NASA-CR-86272
N70-12215

INVESTIGATIONS OF BERYLLIUM ANODES IN NONAQUEOUS ELECTROLYTE SOLUTIONS

Final Report

by Richard E. Panzer

October 1969

Prepared under NASA Request ER 9085 by
NAVAL WEAPONS CENTER CORONA LABORATORIES
Corona, California

Electronics Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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By Richard E. Panzer

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SUMMARY

Electrochemical investigations were conducted to find a compatible electrolyte solution for utilization of beryllium as the anode in a reliable and efficient high energy density voltaic cell. Eleven nonaqueous ionizing solvents with various solutes were utilized for measurements of voltaic potentials and the determination of reversibility of the Be/Be(II) couple. Continuing low potentials (calculated to the standard hydrogen electrode) indicated that some side reaction was reducing the potential far below the thermodynamic potential, -1.85 V, calculated from free energy values. Problems of complexation and chemisorption on Be metal surfaces and poorly dissociated Be(II) species of low solubility hindered much of the investigation. Using an Hg pool electrode, reversibility was studied across a limited concentration range of $BeCl_2$ dissolved in propylene carbonate solutions. (See Fig. 22 in text.)

The formation of Be^o in aqueous solution was verified (see Fig. 24 in text), and also observed in nonaqueous systems. This is likely the result of the disproportionation of a solvo-Be(I) species, probably $(Be)_2^{+2}$. The disproportionation reaction, resulting in powdery Be metal, and solvo-Be(II) moieties may explain the many unsuccessful efforts to deposit adherent Be coatings.

The results of these investigations emphasize the fact that the charge to radius ratio of Be(II), highest of any ion, completely dominates the chemistry of this element. The effect is to strongly orient solvent molecules in its vicinity, bringing to them a greater degree of order than they normally possess. Accordingly, Be^{+2} is the most heavily solvated (hydrated in water) of all the ions.

A freshly renewed surface of Be metal, prepared in a dry inert atmosphere, rapidly polarized in a nonaqueous electrochemical cell due to formation of surface coatings. This was shown by successive voltammetry scans on the clean Be anode. (See Fig. 21 in text.)

INTRODUCTION

The objective of this research was to find a compatible electrolyte solution for utilization of beryllium as the anode in a reliable and efficient high energy density voltaic cell. From the standpoint of thermodynamic calculations, Be is one of the most promising anode materials, but its use in aqueous solutions is precluded by its tendency to form passivating films. From these studies we expected to be able to predict the potentialities for using Be anodes in nonaqueous voltaic cells.

In Table I are given the theoretical energy density values for beryllium compared with other light metals. Admittedly, some of them have little promise as anodes because of their high activation energy of ionization and tendency to complexation. However, the table indicates the theoretical possibilities of anode metals for comparison with what is actually achieved in the investigations reported here and elsewhere. Gmelin's Handbuch (Ref. 1) provides a summary of beryllium electrochemistry, both in aqueous and nonaqueous systems, to 1930. In spite of the predicted -1.85 V potential for Be, it is noteworthy that observed aqueous potentials, versus the standard hydrogen electrode (SHE), have been in the range of -0.54 to -0.75 V. In the nonaqueous solvents amyl alcohol, ethanol, and pyridine, Schmidt (Ref. 2) obtained potentials of -0.41, -0.91, and 1.20 V, versus standard hydrogen electrode (SHE), for the half cell, $Be/BeCl_2$, 1 N in the solvent used. The same investigator gives a potential of -1.077 V for amalgamated Be in ethanol. Apparently Bodforss (Ref. 3) first suggested that the potential determining species in aqueous beryllium half-cells might be a Be(I) species, most likely $(Be)_2^{+2}$.

More recently, Wood and Brenner (Ref. 4) have conducted extensive experiments to deposit beryllium and other metals from nonaqueous solutions. In common with previous efforts, their work produced black powdery deposits containing less than 100% Be. Experimentation by Lui, et al. (Ref. 5) to form massive structures of electrodeposited Be under a broad spectrum of environmental conditions in nonaqueous solutions has been singularly unsuccessful.

TABLE I
THEORETICAL ENERGY DENSITY VALUES FOR SELECTED METALS

Element	E_o	Electrons	Energy density	
			joules/mg	joules/mm^3
Li	3.05	1	42.4	0.73
Be	1.85	2	39.5	7.27
B	0.87	3	23.3	5.45
Mg	2.37	2	18.8	3.27
Al	2.07	3	22.2	5.99
Ca	2.87	2	13.8	2.13
Na	2.72	1	11.4	1.10

Note: 7.93 joules/mg = 1 W-hr/lb.

Strohmeier and Popp (Ref. 6), using many combinations of complex beryllium salts and alkyl beryllium compounds in carefully dried toluene or di-n-butyl ether, were able to produce only the compound Be_2C. These authors quote the German patent (Ref. 7) of Dotzer, Engelbrecht, and Todt, where it is claimed that dendritic deposits of Be could be formed under the same conditions utilized by Strohmeier and Popp. As seems often the case with Be, this claim could not be verified; only black, impure deposits were obtained.

In recent years, interest in the complex chemistry of beryllium has led to preparation of many previously unknown polymers. The general chemistry of beryllium is influenced by its small ionic radius, 0.31 Å, and its correspondingly high charge to radius ratio, z/r = 6.45, the highest of any element. This may be compared to z/r ratios of $Li^+ = 1.67$, $Al^{3+} = 6.00$, $Mg^{2+} = 3.07$, $Ca^{2+} = 2.02$, and $Zn^{+2} = 2.41$. From these, the similarity of Be to Al can be seen; additionally, Be resists oxidation in spite of its heat of oxidation of -143.1 kcal/mol. This is a kinetic effect which arises because the volume of the oxide is larger than that of the metal from which it is formed, producing a surface film which resists further attack. Beryllium is also very similar to zinc in its mineral occurrence, and their first and second ionization potentials differ by only a small fraction of an electron volt. In spite of such similarities, the high charge to radius ratio of the Be^{2+} ion completely governs the chemistry of this element.

A consequence of this is that the Be^{2+} ion is a strong "order-producing ion," according to Gurney (Ref. 8). That is, it strongly orients the solvent molecules in its vicinity, bringing to them a greater degree of order than they normally possess. This has been proven through the discovery that Be^{2+} is the most heavily hydrated of all the ions.

As will be discussed in detail later, it is this hydrating capacity which has precluded preparation of certain Be compounds which were desirable for use in this project. The extreme capability of Be to solvolyze is a direct result of its high charge to radius ratio. The high charge density on the Be(II) ion surface polarizes the surrounding solvent molecules, causing them to orient with the negative ends of their dipoles towards the Be ion. Any protons present are repelled to such an extent that sooner or later thermal energy will transfer the positive species to a more distant molecule. The result is formation of a polynuclear species, such as is illustrated with $BeCl_2$ below. The complexing power of Be has been a hindrance in studies of solubilities of its compounds in nonaqueous solvents, since nothing is known of the species resulting from dissolution of even a simple binary salt, such as $BeCl_2$, in a given solvent. Since the chloride is itself a polymeric structure, i. e., $>\mathrm{Be}<\substack{\mathrm{Cl}\\ \mathrm{Cl}}>\mathrm{Be}<\substack{\mathrm{Cl}\\ \mathrm{Cl}}>\mathrm{Be}<$, etc., the identity and activity of the charged species in solution are unpredictable. An additional factor is that Be is amphoteric and the formation of many of its complex compounds is a direct result of this situation.

Noteworthy is the high melting point of Be metal, 1284°C, to be compared with Mg = 651°C, Al = 660°C. This property is a direct result of the close-packed hexagonal structure of the metal, combined with the small atomic radius (1.12 Å) producing a very stable structure which is not easily disrupted.

It is a pleasure to acknowledge the many discussions with my colleague, Dr. Peter J. Slota, Jr., and his supervision of the solvent purification processes. Oral contributions from Mr. W. C. Spindler, Head, Electrochemistry Branch, and from Drs. Fetter, Haber, Harris, and Miles of the Chemistry Division were invaluable. The beryllium wire was furnished by Miss Betty Del Duca of the NASA-Lewis Research Center.

EXPERIMENTAL

Solvents utilized in these investigations were chosen on the basis of several criteria listed by other investigators who have used ionizing nonaqueous solvents (Ref. 9, 10, 11, and 12). Practically all of the previous investigations concern anodic reactions of alkali and alkaline earth metals in various solvents, and the results are not readily comparable to beryllium electrochemistry. Our final criteria for selecting a solvo-system for a Be anode are based on the broad knowledge of beryllium chemistry of Dr. P. J. Slota, Jr., and his group in the Synthetic Chemistry Branch at the NWC Corona Laboratories. Additionally, the Electrochemistry Branch has maintained (for over a decade) a continual survey of nonaqueous electrochemistry and related chemical investigations.

In the present investigations, we have used the full range of acid-neutral-basic solvents defined by G. N. Lewis (Ref. 13). In Table II are listed the solvents, area of investigations, and types. It is manifestly impossible to list all the techniques used to purify the solvents. Generally, this has consisted of a pretreatment of the solvent with molecular sieves to remove water; the solvent is then distilled under vacuum, the middle fraction being retained for use in the electrochemical investigations. When possible, we have used a Model 775 F & M Scientific (Hewlett-Packard) preparative gas chromatograph to determine solvent purity. However, as demonstrated by Burrows and Kirland (Ref. 14) with propylene carbonate, this technique may decompose the solvent, resulting in a poorer material than was injected into the machine. We have determined conductivities of "as received" and of the purified solvents and solutions. Generally, values of specific conductivity have agreed well with those reported by other investigators, and have served as a check on the purification techniques. All solutions were prepared in a Vac/Atmospheres drybox, with a recirculating argon atmosphere maintained at less than one part per million of oxygen and moisture.

Supporting electrolytes were of reagent grade, dried under vacuum at a temperature appropriate for the chemical, then stored and weighed in the drybox. Solutes used were lithium chloride, lithium perchlorate, potassium hexafluorophosphate, lithium fluorborate, and tetraethyl ammonium perchlorate. Although LiCl is not always soluble in certain solvents, to provide adequate supporting electrolyte concentration, we have been able to use $LiClO_4$ regularly (G. F. Smith Co.). Concentration was limited to 0.1 molar whenever possible, as it was

TABLE II
SOLVENTS UTILIZED IN STUDIES OF BERYLLIUM ELECTROCHEMISTRY

Solvent	Lewis class	Usage
Phosphorus oxychloride	Acid	Voltammetry, anode disch.
Propylene carbonate	Neutr-basic	Voltammetry, anode disch., disprop. reaction study
Tetrahydrofurane	Basic	Voltammetry, anode disch.
Dimethylformamide	Basic	Voltammetry, anode disch.
Hexamethylphosphoramide	Basic	Voltammetry, anode disch., disprop. reaction study
4-butyrolactone	Neutr-basic	Voltammetry, anode disch.
Acetonitrile	Neutral	Voltammetry, anode disch., disprop. reaction study
Ammonia	Basic	Voltammetry, anode disch., disprop. reaction study (3 different environments)
Methyl pyrollidone	Basic	Voltammetry, anode disch.
Pyridine	Basic	Voltammetry, anode disch., disprop. reaction study
Methanol	Basic	Disproportionation reaction

found that higher concentrations of the background electrolyte would sometimes reduce the solubility of the beryllium compounds. Solvent choice for this work has often been a matter of balancing one complicating factor against another. Because beryllium chloride is the only salt of the element available in anhydrous form, we found on occasion that some interaction with the supporting solute would precipitate the Be species out in a new complex form. Sometimes the metathetical reaction was slow enough to allow some voltammetry studies, but concentrations of Be species were obviously unstable. In voltaic cells, constant current discharge of Be metal occasionally produced instantaneous passivation due to formation of some solvated or solvolyzed species on the metal surface. We would have preferred to use beryllium perchlorate as the source of Be species in voltammetric work, but the tetrahydrate is the only compound available, and the perchlorate ion decomposes before the water can be driven off. We have some trepidation about reacting Be metal with anhydrous perchloric acid.

Beryllium metal electrodes were made from wire of various sizes, and disks cut from a sheet or a rod. The sheet beryllium (Beryllium Corp.) was HR-700, having an assay of 98.3% Be, 1.93% BeO, the remainder being small percentages of Fe, Mg, Al, and Si. Disks were also cut from an ingot of Pechiney, SR grade Be metal. Impurities in it are BeO_2 = 0.6%, C = 0.01%, and other metals present in a few parts per million.

The disks of Berylco metal were 4 mm in diameter and mounted with Hysol Epoxy cement (which is unaffected by the solvents utilized) in the end of a 4 mm ID × 300 mm long Pyrex tube. Connection to the back of the Be disk was made with a drop of mercury to contact a strip nickel conductor leading out the other end of the glass tube, where the strip was sealed with melted polyethylene. Disks of the Pechiney metal were 12.5 mm in diameter and were mounted in the same way, in a correspondingly larger tube. Beryllium disk electrodes for use in pressurized ammonia voltaic cells were 10 mm in diameter, and were welded to the face of a stainless steel disk to which a connector pin was attached. Details of this cell electrode assembly have been described elsewhere (Ref. 15) and will be published in detail later. The Be electrode surface was degreased, then cleaned by stripping with a mixture of 2% HF, 48% concentrated HNO_3, and 50% H_2O. After thorough rinsing with distilled water and acetone, the electrodes were quickly dried and placed in the drybox. Just prior to use in the electrochemical cells, the Be was treated with a saturated solution of HCl (gas) in dimethylformamide, then rinsed with portions of the solvent in use. This treatment stripped off the last traces of oxides, and gave a smooth, uniform surface. Chemical was preferred to mechanical surface preparation, since a recent paper by James (Ref. 16) indicates that mechanical polishing leads to selective erosion at incipient centers created by the polishing.

All cells used in the drybox were of a three-compartment type as shown in Fig. 1. The indicator electrode was placed in the center compartment, the platinum disk counter electrode was in one side compartment, and the reference electrode half cell assembly was in the other side. Two sizes of cells were made; the one illustrated has 18/9 ball and socket joints, while the larger cell has 28/15 joints. The second

