Electrochemical Reduction of Titanium in Nonaqueous Solvents

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Report of Investigations 9592

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By P. L. Sibrell

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ILLUSTRATIONS

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT			
A	ampere	nA	nanoampere
cm^2	square centimeter	pct	percent
h	hour	ppm	part per million
M	molar concentration	s	second
mA	milliampere	V	volt
mm	millimeter	°C	degree Celsius
mV	millivolt			

ELECTROCHEMICAL REDUCTION OF TITANIUM IN NONAQUEOUS SOLVENTS

By P. L. Sibrell[1]

ABSTRACT

Electrorefining of Ti in nonaqueous solvents has been studied by the U.S. Bureau of Mines as a method for recycling impure scrap Ti. Electrochemical behavior of Ti species was investigated using cyclic voltammetry. Research results showed that Ti metal can be dissolved in polar solvents such as dimethylformamide or dimethyl sulfoxide. However, deposition of Ti from these solvents was not successful. Several solvent systems were investigated for electrodeposition of Ti but no deposits were obtained. Reduction of Ti^{4+} complexes to Ti^{3+} proved to be straightforward, but reduction to lower oxidation states could not be confirmed. In dimethylformamide solutions, cyclic voltammetry results demonstrated the reduction of Ti to an oxidation state of less than three, but no Ti metal was identified. In dimethyl sulfoxide solutions containing LiCl, it was possible to deposit Li metal. After adding Ti salts to the solution, electrolysis quickly passivated the electrode. Deposition of Ti was also investigated in solutions of dimethoxyethane and propylene carbonate but, again, no reduction of Ti to oxidation states of less than three occurred. Therefore, the prospects for a nonaqueous electrorefining system for Ti metal do not appear promising.

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INTRODUCTION

Titanium is a light, strong metal used primarily in the aerospace industry. In 1991, the last year for which data was available, U.S. production of Ti metal was 13,000 tons from two plants (1).[2] Currently, Ti is produced by chemical reduction of titanium tetrachloride ($TiCl_4$) with Na or Mg under an inert atmosphere in sealed vessels. Titanium sponge metal produced in this operation is commonly remelted in an arc or electron beam furnace to produce Ti ingot for further processing. The affinity of Ti for O_2 and other atmospheric gases at elevated temperatures necessitates the use of inert atmospheres at all stages of production, which contributes significantly to the cost of finished mill products.

Most end-use Ti pieces are fabricated by machining of bulk forgings, leading to a high rate of scrap production. In some applications, as much as 90 pct of the original forging weight is removed by machining to produce the finished product. Much of the scrap generated during the finishing process is too contaminated for recycling, and is disposed of by landfilling. This represents an enormous waste of a highly energy intensive resource. If a method could be developed to recycle contaminated Ti scrap, significant reductions in the price of Ti parts should occur. In this paper, electrochemical refining of scrap Ti at room temperature in organic solvents was investigated. The Bureau of Mines investigated this technology as a means of recycling Ti alloys, which would conserve raw materials and energy, while also decreasing the nation's waste material burden.

Literature Survey

In electrorefining, impure metal is anodically dissolved, leaving behind more noble impurities as a solid residue, and pure metal is deposited on the cathode, leaving less noble impurities in solution. This technique is applied on an industrial scale for Cu purification (2).

Pourbaix (3) gives the standard potentials ($E°$) for the stepwise reduction of Ti in aqueous solutions as follows:

$$TiO^{2+} + 2H^+ + e^- = Ti^{3+} + H_2O \qquad E° = 0.100 \text{ V}$$

$$Ti^{3+} + e^- = Ti^{2+} \qquad E° = -0.368 \text{ V}$$

$$Ti^{2+} + 2e^- = Ti \qquad E° = -1.63 \text{ V}$$
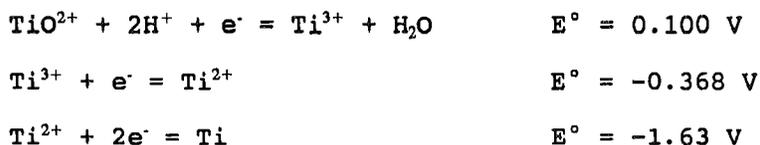
However, others have questioned the above value for the reduction of Ti^{3+} to Ti^{2+}, suggesting that a potential of -2.3 V is more accurate (4). The value given for the reduction of Ti^{2+} to metal is calculated based on the potential for the reduction of TiO^{2+} directly to Ti metal, which can be calculated from the free energies of the reactants and products. Ti^{2+} is unstable in aqueous solutions, so a direct measurement is not possible. Because of solvation and complexation effects, potentials for Ti reduction in nonaqueous solvents may be very different. In addition, kinetic limitations often further increase overvoltages required to obtain appreciable reaction rates.

