} + \frac{1}{\alpha_c n_f}\right) \ln \left(\frac{i}{i^0}\right). \]

Sample data are presented in table II.

The behavior shown in figure 22 agrees with the data obtained with the transient method only in the shape of the curve. If it is assumed that $\alpha_a = \alpha_c$, the value of the transfer coefficient is 0.68. This value is more than the double of the values obtained by the other method. The exchange current determined by extrapolation is 0.0002m A/cm² very much smaller than the values measured by the simple step galvanostatic method.
Fig. 22. Cell overpotential measurements using steady state galvanostatic method KA1Cl4 (0.5m) in PC.
Temperature: 25°C.
Table II. Run 27, cell voltage, ohmic drop, and cell overpotential. (0.5m KAlCl₄ solution).

<table>
<thead>
<tr>
<th>Current (mA/cm²)</th>
<th>Cell Voltage (volts)</th>
<th>Ohmic Drop calc. (volts)</th>
<th>Cell Overp. (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>0.572</td>
<td>0.058</td>
<td>0.514</td>
</tr>
<tr>
<td>0.322</td>
<td>0.792</td>
<td>0.174</td>
<td>0.618</td>
</tr>
<tr>
<td>0.5</td>
<td>0.953</td>
<td>0.291</td>
<td>0.662</td>
</tr>
<tr>
<td>1.07</td>
<td>1.300</td>
<td>0.583</td>
<td>0.717</td>
</tr>
<tr>
<td>2.14</td>
<td>2.035</td>
<td>1.166</td>
<td>0.869</td>
</tr>
<tr>
<td>4.34</td>
<td>3.290</td>
<td>2.361</td>
<td>0.921</td>
</tr>
<tr>
<td>8.63</td>
<td>5.800</td>
<td>4.693</td>
<td>1.107</td>
</tr>
<tr>
<td>10.04</td>
<td>7.000</td>
<td>5.853</td>
<td>1.147</td>
</tr>
<tr>
<td>15.30</td>
<td>10.200</td>
<td>8.920</td>
<td>1.280</td>
</tr>
<tr>
<td>21.75</td>
<td>13.200</td>
<td>11.835</td>
<td>1.367</td>
</tr>
</tbody>
</table>

T = 25°C

Interelectrode distance = 7.5 cm.

Electrode areas = 0.93 cm² each.

Cell resistance = 583 ohms (by a.c. method).

At each current density the duration of electrolysis was approximately 15 minutes.
The results described above indicate that the rate controlling step in the mechanism of dissolution and deposition of potassium in the PC electrolytes investigated cannot be adequately represented by a simple charge transfer process. The limited scope of the experimental investigation reported here does not allow advancing even a tentative proposal for the rate controlling step (or steps) in the reaction mechanism.

As discussed above the overpotential behavior depend on the history of the electrode surface. This may be the reason for the large difference between the data obtained using the transient and steady state methods. Each steady state measurement was taken after 15 minutes following the closing the circuit while the transient measurements involved only 100 ms galvanostatic pulses. Future works should be done with renewal of the surface after each measurement. Also, fast transient methods may have to be used with cells designed to provide a uniform current distribution on the electrodes to eliminate the uncertainty in the magnitude of the ohmic drop.

3.5 Current Efficiency Measurements

On the basis of visual observation of the metal deposit, the absence of any gas evolution during deposition, and because there was no visible evidence of any chemical attack of the electrolyte, we assume that the only reaction occurring was that of the reduction of potassium to the metal. It is to be remembered that X-ray diffraction patterns did not show any other lines besides those of potassium.

Current efficiency measurements were attempted in the same cell described in section 2.3.1 using Pt cathodes. After passing an
appropriate number of coulombs (typically 50-100) through the cell, the cathode was washed several times with PC and cyclohexene. Following washing, the electrode was enclosed in a container which was evacuated to 1μHg for two hours. The amount of potassium was determined by weighing the dry electrode.

The results obtained with the above method were not reliable because of two reasons: 1) The potassium does not stick well to the Pt surface and some of deposit was always lost when the electrode was taken out of the cell. 2) It is not possible to eliminate all the PC contained in the porous deposit structure.

Regrettably the time assigned to this project did not allow to make further experiments on this subject. Future current efficiency measurements may have to be done dissolving the deposited potassium in an appropriate reactant instead of weighing it. The amount of potassium in the solution could be determined by a suitable quantitative analytical method. Also, the appropriate means will have to be taken to prevent mechanical losses of the metal during electrolysis and also when the cathode is transferred out of the cell.

IV. CONCLUSIONS

The following conclusions can be extracted from the reported work:

1. Potassium metal was obtained up to gram quantities by cathodic deposition at room temperature, using current densities up to 30mA/cm². Electrolysis periods ranged up to 160 hours. X-ray diffraction powder patterns and spark emission spectra showed no aluminum co-deposition.
2. Anodic dissolution of potassium occurred smoothly by uniform etching of the surface.

3. Provided the solutions were carefully purified before electrolysis there were no indications whatever of side reactions, including decomposition of the solvent. Cyclic deposition-dissolution was conducted over 100 hours without showing any deterioration of the electrolyte, or change in the character of the metal.

4. Even after careful application of a sequence of purification techniques for the solvent and the salts used, metal deposits of good appearance were not consistently obtained from each batch of freshly prepared electrolyte. This indicates, that in the course of the dissolution of $\text{AlCl}_3$, (a high exothermic process) the solvent possibly undergoes chemical decomposition. Products of these reactions, even at very low levels of concentration may seriously interfere in the electrode process. A systematic search for the identification of the agent(s) responsible for the malfunction of batches of electrolyte is necessary before technological application of this process is contemplated.

5. The overpotential data obtained do not allow reliable determination of the exchange current, or of the transfer coefficients. The exchange current in these solutions was found to be lower than $4 \times 10^{-5}$ amp/cm$^2$ and possibly as low as $1 \times 10^{-7}$ amp/cm$^2$. However, at high current densities (10 mA/cm$^2$) Tafel behavior was not followed by either the anodic or the cathodic process, rather the overpotentials tended to be larger than expected on basis of Tafel extrapolation.
However, since the overpotentials observed in the practical range of current densities are not prohibitively large, a practical process for the refining, or winning of potassium still appears an attractive possibility.

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