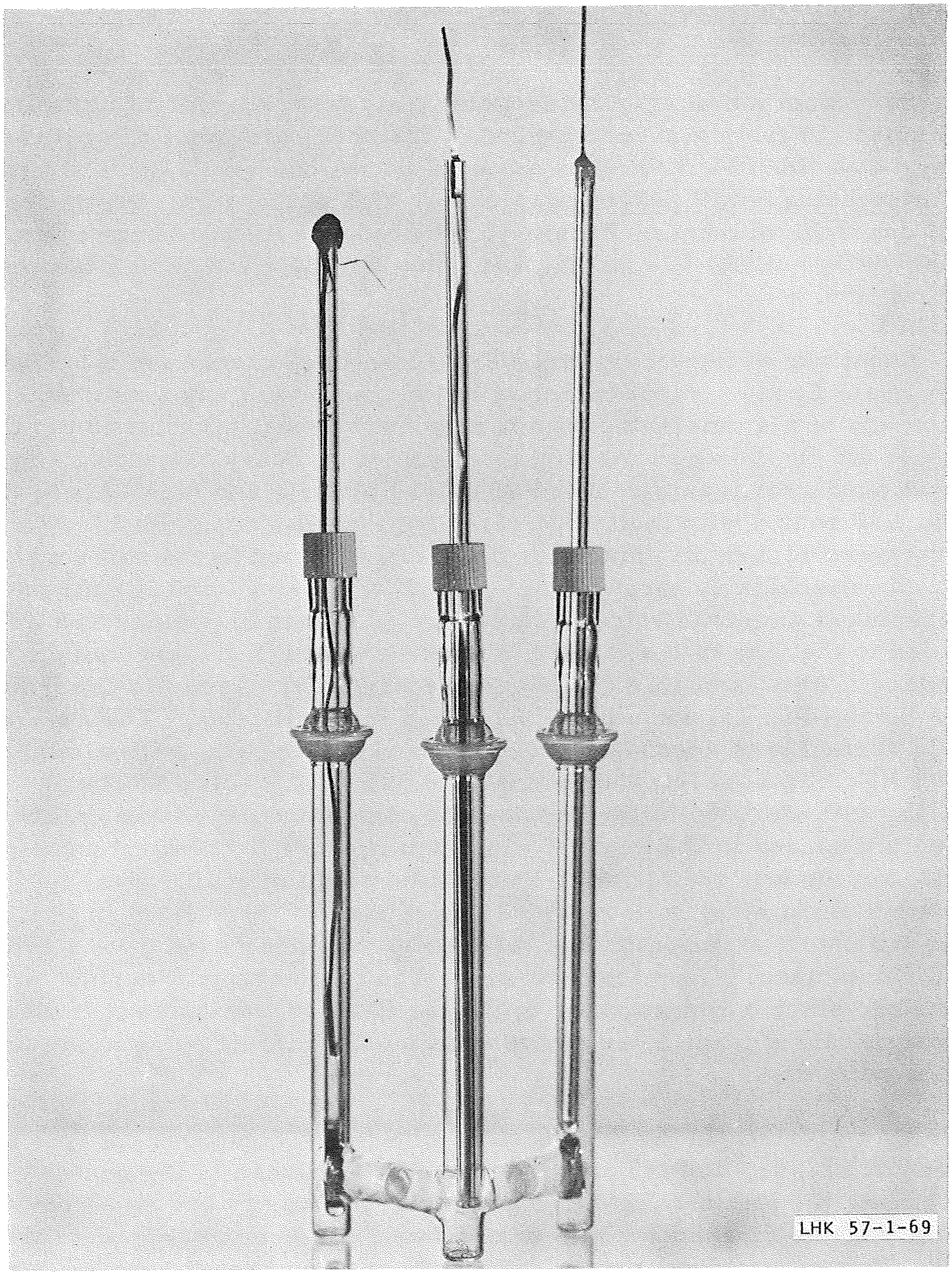
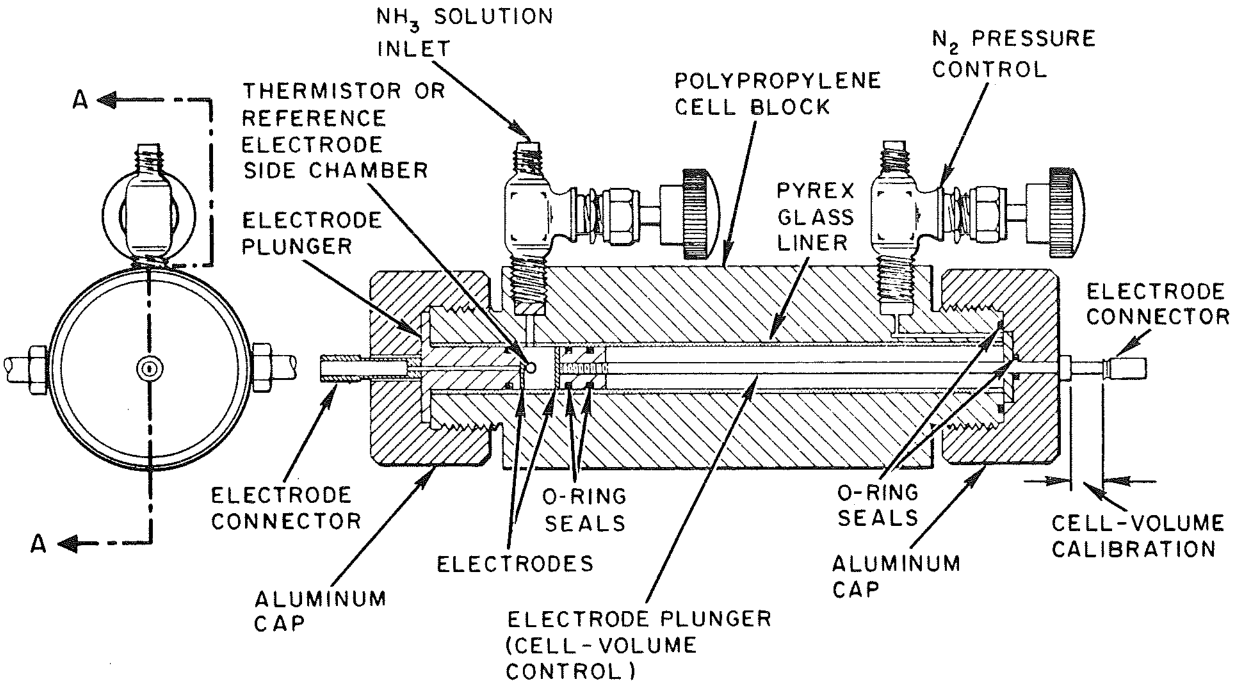


FIG. 1. Three-Compartment Cell Used in Nonaqueous Electrochemical Investigations.

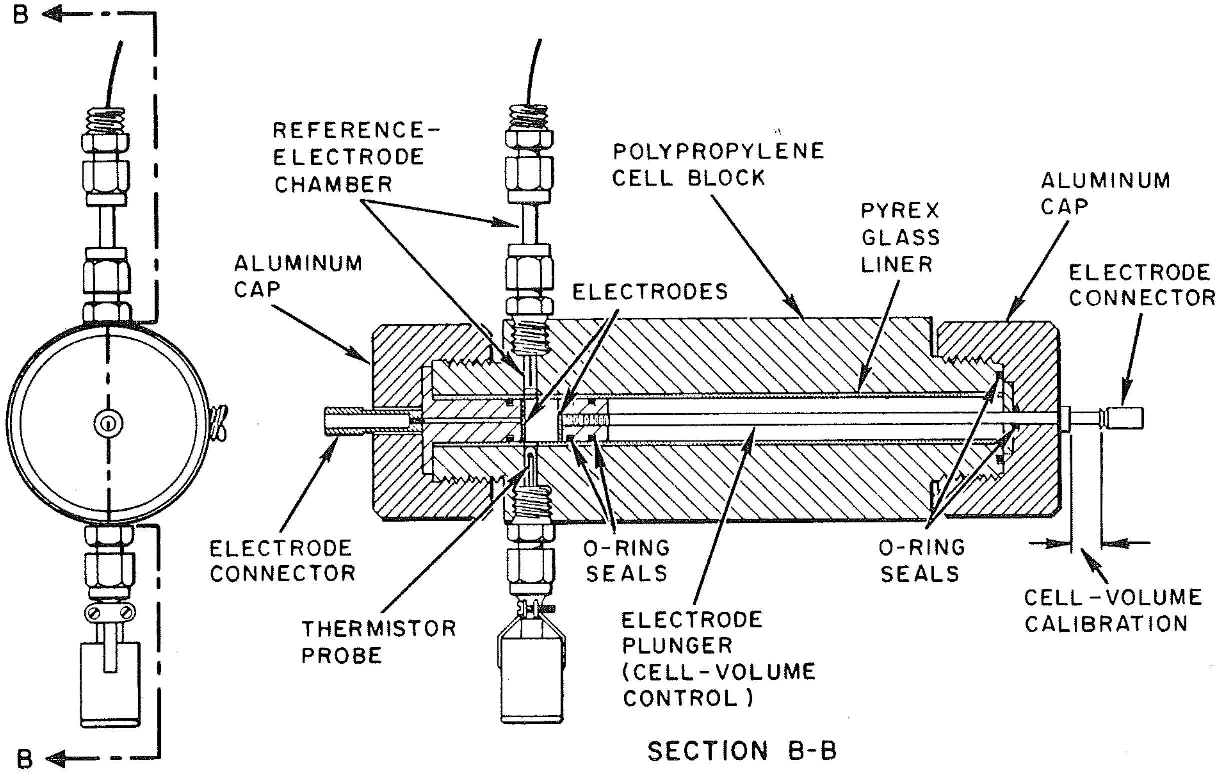
figure indicates the inside diameter of the cell tubing. Pyrex frits separating the compartments are of fine porosity, with pore size in the range of 4-5.5 μ. Cell compartments are approximately 150 mm high; the thermometer slip joints closing off the compartments have O-ring seals which hold the 6 mm OD electrode glass tubing tightly in place.

The cell assembly shown in Fig. 2 was designed for use with pressurized liquid ammonia systems and has been described previously (Ref. 17). This assembly incorporates a platinum counter electrode on one end, the indicator disk electrode on the other, and the reference electrode is inserted into one of the side gland seals on the chamber. Separation between electrodes can be achieved by moving the electrodes farther apart, or by inserting a fritted glass or polypropylene separator between the electrodes. The detailed operation of this cell is to be described in a later publication.

Reference electrodes were generally based on some form of a silver system, with exceptions as indicated in Table III, which lists the electrodes used in various solvent systems. Although the fritted separators in the compartmented cells restrict diffusion of the electrode products, we have adopted the microcracked system as a means of preventing the reference electrode solution from contaminating the rest of the cell. This system is an adaptation of the controlled crack first utilized by Perley (Ref. 18). These have been developed for high-pressure systems with liquid ammonia and used extensively by Panzer in work in nonaqueous solvents (Ref. 19). The microcrack is made by sealing a 0.1 mm diameter piece of soft glass in the end of a Pyrex tube of suitable diameter and length depending on the cell usage. The differential expansion of the soft and Pyrex glasses causes a fine crack to appear along the sealed piece of soft glass in the end of the tube. If the assembly is made correctly, resistivity through it (using KCl, aq.) will be on the order of 0.5 to 1.5 MΩ. The half cell is then made up in the tube behind the microcrack, using the appropriate solution and metal wire. The resulting half-cell is very stable; the reference solution remains uncontaminated, and there is no detectable flow of the reference solution into the indicator electrode compartment. In either three-electrode voltammetry or controlled current discharge, the current passes between the indicator and counter electrodes, and the potential change on the indicator electrode is monitored with the reference electrode. With high impedance of the microcracked separator it is necessary to use a follower (unity-gain amplifier) in that portion of the circuit. The versatility of the microcracked configuration allows one to place the reference assembly anywhere in the cell, to monitor



SECTION A-A



SECTION B-B

FIG. 2. Cell Fixture. Section A-A shows valves; Section B-B shows side chambers.

TABLE III
POTENTIALS OF NONAQUEOUS REFERENCE HALF-CELLS VERSUS SATURATED CALOMEL AND STANDARD HYDROGEN ELECTRODES

Solvent	Potential vs SCE, volts	Potential vs SHE, volts	Notes
HMPA (0.1 M $LiClO_4$)	+0.26	+0.50	Ag/Ag^+ (0.1 M)
NH_3	-0.76	-0.52	$Pb/Pb(NO_3)_2$(sat'd)-$LiNO_3$(sat'd)NH_3
Acetonitrile (0.1 M $LiClO_4$)	+0.32	+0.56	Ag/Ag^+ (0.1 M)
DMF (0.1 M KPF_6)	+0.42	+0.66	Ag/Ag^+ (0.1 M)
4-Bu Lac (0.1 M KPF_6)	+0.53	+0.77	Ag/Ag^+ (sat'd)
(0.1 M $LiClO_4$)	+0.57	+0.81	Ag/Ag^+ (sat'd)
M-Pyrol (0.1 M $LiClO_4$)	+0.35	+0.79	Ag/Ag^+ (0.1 M)
THF (0.1 M $LiClO_4$)	+0.065	+0.30	Ag wire in 0.1 M $LiClO_4$ contained in a microcrack tube
Propylene Carbonate	-2.92	-2.68	Li/Li^+ (1 M $LiClO_4$)
$POCl_3$	+0.94	+1.18	Mo wire in $POCl_3$ contained in a microcracked tube

the potential at that point. When cleaning the cell, the reference half-cell can be lifted out of the cell assembly and reused.

In the table of reference half-cell assemblies are listed a few which are not based on a silver system. The electrode used for $POCl_3$ investigations is one used by Gutmann and Mairinger (Ref. 20); it consists of a freshly cleaned molybdenum wire immersed in the solvent contained in a microcracked tube. The environment of the wire does not vary, and it provided a stable reference half-cell. Another half-cell listed is the Li/Li^+(1M $LiClO_4$-PC), which is the same system that was utilized by Burrows and Kirkland (Ref. 14). For certain solvents (DMSO, MeCN) we have been able to use an aqueous calomel electrode (Beckman #39402) with ceramic junction. Following a suggestion by Dr. P. J. Elving (Ref. 21), we have measured all reference half-cell potentials against the SCE. Although such measurements include an unknown junction potential, these are usually quite small. Nelson (Ref. 22) has shown that only for very basic or very acidic solvents will the junction potential be over a few millivolts. In the present case, we would expect them to be greatest with NH_3, $POCl_3$, and, possibly, pyridine.

Conductivities of solvents and solutions were determined using a dip-type cell which was calibrated in the usual manner with KCl, aq. A General Radio Type 1650-A impedance bridge operating at 1.0 kHz was used for determining specific conductance.

Cyclic voltammetry instrumentation consisted of a triangular wave generator (Astrophysics Research Corp.), two Philbrick Q-3A1P Stabilized Operational Amplifier modules, and a Hewlett-Packard Power Amplifier Type 467A. One of the opamp modules is set up in the follower mode, while the other operates as a control amplifier, driven by the triangular wave generator. The control amplifier drives the H/P power amplifier, which can provide 500 mA maximum current.

For electrode polarization measurements, a power supply system consisting of a Kepco Model CK-60-0.5 was used to operate the beryllium anodes at constant currents over 20 mA. Below this value, the output of the Kepco supply was fed into a transistorized current regulator which allows precise adjustment of the current passed through the anode, to a minimum value of 80 μA. In both cyclic voltammetry and anode polarization measurements, readout is done (via appropriate resistances on a decade box for currents) onto a 25 × 38 cm X-Y Recorder, Moseley Model 7001 AM.

RESULTS AND DISCUSSION

Selection of Promising Solvo-Systems

Initial investigations were performed to screen solvo-systems in the most direct way to determine if they could be used with beryllium anodes. Specific conductivities of purified solvents and of solutions were determined to check the purity level, as far as this can be indicated by conductivity. In one solvent, hexamethylphosphoramide (HMPA), which had not been extensively used in electrochemistry, some work was conducted on solutions of $Be(NO_3)_2$ and $BeCl_2$ to determine if complexes formed readily. The treatment of $BeCl_2$ and $Be(NO_3)_2 \cdot 3H_2O$ with HMPA gave the white solid complexes $BeCl_2 \cdot 2OP[N(CH_3)_2]_3$ and $Be(NO_3)_2 \cdot 2OP\text{-}[N(CH_3)_2]_3$. When only a slight excess of the solvent was used, the chloride complex separated shortly after the reagents were mixed. The nitrate complex separated rapidly when the water from the hydrated salt was removed from the mixture. The latter fact indicated that the HMPA complex completely displaced the solvated water, providing an estimate of relative solvation power.

Measurement of Be Electrode Polarization in Selected Systems

Voltammetry discharge curves (polarization curves) for Be in various solutions were run to determine the most promising systems for more detailed investigations. It was the polarization curves which first indicated that the expected potentials for beryllium were not obtained in the various solvo-systems. Early work by Schmidt (Ref. 2) had indicated that potentials of Be in nonaqueous solvents were much lower than the thermodynamically predicted values.[1]

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[1] In order to compare all previous data with our own potentials, we have calculated them all to the zero standard of the Standard Hydrogen Electrode (SHE). Since much of the earlier data have been listed on the normal calomel scale, the conversion to the SHE scale is a matter of subtraction. Signs of potentials are according to the IUPAC Stockholm Convention.

For the half cell Be/1N-$BeCl_2$, Schmidt obtained the following potentials.

Amyl alcohol	$E_h = -0.38$
Pyridine	$E_h = -1.17$
Ethanol	$E_h = -0.88$
Ethanol (Amalgamated Be)	$E_h = -0.897$

These low values were obtained prior to 1930 when dry, inert atmospheres were not usually available, and we were reluctant to accept them as a prediction of potentials to be expected in nonaqueous solvents. In Table IV is presented a summary of our potential measurements of beryllium anodes in various solutions. The "Derived Potentials" were obtained by relating the measured electrode potentials (versus the SCE potential-Table III) and the potential of the standard hydrogen electrode. The resulting values include a small junction potential, as previously discussed, but provide a common base for comparison of the measured OCV values. Although the open circuit potential has little thermodynamic significance, from a practical standpoint it is the potential one would observe in a voltaic cell when no Be ionic species is present in solution. In that situation, the OCV will initially be higher than the reversible potential obtained in a cell where the Be ionic species is, for example, 0.1 molar. As the Be concentration builds up, the OCV would gradually become less, as a consequence of the relationships expressed in the Nernst equation, and there may be a contribution from the free energies of solvation. The latter will be different for each solvo-system, but will undoubtedly make a maximum contribution of only a few tenths of a volt in any case.

As mentioned previously, the problems of preparing solutions of known activity, or concentrations of Be species, make the situation of a "reversible" potential somewhat problematical in the present case. Throughout the investigations, the continuing low potentials measured indicated that some complicating process was taking place. In Fig. 3-14 are shown the polarization curves for beryllium metal in various cells. Increasing amounts of current were drawn through the electrode and the potential measured as a function of the current. The time for the sweep from OCV to-0.5 V was about 1 minute. After the initial sweep and at indicated cursities, the current was held constant and the potential monitored for several minutes to determine the behavior of the Be anode under steady polarization conditions.

TABLE IV
SUMMARY OF MEASURED AND DERIVED Be POTENTIALS

SCE indicates saturated calomel electrode, SHE indicates standard hydrogen electrode. On the thermodynamic scale at 25°C the potential of SHE = 0.00 V and the potential of SCE = +0.244.

Solvent	Solute	Measured OCV vs ref. electr.	Derived OCV vs SCE	Derived OCV vs SHE	CCV vs ref. electr.	Cursity, mA/cm^2	Notes
HMPA	LiCl	-1.73	-1.47	-1.23	-0.45	1.0	
	$LiClO_4$	-1.55	-1.29	-1.05			Extreme polarization
NH_3	KSCN	-1.53	-2.29	-2.05	-1.35	1.0	
	KBr	-1.45	-2.21	-1.97	-1.75	1.0	
	$NaNO_3$	-0.36	-1.12	-0.88			Extreme polarization
	NH_4Br	-0.90	-1.66	-1.42			Extreme polarization
AN	$LiClO_4$	-1.44	-1.12	-0.88	-1.18	1.0	
DMF	KPF_6	-1.53	-1.12	-0.88	-1.18	1.0	
	$LiClO_4$	-1.57	-1.05	-0.81	-0.95	1.0	
4BL	KPF_6	-1.55	-1.03	-0.79	-0.78	1.0	
M-Pyrol	KPF_6	-1.29	-0.94	-0.70	-0.96	1.0	
	LiI	-1.42	-1.07	-0.83			Extreme polarization
	$LiClO_4$	-0.92	-0.57	-0.33			Extreme polarization
	$LiClO_4$	-1.05	-0.99	-0.75			Extreme polarization

TABLE IV (contd.)

Solvent	Solute	Measured OCV vs ref. electr.	Derived OCV vs SCE	Derived OCV vs SHE	CCV vs ref. electr.	Cursity, mA/cm^2	Notes
THF	KPF_6(sat'd)	-1.20	-1.19	-0.95			Extreme polarization
P.C.	KPF_6	+2.02	-0.90	-0.66	+3.40	0.5	Pechiney SR grade Be anode
	$LiClO_4$	+1.98	-0.94	-0.70	+3.55	0.5	Berylco HR-700 grade Be anode
$POCl_3$	$SbCl_5$	-1.48	-0.54	-0.30	-0.69	0.10	CCV reading after an initial anodization
	$LiBF_4$	-1.73	-0.79	-0.55	-1.40	0.10	$POCl_3$ solution resistivity is very high, requires high applied pot'l between working and counter electrodes.
	$LiClO_4$	-1.92	-0.98	-0.74	-1.00	0.10	

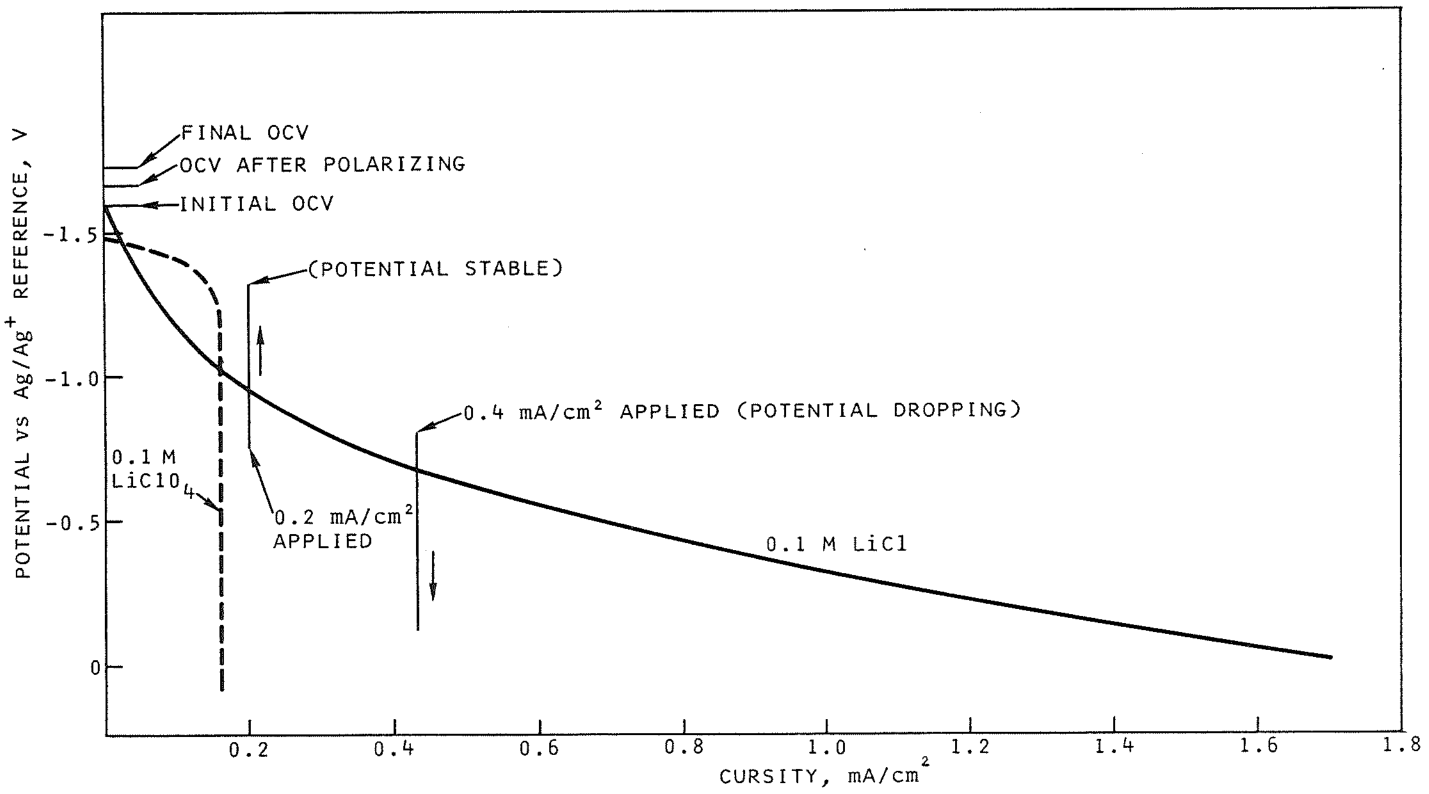

FIG. 3. Electrochemical Polarization Curves of Be in HMPA Solutions.

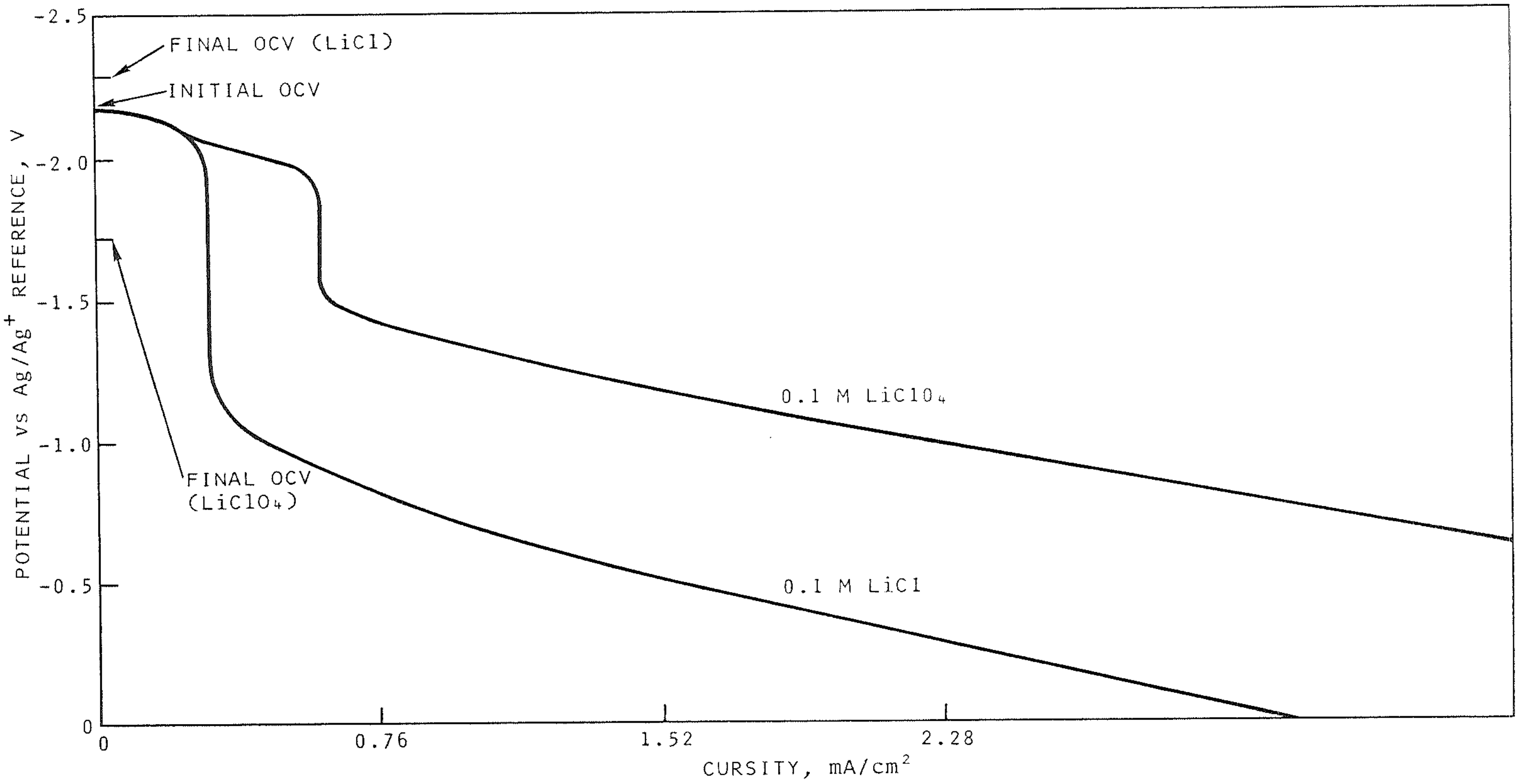

FIG. 4. Electrochemical Polarization Curves of Mg in HMPA Solutions.

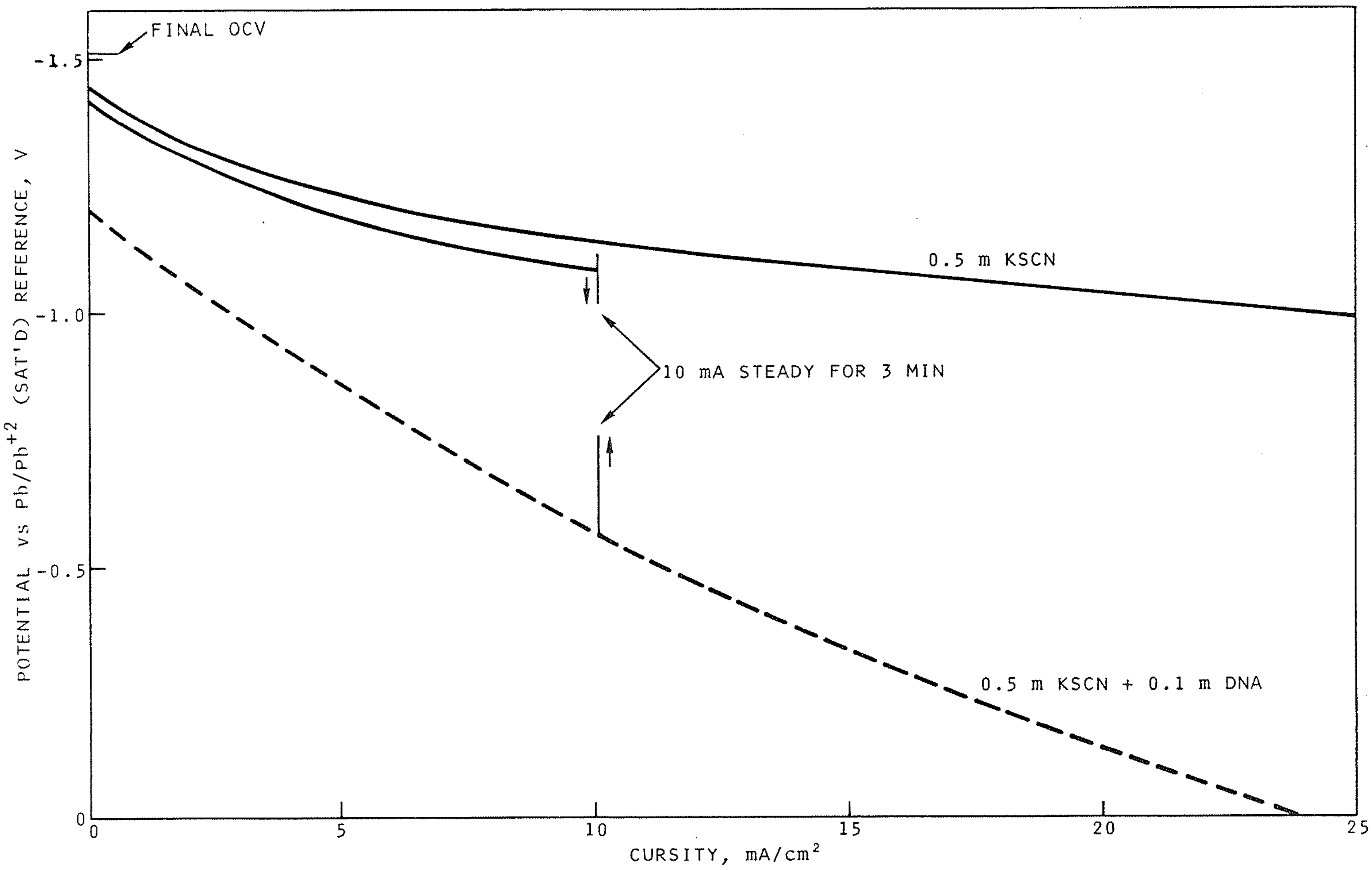

FIG. 5. Electrochemical Polarization Curves of Be in Liquid NH_3 Solutions of KSCN and KSCN + 2, 4, DNA.

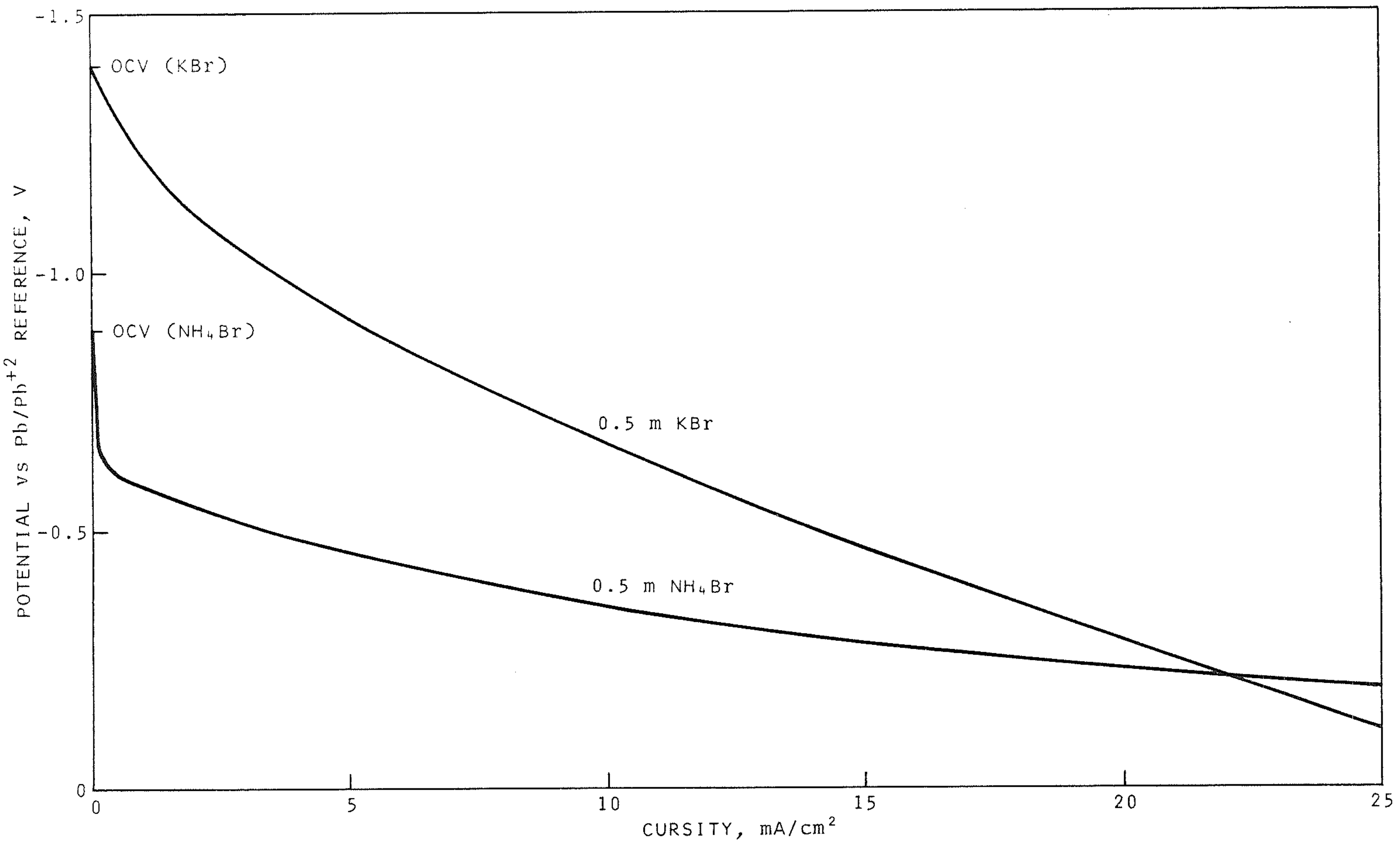

FIG. 6. Electrochemical Polarization Curves of Be in Liquid NH_3 Solutions of KBr and NH_4Br.

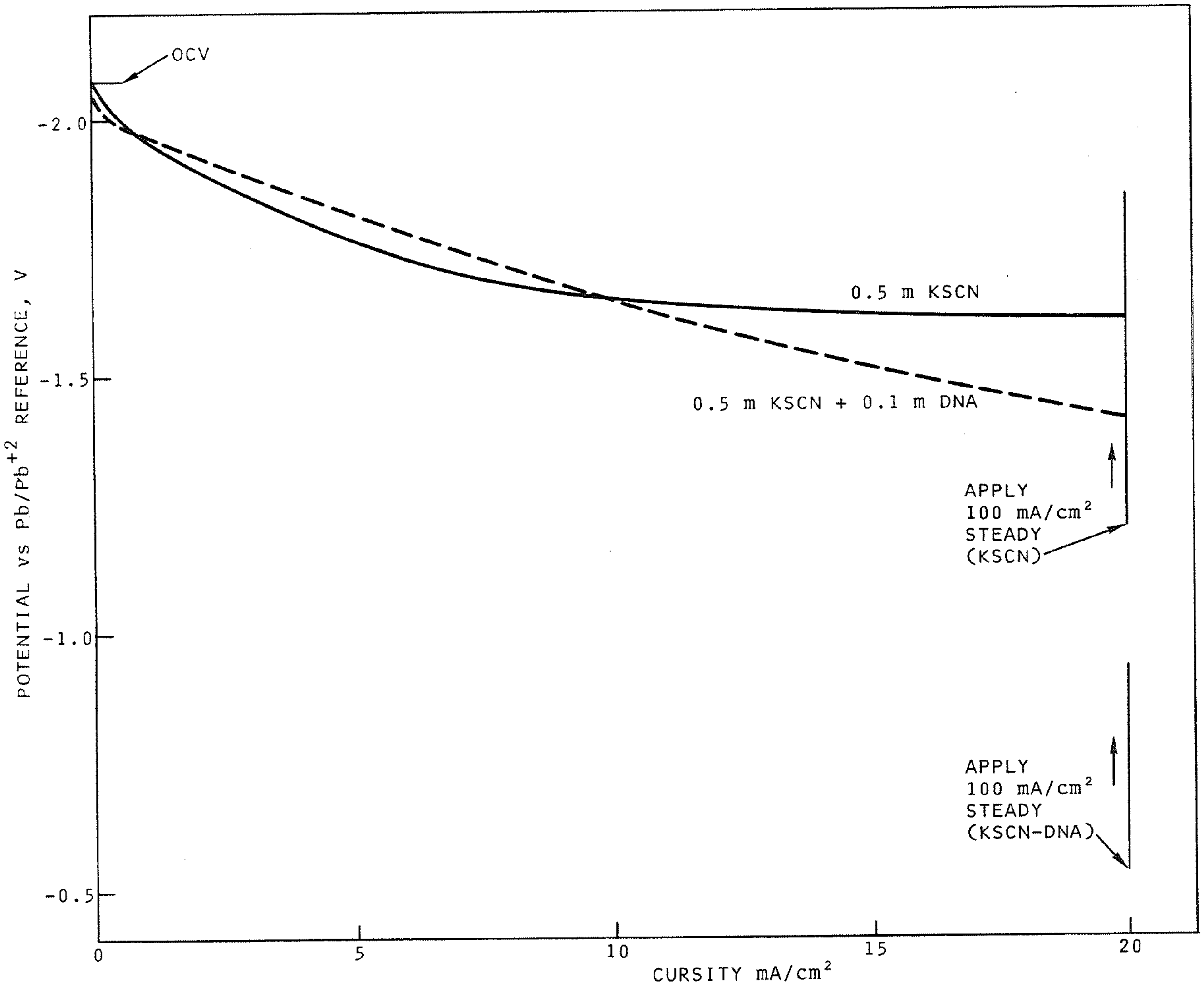

FIG. 7. Electrochemical Polarization Curves for Mg in Liquid NH_3 Solutions of KSCN and KSCN + 2, 4, DNA.

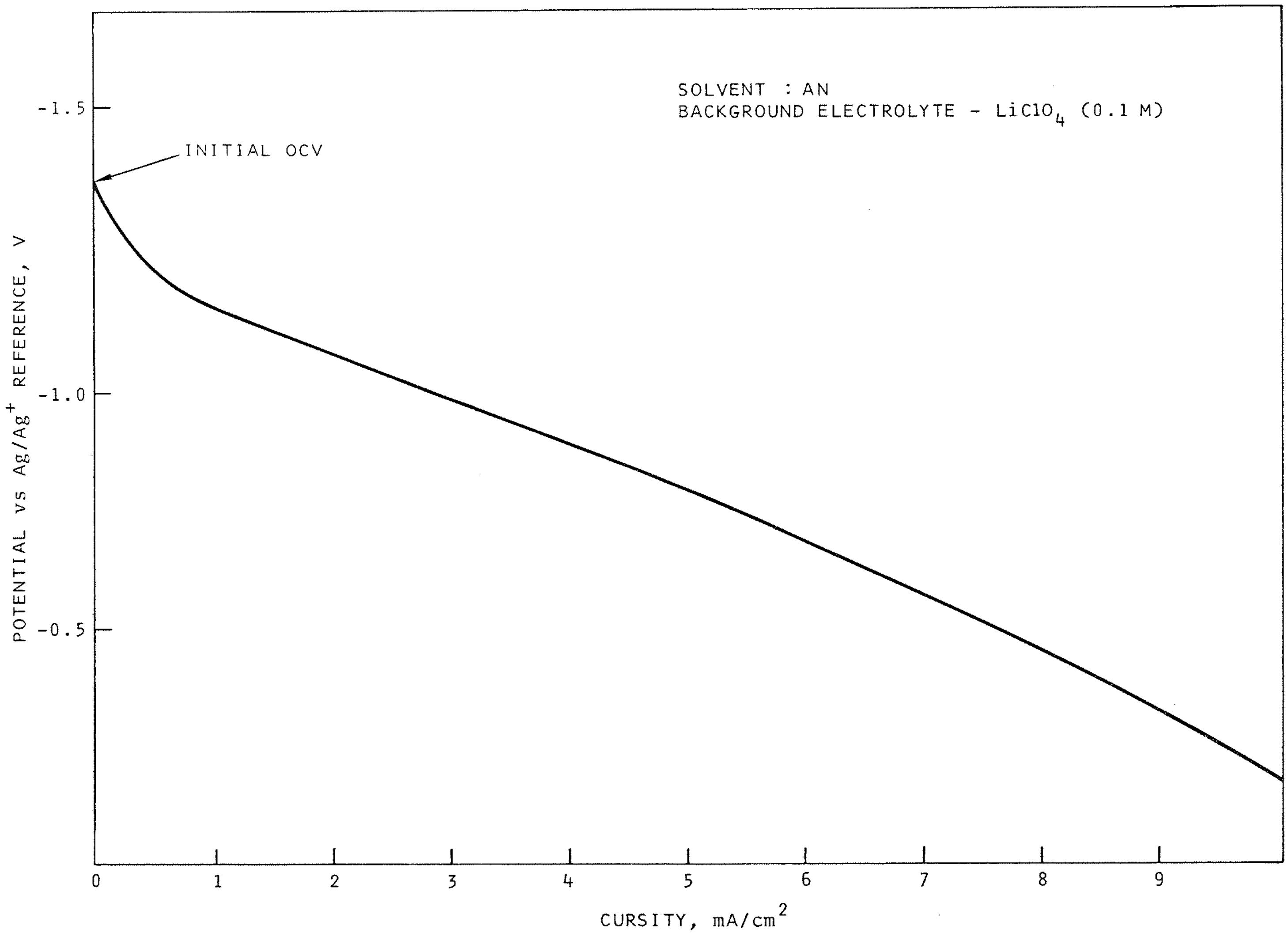

FIG. 8. Electrochemical Polarization Curves for Be in Acetronitrile Solutions.

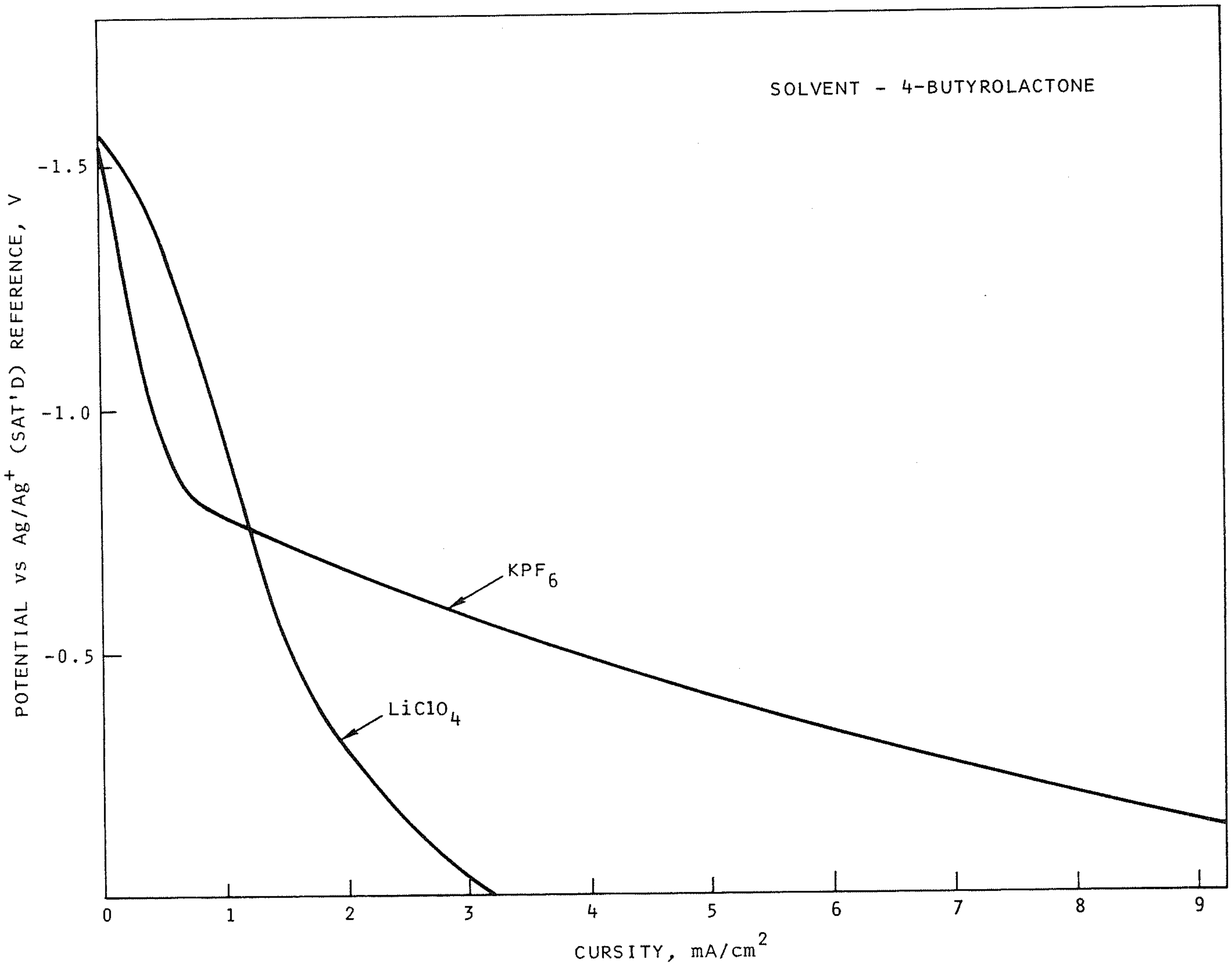

FIG. 9. Electrochemical Polarization Curves for Be in 4-Butyrolactone.

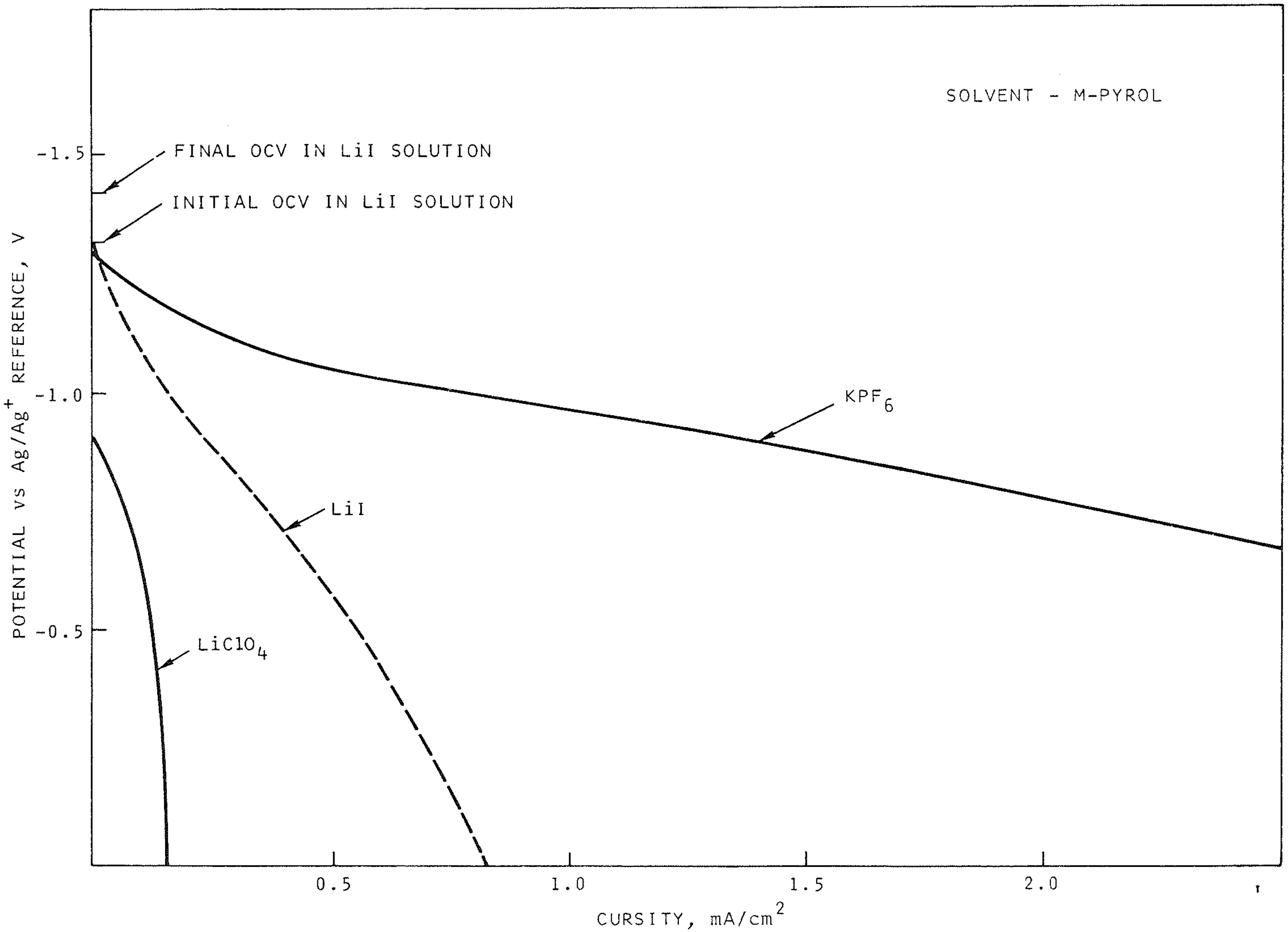

FIG. 10. Electrochemical Polarization Curves for Be in M-Pyrol Solutions.

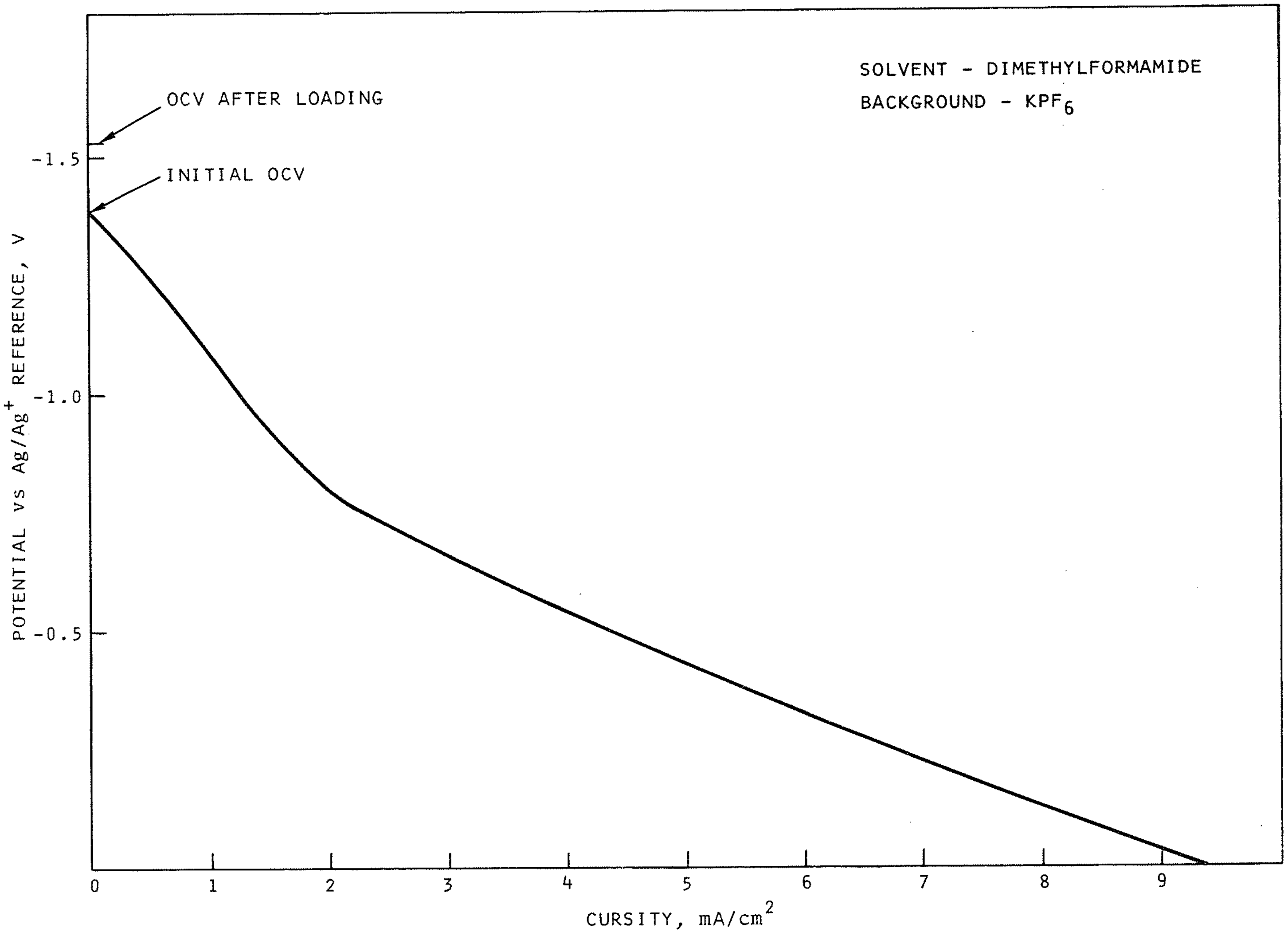

FIG. 11. Electrochemical Polarization Curves for Be in Dimethylformamide Solutions.

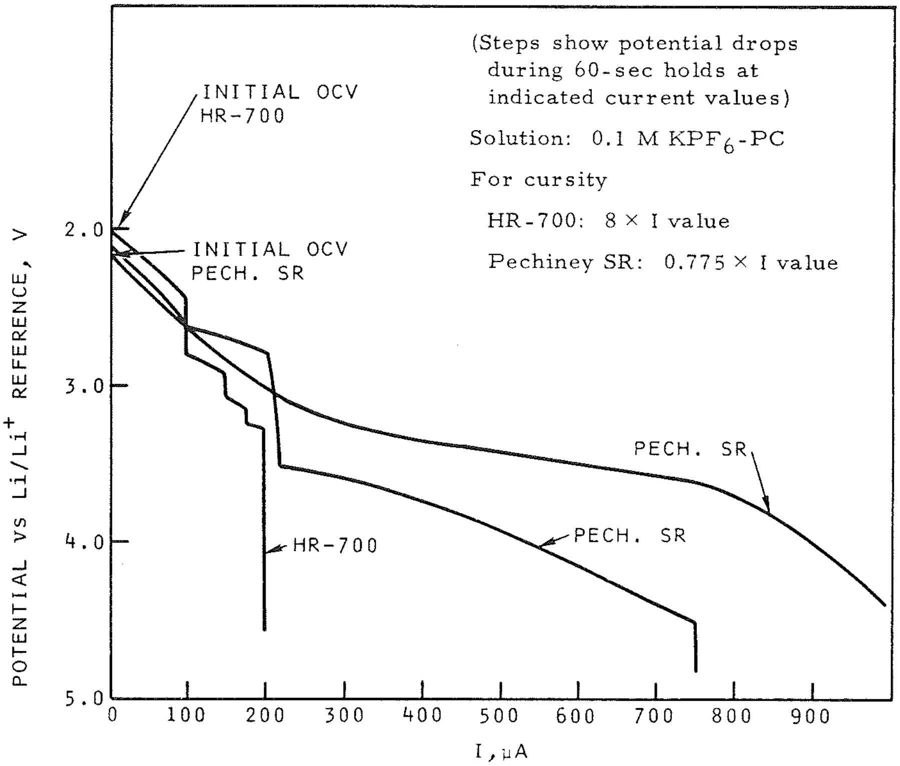

FIG. 12. Electrochemical Polarization Curve of Be Anode in $LiClO_4$-PC Solution.

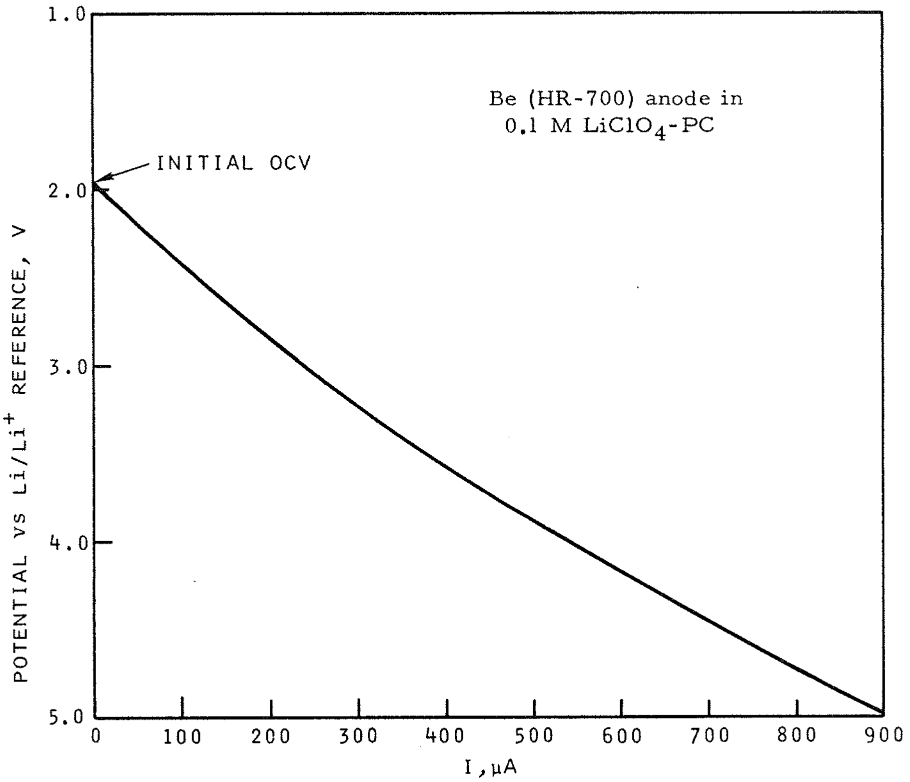

FIG. 13. Electrochemical Polarization Curve of Be in KPF$_6$-PC Solutions.

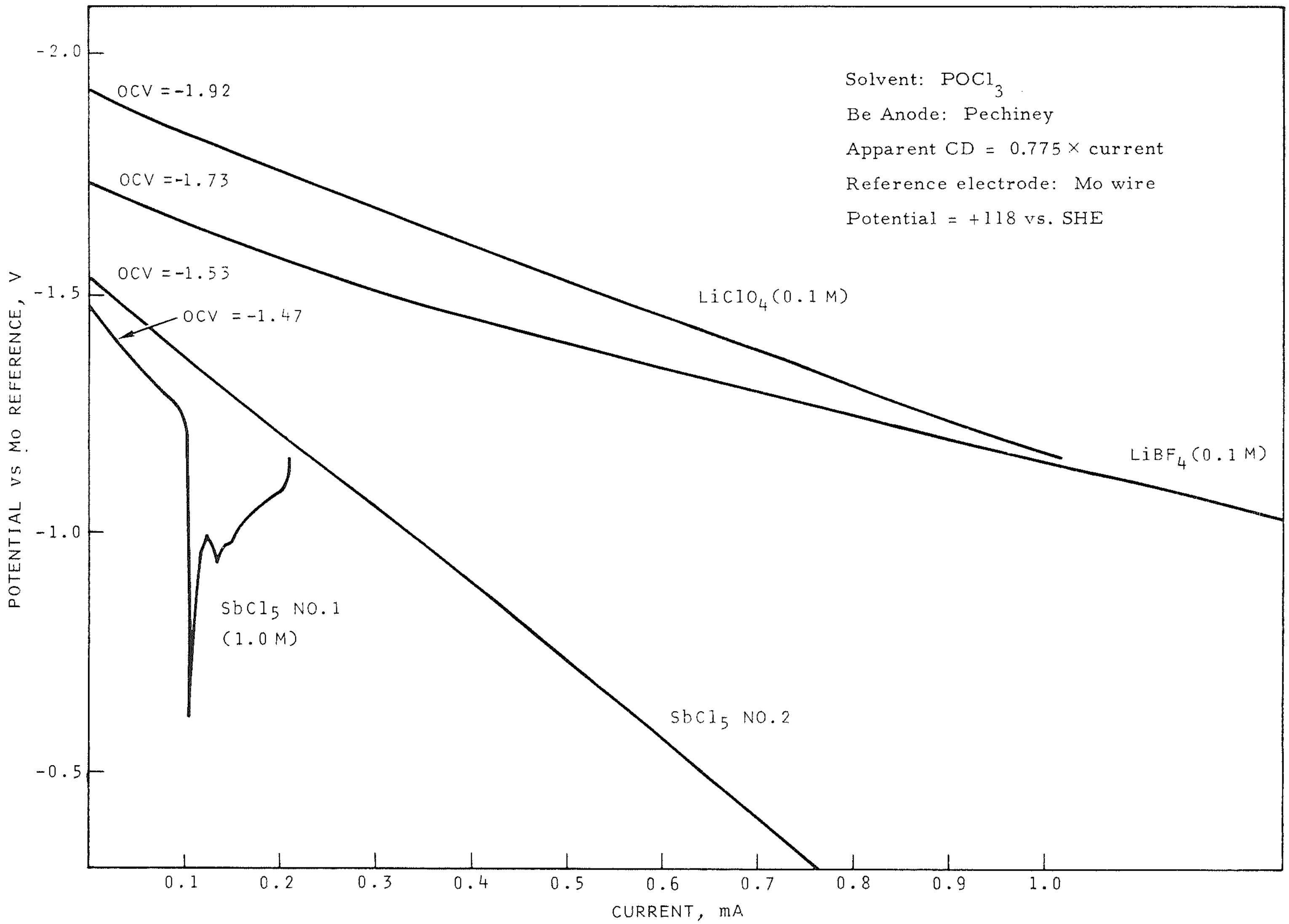

FIG. 14. Electrochemical Polarization Curves of Be in Phosphorus Oxychloride Solutions.

Within the limits of the solvent purification techniques, the inert atmosphere of the drybox system and the handling and cleaning of the Be metal, we are certain that the polarization of the Be anodes is essentially due to phenomena connected with the given solvo-system. However, there remains some small (but finite) possibility that even the very low levels of oxygen and moisture in our systems, as attainable at the present time, may indeed still be too high for one to speak of absolute results. Nevertheless, the results here indicate that the behavior of Be is a function of the solvo-system, and as is noted later, one can actually observe progressive polarization with successive scans of the electrochemical polarization current. Concurrently with the Be anodes, we conducted some experiments with magnesium anodes to compare their performance with that obtained from Be. Along with previous results from Mg in liquid ammonia systems (and via the measured potentials versus the SCE), we could make a direct comparison with theoretical potentials listed by DeBethune (Ref. 23) or Jolly (Ref. 24).

In a 0.5 molal solution of KSCN in liquid ammonia, Mg gives an OCV of -2.06 V, and Be gives -1.53 V, versus the Pb/Pb^+ electrode. Jolly's table of potentials gives a value of -2.02 V for Mg/Mg^{+2} ($a = 1$). Allowing for environmental differences and variations in activity, it is obvious that our Mg/Mg^{+2} potentials are very closely comparable to the theoretical values. Unfortunately, we have no published value for the potential of the Be/Be^{2+} couple in liquid NH_3 solutions. The low potentials for Be in ammonia (later observed for Be in other solvo-systems) led us to believe that Be was not providing the potential expected for it. In the ammonia systems, Be behaved very much like Mg (except for the potential); they both polarized badly in $NaNO_3$ solutions, both gassed under the same cell operating conditions, and both provided their best cell performance in KSCN solutions.

Determination of Reversible Potentials

In some solvents, solutions of $BeCl_2$ were made up and the reversibility of the Be electrode was determined. Generally, solution concentration was attempted at 0.01 M, and diluted to lower concentrations by quantitative additions of the supporting electrolyte solvent mixture. For some solvents, either Pt or glassy carbon was used as the indicator electrode material. A mercury pool electrode was constructed which provided an electrode area of approximately 10 mm^2, but it could not be used with certain solvents (for example, $POCl_3$) due to reactivity. In only a few of the solvo-systems was there any evidence of an electroreduction of the Be species. A comparison of background currents of the supporting electrolyte solutions with those from the same solution, but with added $BeCl_2$, should indicate when the solvo-Be species was electroactive.

In the solvent HMPA no current peaks were observed which would indicate that the reduction of Be was reversible. When a saturated solution of $BeCl_2$ in HMPA was electrolyzed using a Pt indicator electrode, a small amount of the dark blue coloration due to solvated electrons was formed. In this reaction Be shows its similarity to other alkaline earth metals which also are reduced, then reoxidized by reaction with the solvent. However, the Be reaction is very slow and not very extensive. These reactions have been discussed in detail by Normant (Ref. 25) for other active metals.

When a Be anode was used in $POCl_3$ solutions, it behaved as though the freshly cleaned metal surface had a thick coating of some adsorbed material. As the potential was applied, the coating seemed to break, and the current increased suddenly as the polarization was reduced. After each sweep, the coating reformed spontaneously. In all the solutions in $POCl_3$ a bright orange coating formed during anodization, regardless of the supporting electrolyte used. It is, apparently, a reaction product between the solvent and Be metal. These $POCl_3$ solutions required a very high power from the power supply to overcome IR drop. During the electrolysis in $LiClO_4$-$POCl_3$ a white material grew downward from the Be anode disk, forming long dendrites which eventually filled the anode compartment.

Detailed Investigation in Propylene Carbonate

As it turned out, only in solutions of $BeCl_2$ in propylene carbonate (PC) was there any reproducible evidence of reversible electrode reactions of the solvo-Be species. This was a particularly fortuitous circumstance because the paper by Burrows and Kirkland (Ref. 14) appeared at the time this work was in progress and provided a direct comparison of background residual currents and results of solute-solution purification techniques. We were able to duplicate exactly the voltammetry curves these authors have presented for highly purified solutions of $LiClO_4$ in PC. However, our best electrochemical data appeared when we used the Hg pool indicator electrode in PC, although the solid electrodes provided first indications of an electrode reaction of the Be species. The results of the investigations of beryllium electrochemistry in propylene carbonate are given below.

Burrows and Kirkland indicated that interaction of their Pt indicator electrode with lithium deposited from $LiClO_4$-PC resulted in Li-Pt alloy formation which gave peaks on the voltammograms. To prevent these interferences, we used another solute, KPF_6, but with only partial success as noted below. Propylene carbonate used in the present work was purified by distillation after drying over molecular sieves. It did not tarnish freshly cut sodium immersed in it for many hours, and the lithium ribbon used in Li/Li^+-1M $LiClO_4$ reference electrodes did not tarnish over a period of many weeks. In Fig. 15 and 16 are shown the background residual currents for solutions of $LiClO_4$ and KPF_6 in PC, using an Hg pool electrode. Comparing these with the curves published by Burrows and Kirkland provides a clear indication of differences due to indicator electrodes and solutes. From their work (with the Pt electrode) it was evident that the peaks due to Li-Pt alloy formation would be in the same potential region as those we obtained when a beryllium species was present (Fig. 17). In Fig. 18 is shown the voltammogram resulting from a trace addition of $BeCl_2$ in 0.1M KPF_6-PC. Investigations were begun using quantitative solutions of $BeCl_2$ in KPF_6-PC electrolyte solutions. As this work progressed, it became evident that some side reaction was occurring that led to anomalous results.[2] The reaction became evident when a saturated solution of $BeCl_2$ in KPF_6-PC was prepared. A voltammogram from this solution obtained with the Hg pool electrode is shown in Fig. 19. Although the initial scans provided a very symmetrical curve, peak heights proved to be time dependent, and eventually a light gelatinous precipitate separated out of the solution. Analysis indicated the material to be a mixture of $Be(PF_6)_2$ (solvated) and KPF_6. The occurrence of the PF_6^- complex explained an observation seen with Be indicator electrodes in these solutions. When a cyclic scan is applied to the Be, the potential increases to some value (not always reproducible) when the current suddenly increases to overload the amplifiers. One gains the impression that the anodization of the metal results in breaking a film which has formed on the metal when it is immersed in the solution. Since no $BeCl_2$ was initially present, it seems that some species is strongly adsorbed or reacts with the clean Be, and the resulting film requires a high potential to strip it off. No evidence of reversibility of the Be anode itself was found in these solutions, but two anodic peaks are observed, as shown in Fig. 20. When a solution of $LiClO_4$-PC was used and successive scans were made on

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[2] Potentials in the propylene carbonate systems can be compared to the SHE by algebraic addition of the value -2.68 V to the potentials on the figures.

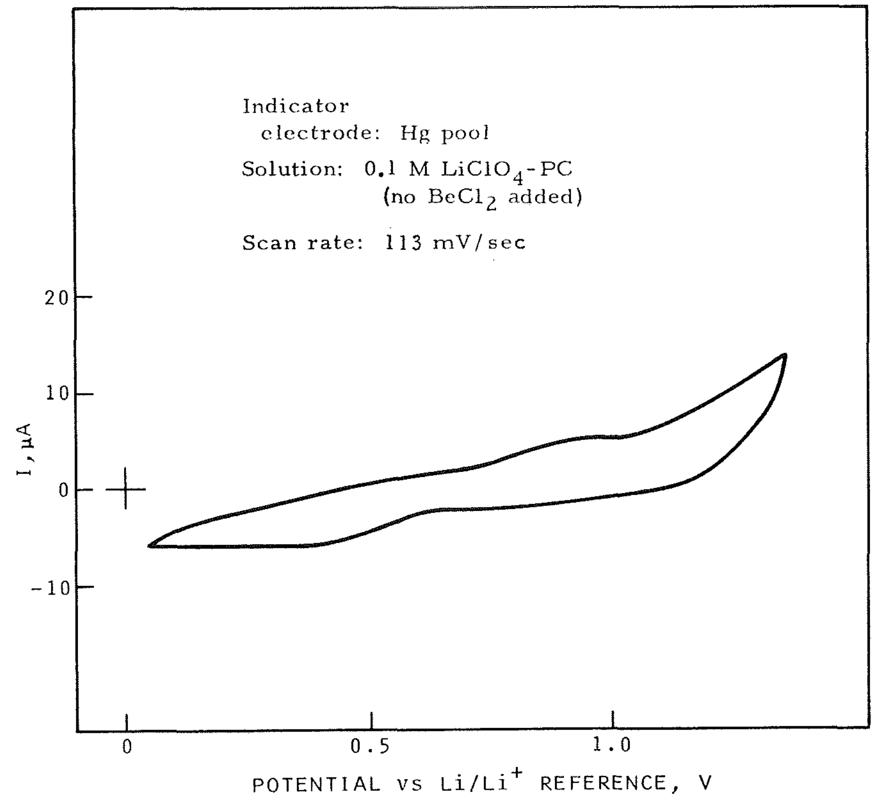

FIG. 15. Background Residual Current for Solution of $LiClO_4$ in Propylene Carbonate on Hg Pool Electrode.

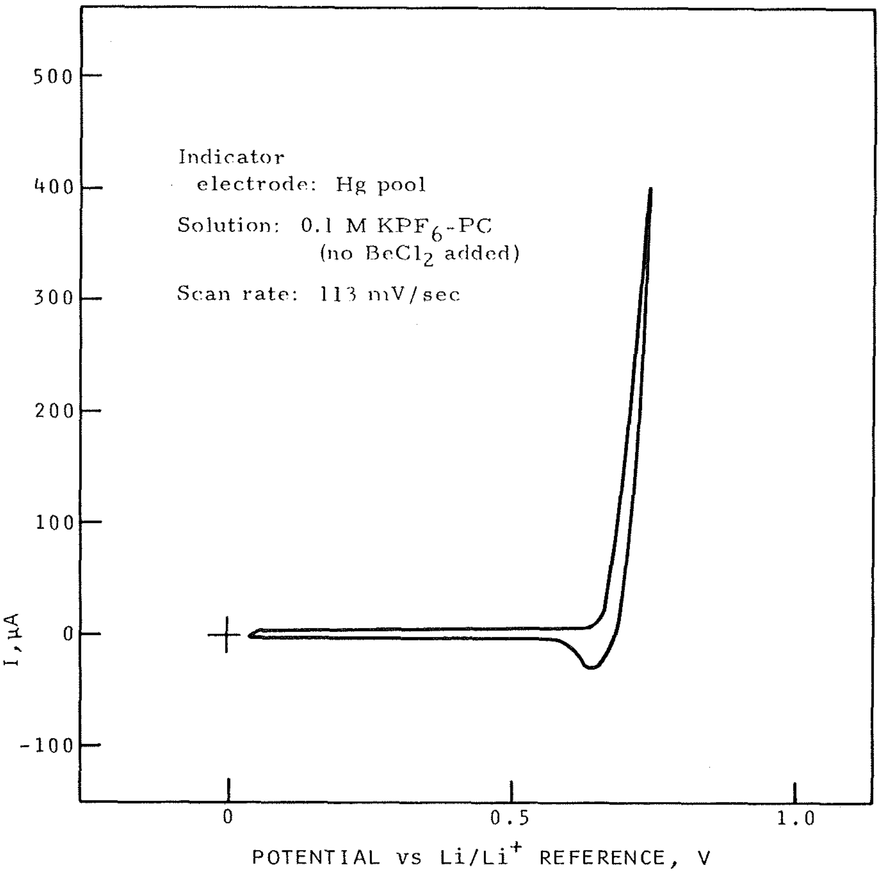

FIG. 16. Background Residual Current for Solutions of KPF_6 in Propylene Carbonate on Hg Pool Electrode.

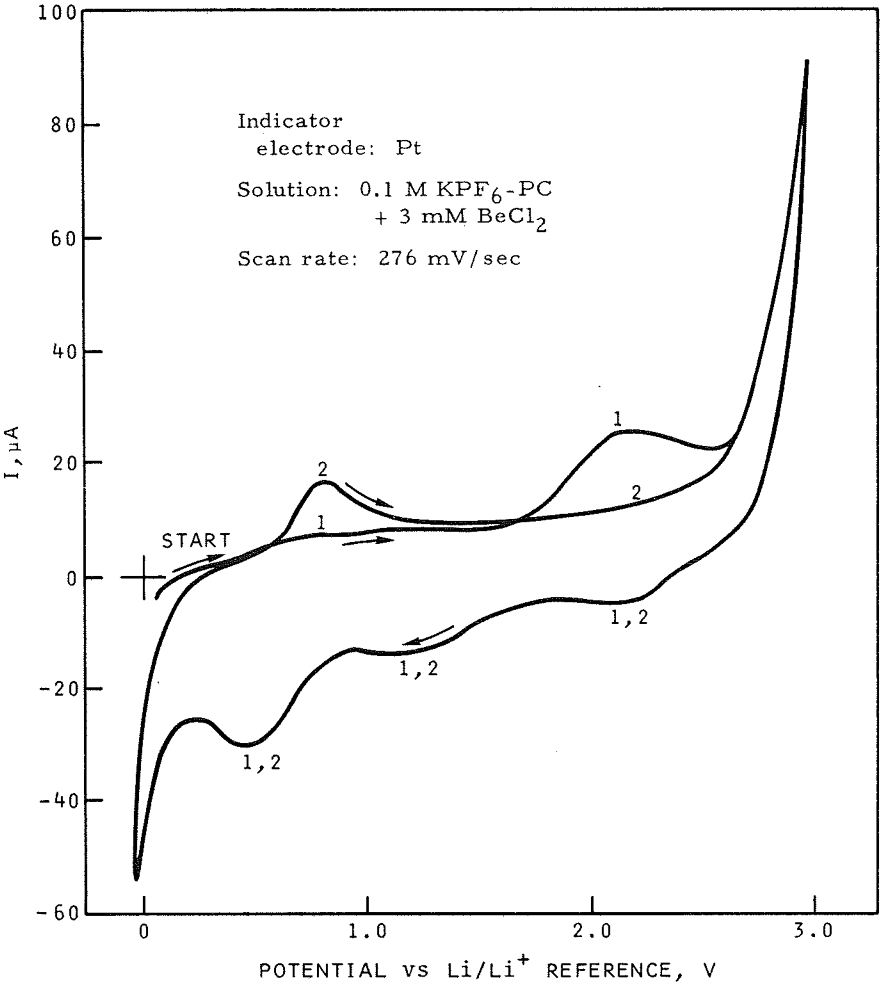

FIG. 17. Voltammogram of Propylene Carbonate Solution with $BeCl_2$ Added, Pt Indicator Electrode.

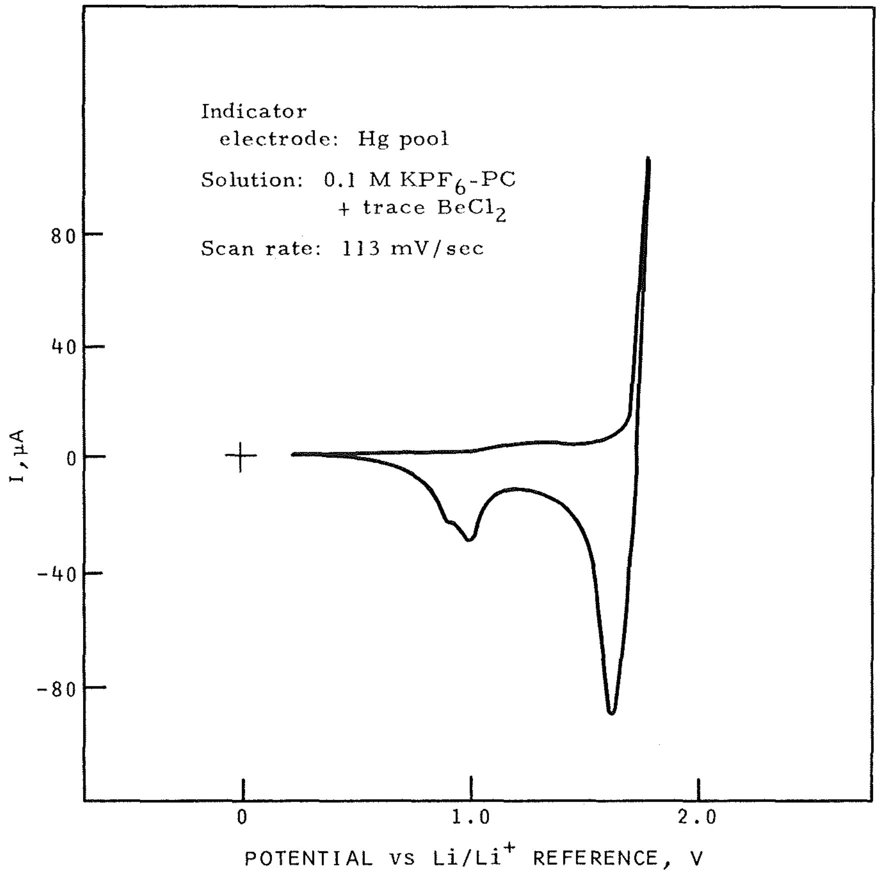

FIG. 18. Voltammogram of Propylene Carbonate Solution with Trace of $BeCl_2$ Added. Compare with background trace, Fig. 16.

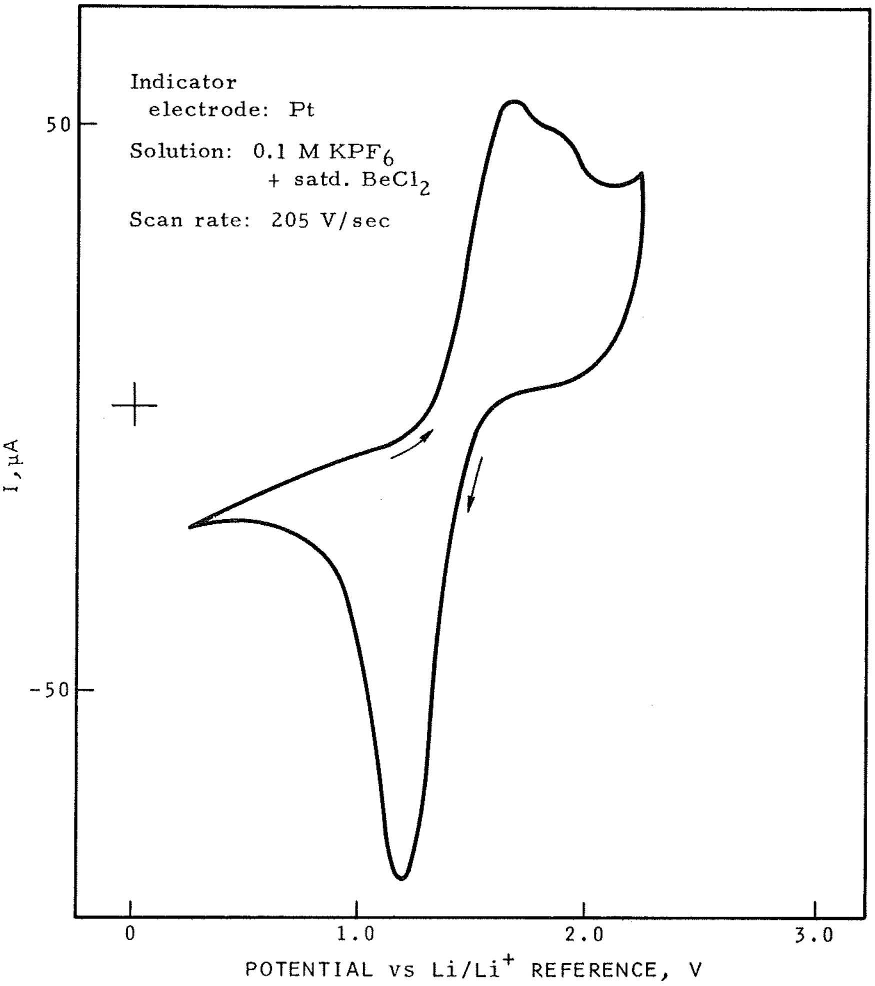

FIG. 19. Voltammogram of Sat'd $BeCl_2$ Solution in KPF_6-PC Using Pt Indicator Electrode.

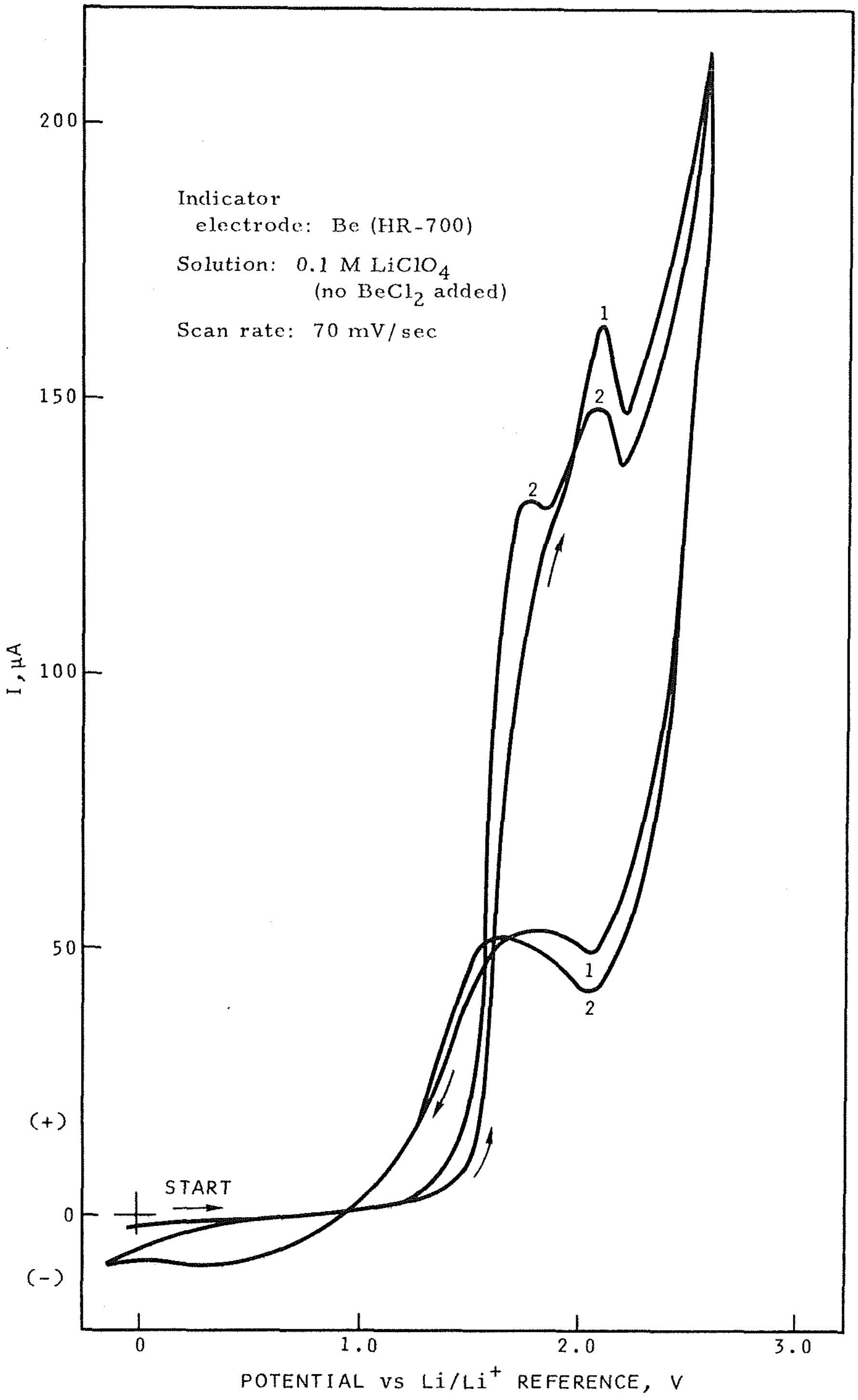

FIG. 20. Voltammograms for Be Indicator Electrode Showing Double Peaks. Numbers indicate Scan 1 and 2.

a freshly cleaned Be anode, the curves of Fig. 21 resulted. These indicate the gradual covering of the Be surface, reducing its effective electroactive area. Note that the current scale here is very high compared to many of the other traces. Although the precipitation of the Be species cut short the investigations in KPF_6-PC solutions, voltammograms taken therein first provided the double peaks on both cathodic and anodic scans. The cathodic peaks are separated by 90 to 120 mV; they show a decreasing peak height difference with increasing scan rate to 113 mV/sec; at higher scan rate the peaks tended toward the same height, though never becoming exactly equal.

In the $LiClO_4$-$BeCl_2$-PC solutions, very different behavior was observed, undoubtedly due to the fact that different species of solvo-Be were present. The effect of varying scan rate and concentration of $BeCl_2$ was studied; scan rates were varied from 14 mV/sec to 276 mV/sec, while the concentrations used were 0.5 mmolar, 1.0 mM, 2.0 mM, 5.0 mM, and 10 mM. Again, it must be emphasized that these are apparent concentrations, as we have no way of determining the dissociation of Be complexes in these solutions. Indeed, it can be stated without reservation that Be ions are present in these solutions only in a solvo-Be(II) species, possibly polymerized. At the lowest concentration it was evident that adsorption effects were determining the electrode behavior, and at scan rates greater than 56 mV/sec the two anodic peaks tended to merge as a plateau, with an E_p of +0.78 mV. Since the anodic peaks will be controlled by the availability for oxidation of deposited Be in the Hg pool, one would expect the peak A-I to be diffusion controlled. The plateau observed at the lowest concentration indicates that not much Be is deposited in the Hg during the period of the faster scan rates.

At a concentration of 1.0 mM, the two cathodic peaks became more pronounced, varying with scan rate in a predictable way. Plots of peak current (I_p) versus the square root of the scan rate ($V^{\frac{1}{2}}$) show that the peaks C-II and A-I are diffusion controlled, while C-I and A-II are not entirely so. Reproducibility was observed at apparent concentrations of 1 mM and above, but peak C-II was also diffusion controlled at 0.5 mM. Occasionally a pre-peak before C-I was observed, disappearing with increased scan rate. This is the behavior expected for an adsorption peak, and it is probable that C-I is partially adsorption and kinetically controlled, as evidenced by $I_p/V^{\frac{1}{2}}$ plots. A typical voltammogram is shown in Fig. 22. Since peaks C-II and A-I were diffusion controlled across all scan rates and at most concentrations used, it is instructive that the ratios of their peak heights were unity for many values of the

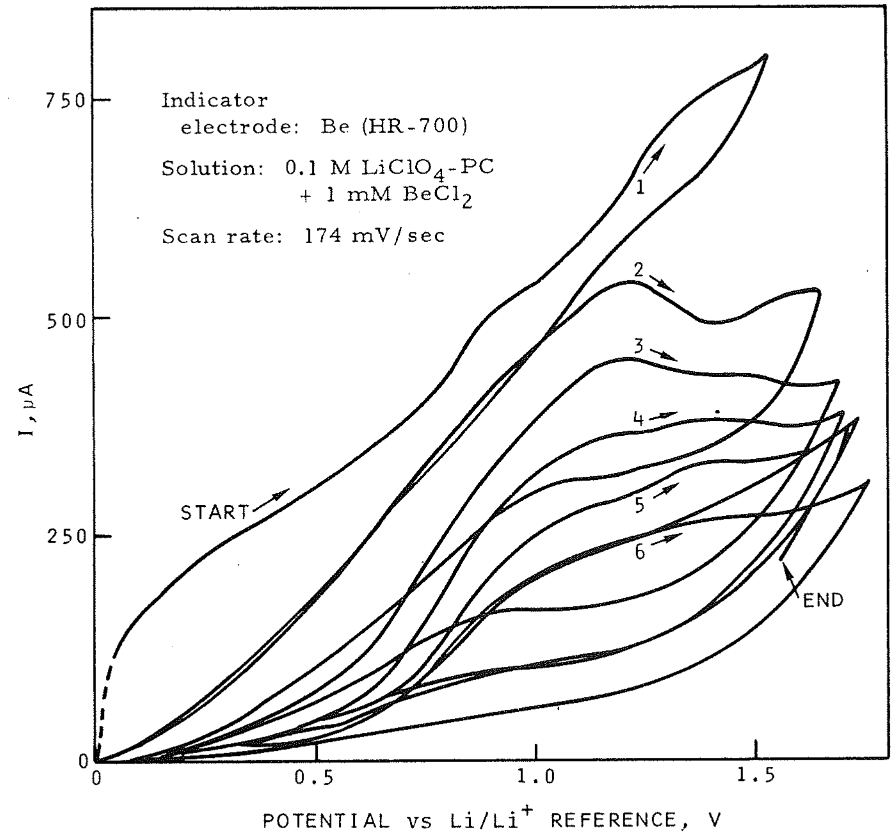

FIG. 21. Multiple Scan Voltammograms on Be Indicator Electrode.

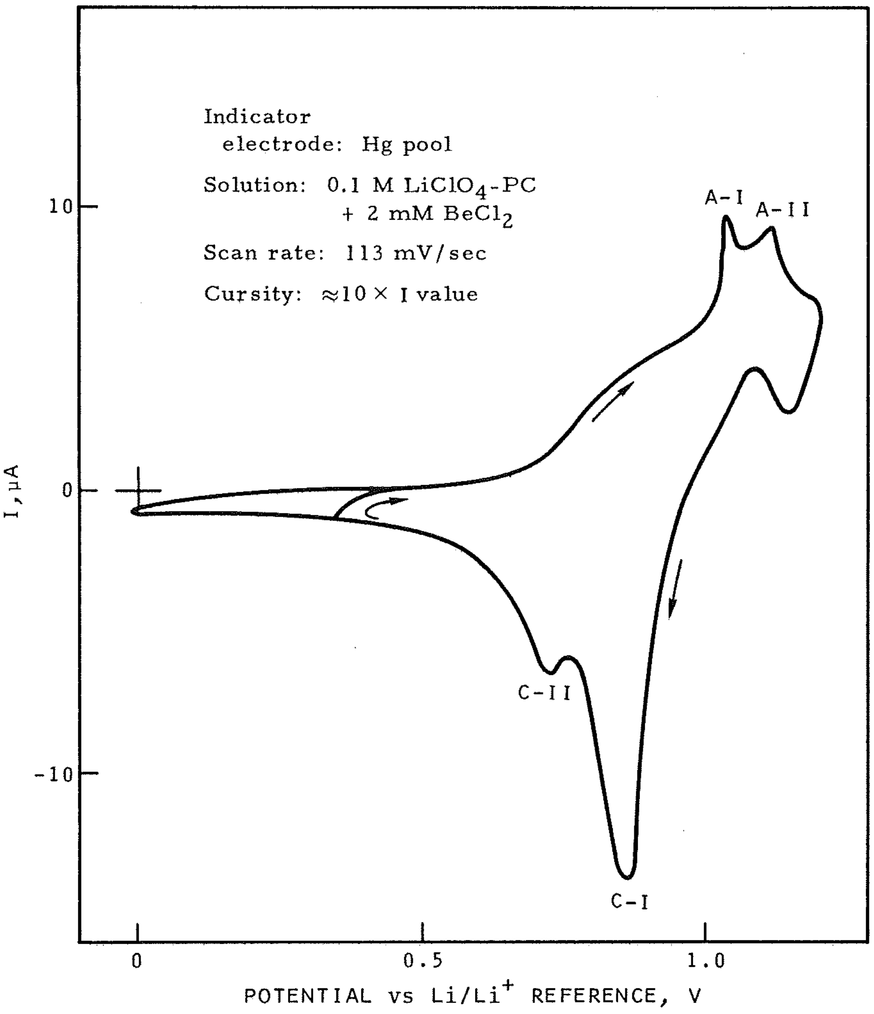

FIG. 22. Typical Voltammogram from $BeCl_2$ Solutions in $LiClO_4$-PC.

concentration and scan rate. This indicates reversibility, but the peak separation of 300 mV is not particularly good; for a one-electron change, one expects a peak separation of 59 mV if exact reversibility is obtained.

In the 5.0 mM $BeCl_2$ solutions the double cathodic and anodic peaks tend to merge, especially at the high scan rates shown in Fig. 23. We have studied the work of Wopschall and Shain (Ref. 26) on the effects of adsorption of electroactive species as well as earlier papers by Nicholson and Shain (Ref. 27 and 28). It is quite apparent that the electroactive Be species is weakly adsorbed; on the cathodic scan, it is reduced in two steps at $E_p = +0.86$ and 0.73, and on the anodic scan is reoxidized in two steps at $E_p = +1.03$ and 1.12. The switching potential is important to observation of these various peaks, since if the anodic switching is done too far positive, irreversible changes may occur, while if done too far cathodic, lithium metal may co-deposit.

An interpretation of the double cathodic peaks narrows down to a few possible explanations for the observed behavior. Shirvington, Florence, and Harle (Ref. 29) have postulated that their observed polarographic steps and presteps may be due to reduction of hydrogen halides formed when beryllium halides are solvolyzed by residual water in acetonitrile solutions. However, they were unable to obtain sufficient evidence to prove this postulate conclusively. A recent publication on the analytical chemistry of beryllium discloses that this element can be reduced polarographically on the dropping mercury electrode in acid aqueous medium with 0.5 M LiCl as the supporting electrolyte (Ref. 30). Two waves at $E_{\frac{1}{2}}$ - -1.79 and -2.00 V (vs SCE) are obtained (Ref. 31). At pH 3.3 and below, the diffusion current at the first stage of the reduction remains proportional to the concentration of beryllium in solution up to 8.0×10^{-3} molar. This reduction involves a hydrolysis reaction, which would not occur in our nonaqueous systems, but formation of some other complex could take place. A more plausible explanation of our double peaks is the formation of a lower oxidation state of beryllium.

It has been long known that Be(I) can be formed (even in aqueous solution), and it disproportionates, forming Be metal and the aquo-Be(II) species. This reaction, observed by Laughlin, Kleinberg, and Davidson (Ref. 32), has been studied in the present series of investigations as outlined below. Much earlier, in 1926, Bodforss (Ref. 3) suggested that the observed potentials of beryllium were due to the reaction

$$Be \rightarrow (Be)_2^{+2} + 2e^- \qquad (1)$$

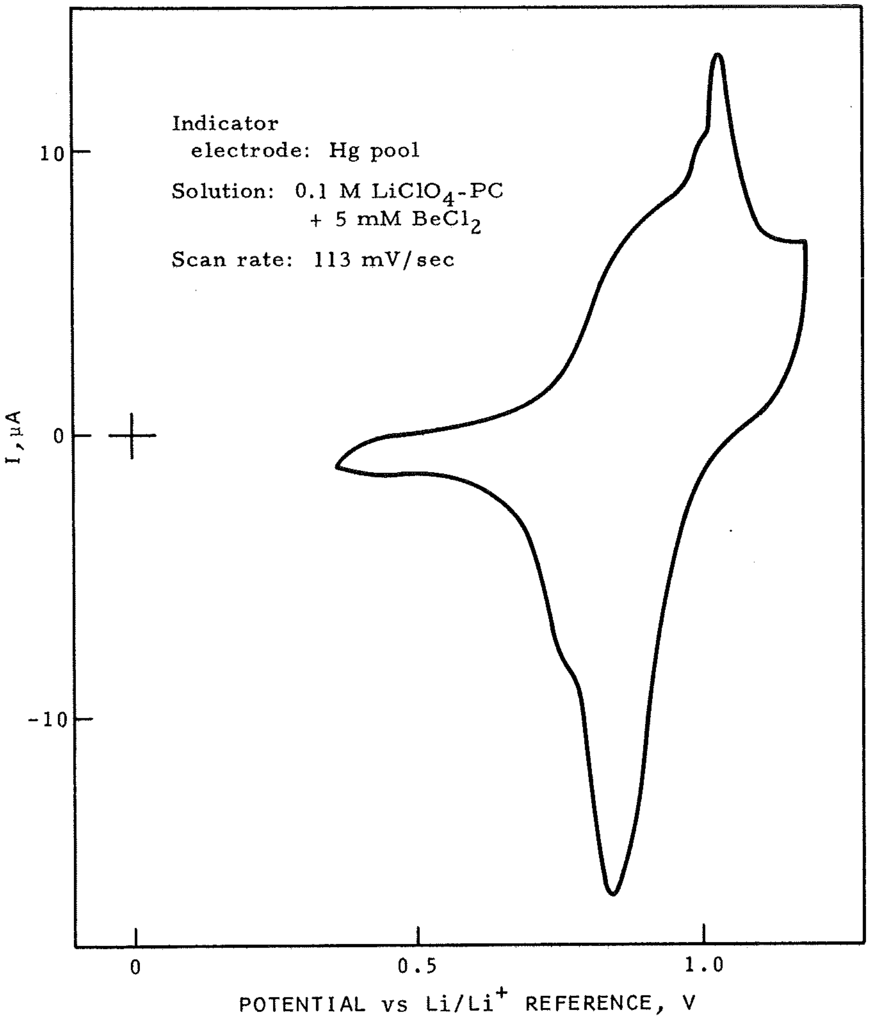

FIG. 23. Voltammogram of $BeCl_2$ in $LiClO_4$-PC.

In the present research, if the peak C-I is due to the formation of Be(I) [or $(Be\text{-}Be)^{+2}$] during the cathodic scan, and this species disproportionates, then the second cathodic peak, C-II, should have a lower peak height. As the scan rate is increased, barring complications due to other phenomena, the peak height difference of the two cathodic peaks should become less. These relationships have been observed in the present investigations, for at low scan rates the peak height difference is greatest, lessening as the scan rate increased. The disproportionation reaction and the proposed electrochemical reactions in PC are given in the following equations:

$$Be(II) + e^- \rightarrow Be(I) \qquad E = 0.86^* \qquad (2)$$

$$2\ Be(I) \rightarrow Be^o + Be(II) \qquad (3)$$

$$Be(I) + e^- \rightarrow Be^o \qquad E = +0.73^* \qquad (4)$$

*Versus Li/Li^+.

Equation 2 is the first electrochemical reduction and is followed by the disproportionation reaction, Eq. 3. The final reduction of unreacted Be(I) to Be metal takes place by the second electrochemical reaction, Eq. 4. The disproportionation reaction takes place relatively slowly, and from the voltammetry data one can calculate a half-time for the reaction. At a scan rate of 113 mV/sec, cathodic peak separation is 0.12 to 0.14 V, and the peak heights are in the ratio of 2:1, indicating that half of the Be(I) species is not available for the reduction to the metal. From these data one obtains the value of $t_{\frac{1}{2}} = 1.3$ seconds; calculations from other scan rate peak height values fall in the same order. If the disproportionation reaction is first order, then the rate constant would be $K = 0.693/t_{\frac{1}{2}} = 0.53\ sec^{-1}$ in the present circumstances. Although investigations have been conducted across a limited range of concentrations, the double peaks have been a distinctive feature of all the curves; at the least, an inflection is always observed.

One immediate ramification of the disproportionation reaction appears in consideration of the numerous attempts to deposit beryllium metal summarized by Brenner (Ref. 33). On solid substrates the effect would be to produce random nuclei over the electrode surface. The resulting deposit would be powdery and incoherent, since the metal atoms would be depositing not at the most optimum sites for crystal growth (i.e., at step or screw dislocations) but randomly depending on the time between formation of the $(Be\text{-}Be)^{+2}$ species and its disproportionation.

Following the voltammetric studies in PC, we attempted to prepare more concentrated amalgams of Be. Electrolysis of a saturated solution of $BeCl_2$ in $LiClO_4$-PC was conducted for a period of 24-36 hours. Current between the Hg pool electrode and the Pt counter electrode was about 5 mA. Potential was +1.0 V with respect to the Li/Li^+ reference electrode. Although an amalgam was formed during this period, it proved to be not very concentrated. Analysis, done by a contractor, showed only 0.055% Be present, thus confirming, in a nonaqueous solvent, the 1926 observation of Bodforss (Ref. 3) that Be does not form amalgams to any great extent.

Investigation of Anodic Dissolution of Be

Following the experimentation described above, we duplicated the investigations of Laughlin, Kleinberg, and Davidson (Ref. 32) by strongly anodizing a Be strip in saturated NaCl, aq. However, we monitored the potential and pH during the several hours of the experiment, and observed substantial changes in pH. Laughlin, et al., reported values of pH = 6 initially, going to pH = 5 at the end. The present cell was run in a water jacketed 3-compartment cell thermostatted at 25°C. The cell assembly shown in Fig. 24 included a Pt disk counter electrode and a Saturated Calomel Electrode (SCE). Initial OCV was -1.11 V versus the SCE (-0.87 vs SHE). Current was passed through the Be and the counter electrode, and the potential between the Be and the SCE was monitored via a General Radio Model 1230 A Electrometer amplifier and recorded on a stripchart. The pH of the compartment holding the Be anode strip was checked periodically with a Beckman Model G pH meter connected to the SCE and a glass electrode in the anode compartment. Current passed was about 27 mA/cm^2 on the Be strip, and the cell was operated for several hours. The photograph shows the cell appearance after the powdered Be had formed heavily in the anode compartment, within the first hour of operation. The first grayness was observed forming throughout the cell within a few minutes of starting the cell current. Initial pH was about 6; within 18 minutes it had dropped to 3.35; at the end of the first hour it was at 2.85. After the end of four hours the pH level was stabilized at around 2.2 to 2.3, holding that level for the duration of the run. All the observations of the previous authors during the cell operation were confirmed; additionally, we found that the polarization of the Be strip was not very great; the potential dropped to -1.04 V with passage of 27 mA/cm^2. Later in the run, the polarization became much greater, requiring higher potential from the power supply to maintain the current at this density. The final OCV was -1.11V; the Be metal powder had become somewhat flocculent.

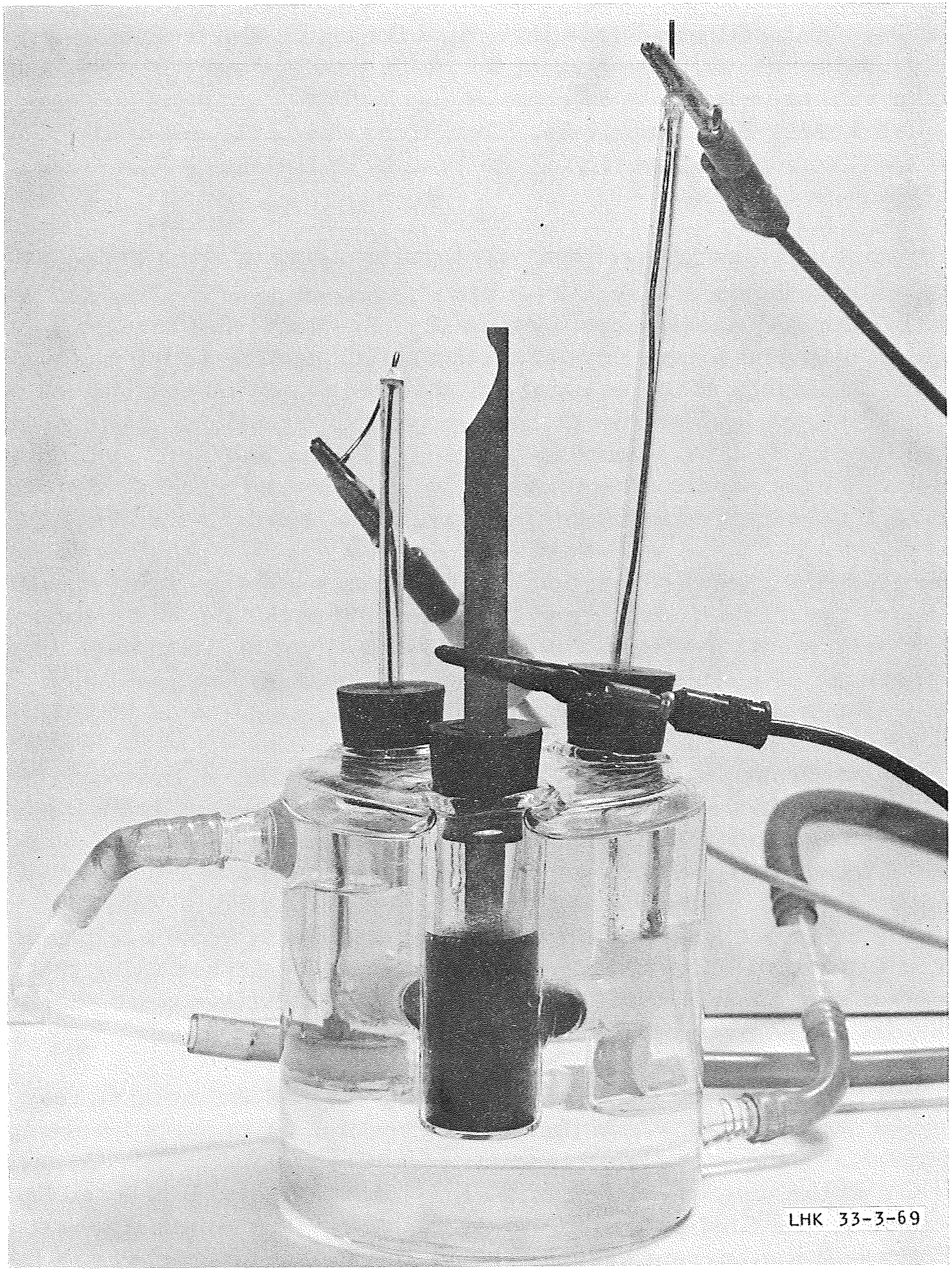

FIG. 24. Water-Jacketed Cell, Showing Be Metal Formation During Disproportionation of Aquo-(Be-Be)$^{+2}$ Species.

It is instructive that if one corrects the above potential to the SHE scale, the resulting potential is -0.87 V. This value is comparable to values obtained by previous investigators on Be electrochemistry in aqueous solutions. Samples of the black product were filtered and washed with acetylacetone to remove any $Be(OH)_2$, then subjected to Debye-Scherrer X-ray analysis. Only lines due to Be metal or BeO (hydrated) were found, verifying the results of Laughlin, Kleinberg, and Davidson (Ref. 32).

Straumanis and Mathis (Ref. 34) have objected to the disproportionation hypothesis of Laughlin et al. on various grounds, but fail to note that the Be^+ species are undoubtedly $(Be-Be)^{2+}$ and that the powdery Be metal forms throughout the solution. The latter observation and the highly reducing nature of the clear solution can only be explained on the basis of the disproportionation reaction. As this report was in its final editing an article by Sheth, Johnson, and James appeared on the anodic dissolution of Be in aqueous solutions (Ref. 35). Apparently the type of anion present largely determines the reaction mechanism, but these authors did not explain why fine grey particles of Be suddenly appear throughout the solution, except to suggest that chunks of the metal dislodge and float away from the Be anode surface. The flowing electrolyte experiments of Laughlin et al. definitely show the presence of a strong reducing agent, most likely the $(Be-Be)^{+2}$ entity. Further investigations on the latter question should be conducted.

Following the investigations in the aqueous cells, solutions in nonaqueous solvents were subjected to electrolysis with beryllium anodes. We wanted to determine if the disproportionation reaction could be carried out extensively in such media with the formation of black, unoxidized Be powder. Solvents and solutes used are listed in Table V. Except for the pressurized ammonia cells and the ammonia cells operated at 223 K, all other cells were operated in the drybox using the 3-compartment cell fixture previously shown. Solutions were prepared in the drybox as previously described.

The table lists the OCV for the freshly cleaned Be metal in the different solvo-systems. In these experiments, as in those involving voltammetry, the true concentrations of $BeCl_2$ are unknown. However, the OCV of the metal has been singularly reproducible; in the cells of this series, the final potential was within 10 mV of the initial potential. In every cell the current passed through the Be anode strip was in the range of 25-30 mA/cm^2.

TABLE V
SOLVENT SYSTEMS USED IN BERYLLIUM DISPROPORTIONATION REACTION INVESTIGATIONS

Solution system and conditions	OCV vs SHE
HMPA-$LiClO_4$ (0.1 M)	-0.87
PC-$LiClO_4$ (0.1 M)	-1.3
NH_3-NaCl (0.5 M) pressure cell	-1.19 vs SHE/NH_3
NH_3-$LiNO_3$ (11 molal) 3 comp. cell	-1.14 vs SHE/NH_3
NH_3-NaCl (sat'd), 223 K	-0.76
CH_3CN-$LiClO_4$ (0.5 M)	-0.70
CH_3CN-LiCl (sat'd)	-0.70
MeOH-NaCl (sat'd)	-1.02
DMSO-$KClO_4$ (1.0 M)	-0.76
Pyridine-LiCl (nearly sat'd)	-0.80
$POCl_3$-LiCl (sat'd)	-0.74

Of the cells operated in this experimentation, only those in acetonitrile and methanol provided any direct evidence for the disproportionation reaction of the oxidized Be species, $(Be-Be)^{+2}$. This does not imply that the Be(I) species does not form in other solvo-systems, but that the disproportionation reaction has not been observed. In the other solutions, there may indeed be a rapid formation and disappearance of the Be(I) species before it can be observed to disproportionate. In CH_3CN and CH_3OH finely divided metal could be seen forming in the bulk of the solution, as was observed in the aqueous cells, but the extent of the metal formation was far less in nonaqueous than in aqueous cells. We had hoped that the PC solution would lend itself to this reaction, but no very active cell reaction was observed beyond formation of a few bubbles on the Be. In spite of the lack of widespread Be metal formation, some of the experiments indicated that the metal was oxidizing to the Be(I) species, as the strip Be gradually accumulated a bulky, powdery formation of the Be metal. This indicated that the strip Be was oxidized to the $(Be-Be)^{+2}$, which quickly disproportionated to the powdery form of the metal and the solvo-Be^{+2} species. In some of the solutions a precipitate formed in the cell compartment as the solvo-Be^{+2}

species were complexing with the other species present in the solution. This was especially noticeable in the methanol, acetonitrile, NH_3-NaCl (pressure cell), NH_3-$LiNO_3$ (drybox cell). In the cases where a chloride was used as the supporting electrolyte, one would expect $BeCl_2$ to form and separate out if a strong anodic reaction oxidizes the Be. In the cells in NH_3, there was gassing at the anode, indicating that oxidation of NH_3 to N_2 occurs in preference to the oxidation of Be metal. In these cells, at the cathode, copious amounts of solvated electrons formed, some of which eventually migrated throughout the cell compartments.

In those solutions in which a small amount of fine Be metal formed, it could be seen with the aid of a low power microscope, and in the acetonitrile there appeared to be a complex forming between the nitrile and the Be^{+2} species. Nitrile complexes have a typical formula $BeCl_2 \cdot 2\ NCCH_3$ and are mentioned by Everest (Ref. 36). In methanol, Be forms a similar complex; only in ammonia and certain amines does the complex have the formula $BeCl_2 \cdot 4NH_3$. Beryllium is tetra-coordinated, never hexa-coordinated, by virtue of there being no 3d orbitals available which are required for sp^3d^2 hybrid bond formation. Some amine compounds with 6 and 12 molecules of NH_3 must have a polymeric structure.

In reviewing these experiments, it is apparent that the copious formation of $(Be-Be)^{+2}$ species in aqueous solution must be a direct result of that environment, as compared to the nonaqueous one. In the presence of a solvent, the Be surface atoms with their unbalanced forces can strongly coordinate the solvent, causing a selective orientation of the solvent molecules with their negative poles toward the Be atoms. When a charge transfer takes place at a given metal atom, the solvent tends to bind closely to the (now ionic) species, separating it from the bulk of the metal. The water molecules, being small and much more closely packed than any other solvent, can then form a complete solvation sheath around the $(Be-Be)^{+2}$ moieties, allowing their migration through the double layer out into the bulk of the solution. Admittedly, it is difficult to visualize these various steps, but it is certain that the high charge on the very small Be ion is the determining factor in these reactions, as it is in so many of the other reactions of this element.

In retrospect, the results of these investigations add to the evidence that beryllium is the most strongly solvated of all the metal ions in solution. This is the ordering effect mentioned by Gurney (Ref. 8), in which the Be ions so strongly polarize the solvent water molecules that any protons are repelled and, sooner or later, thermal agitation will transfer the protons to a more distant molecule. From the standpoint of the theory of hard and soft acids and bases (Pearson, Ref. 37), Be must be considered as the hardest acid of the metallic elements, although these are usually considered as soft acids. Additionally, its divalent ions must be the hardest acids in this group. The melting point of Be, the highest of the light weight elements (1284°C), is indicative of the strength of the intermetallic bonds of the metal. Were it not for the high solvation energy of the beryllium ions, it is doubtful that it could be readily ionized by anodization. This is because the rupture of the intermetallic bonds requires a large activation energy, which must be provided from some source.

Finally, with a solid metal such as Be, which is hexagonal close-packed, the small atomic radius results in a high degree of surface energy and charge on the metal. The growth of a crystal can occur at only a few sites which are energetically favorable, and there must be different rates of transfer of ions at the various sites, depending on the site orientation. Under the circumstances, the exchange current of Be must be very low, as indicated by the data from the voltammetric investigations. Overall, within the limits imposed by its orbital configuration, beryllium tends to be more like a transition metal in its chemical and physical behavior than like an alkali or alkaline earth metal.

In recent years, the adsorption phenomena of solid electrodes have been studied very extensively. Considering factors such as the highly charged Be metal surface, ordering effects on the solvent and solute molecules, and the resulting solvolysis reactions mentioned above, it is not surprising that, thermodynamics notwithstanding, the electrochemistry of beryllium is adsorption and kinetically controlled, probably to a greater extent than that of any other metal.

CONCLUSIONS

Investigations were conducted on the electrochemistry of beryllium using 11 nonaqueous ionizing solvents covering the range of Lewis acid-neutral-basic types. Solutes were generally $LiClO_4$, KPF_6, LiCl, or specialized compounds determined by the solvent used, i.e., $SbCl_5$ in $POCl_3$. Determination of open circuit potentials and polarization curves in the various systems indicated that the potentials observed were not approaching the thermodynamically predicted level of -1.85 V. In neutral nonaqueous electrolytes, the Be potentials were on the order of -0.75 to -0.88 V (vs the standard H_2 electrode); these values are comparable to potentials observed in aqueous systems for the Be/Be(II) couple, depending on the anion of the system. Using a mercury pool electrode, the reversibility of the Be/Be(II) couple in nonaqueous solutions was determined. No very reproducible reversible peaks were obtained in other solvents than propylene carbonate (PC). Two reduction and two oxidation peaks were observed for $BeCl_2$ dissolved in $LiClO_4$-PC. Redox potentials of $BeCl_2$ on Hg were at more negative potentials than the oxidation of Be disks observed in the polarization experiments and in cyclic voltammetry scans. For example, from a dilute Be-Hg amalgam pool electrode oxidation peaks are observed in a 1 millimolar $BeCl_2$ solution at -1.56 and -1.65 V (vs SHE), while a Be disk electrode oxidized at -0.70 to -1.00 V. Chemisorption of species from the solution inhibits the Be electrode surfaces, since many investigations indicated the formation of a film on the freshly cleaned metal surface which was not readily removed. Multiple potential scans on a freshly stripped, anhydrous, oxygen-free Be metal surface caused a rapid progressive polarization of the electrode, due to the coverage of the surface by the solvated Be reaction products.

The exchange current is low, and the activation energy to remove the Be atoms from the solid metal is high, as predicted by the high melting point of the metal, 1284°C. Typical potential values obtained are those from $LiClO_4$-acetonitrile solutions. The open circuit potential was -1.44 V; at 1 mA/cm^2 current the potential was -1.18 V. Potentials are versus the Ag/Ag^+ reference electrode and may be converted to the standard H_2 scale by algebraic addition of +0.56 V.

Since voltammetry experiments had indicated that the double peaks were due to a two-step reduction of the solvo-Be^{+2} species, investigations were conducted to verify the previously reported production of a Be(I) species in aqueous solution. This reaction takes place via a disproportionation of the probable entity, solvo-$(Be-Be)^{+2}$, producing Be metal and a solvo-Be(II) species. We found that the same reaction occurs in several nonaqueous solvent systems.

In this reaction the oxidation of Be metal apparently occurs through the formation of the solvo-Be_2^{+2} species, which then diffuses away from the electrode reaction site, out into the bulk solution. It then spontaneously disproportionates, forming finely divided Be metal throughout the solution. This confirms a postulate by an early beryllium investigator of the stabilized existence of a mono-valent Be species for nonaqueous, as well as aqueous, systems.

The occurrence of the disproportionation reaction may explain why all previous attempts to deposit adherent Be coatings from nonaqueous solutions have been fruitless. The reaction results in powdery deposits which occur randomly over the electrode surface, and not at the optimum growth sites for continuous deposits.

Principal factors in beryllium electrochemistry may be summarized as follows:

1. Freshly cleaned Be metal strongly chemisorbs available species and is inhibited in subsequent electrode reactions.

2. Be metal oxidizes at a much lower potential (-0.88 V) than that predicted by thermodynamics (-1.85 V); this is apparently due to the formation of a Be(I) species, solvo-$(Be-Be)^{+2}$.

3. Be metal forms only dilute amalgams, of approximately 0.05% Be concentration.

4. The behavior of Be^{+2} species in solution is governed by its high charge to radius ratio. It is the most highly solvated bivalent ion, and has a strong orienting effect on solvent molecules. It forms polynuclear species to achieve stable configurations.

5. Monovalent Be species $(Be-Be)^{+2}$ form readily and disproportionate, forming powdery Be metal and solvo-Be^{+2}. This reaction explains the lack of success in producing massive Be deposits.

6. Be electrode reversibility is essentially nil; highly solvated and polynuclear species, chemisorption on Be metal surfaces, very low Be concentration in Hg, and Be_2^{+2} disproportionation drastically complicate the electrochemistry of this element in both aqueous and nonaqueous systems.

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