In any case, the potential required for Ti deposition exceeds the stability of water, making it impossible to deposit Ti metal from aqueous solution. Researchers at many laboratories, including the U.S. Bureau of Mines (5) and Dow-Howmet (6), have shown that molten salt reduction of Ti is technically feasible. However, these processes have not proven to be economic at current Ti prices.

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[2]Italic numbers in parentheses refer to items in the list of references at the end of this report.

Although nonaqueous solvents are commercially used in the electrochemical production of organic chemicals, few if any inorganic products are manufactured in this way. Mann has outlined many of the more common solvents used for electrochemical processing (7). Jayasekera and others demonstrated deposition of Ag on a laboratory scale from dimethyl sulfoxide (DMSO) (8). Morisaki and others investigated metal deposition from DMSO solutions (9). Metals more active than Zn such as Mg and Al could not be deposited. Gregory and others investigated deposition of Mg from organic electrolytes (10). These researchers had no success with inorganic Mg salts, but were able to produce a high purity, adherent deposit using organomagnesium halides. Lithium deposition has been investigated extensively for use in high-energy-density batteries because of its high electromotive potential (11). Solvent systems investigated for Li deposition include cyclic esters and ethers such as propylene carbonate and tetrahydrofuran, respectively. Lithium metal deposition has been documented in these systems, but repeated cycling of deposition and redissolution, as would be required in a rechargeable battery application, has not been satisfactorily demonstrated.

The topic of Ti reduction in organic solvents has been investigated in the past, but no successful systems have emerged. Reid and others tested over fifty different solvent/electrolyte systems for Ti reduction using Ti halides (12). They concluded that electrodeposition of Ti from halide solutions is not feasible. An Al-Ti alloy containing up to 6 pct Ti was produced from an ether solution of Ti and Al hydrides. Kolthoff and Thomas investigated the electroreduction of Ti halides in acetonitrile (AN) by polarographic methods, and claimed that reduction of Ti^{4+} to $Ti(0)$ had taken place at the mercury working electrode (13). Franklin and Seklemian concluded that Ti^{2+} was not stable in AN and, therefore, disproportionated to metal and Ti^{3+} (14). Studies of Ti reduction in DMSO were undertaken by Fanti and Marschoff (15). These investigators claimed that Ti deposition had occurred, but did not produce a verifiable amount of metal. Further investigations by members of this group indicated that the Ti was present as $TiCl(DMSO)_2^{3+}$ in solution (16). Several papers on the topic of Ti reduction have originated in eastern Europe. Koneska and others investigated the reduction of Ti halides in dimethylformamide (DMF) and DMSO and the possibility of electrorefining Ti in DMF (17). No Ti deposits were produced in this study. Lisowska and Biallozor attempted reduction of $TiCl_4$ in AN (18) and DMSO (19). Reduction of Ti^{4+} to Ti^{3+} was accomplished, but further reduction was not documented. In the DMSO system, cathode deposits were obtained, but were found to contain no more than 37 pct Ti, with significant amounts of C and S. These investigators theorized that, at potentials necessary to reduce Ti to the metallic state, DMSO was also decomposed. They concluded that the possibility of Ti reduction in organic solvents was poor. In summary, while several investigators have examined reduction of Ti in organic solvents, none have successfully produced Ti metal, but at the same time, no consensus has emerged as to why Ti was not deposited.

<div align="center">EXPERIMENTAL</div>

<div align="center">Environmental Chamber</div>

Because of extreme sensitivity of Ti to O_2, electrochemical tests were carried out in an environmental chamber, or glovebox. The glovebox was constructed of a clear, rigid acrylic plastic top and a thermoset plastic bottom, and was sealed clamshell-style at the center with a closed foam gasket. The sealing surfaces were coated with silicone vacuum grease before clamping. The gloves were composed of Hypalon. The glovebox had an airlock entrance for introduction of materials without degradation of the inert atmosphere. Materials to be transferred into the glovebox were placed in the airlock, then the airlock was evacuated using a rotary vacuum pump and refilled with commercial grade Ar. Three cycles of purging were completed before transferring into the main chamber. The glovebox was purged with Ar periodically to replace the atmosphere. Oxygen and water vapor impurities were eliminated from the Ar by pumping through a

packed bed of Ti metal held at 700 °C in a stainless steel tube. The O_2 content of a bleed stream from the glovebox was monitored with an O_2 meter which used an aqueous electrochemical cell to measure O_2 content in the gas stream. The O_2 content of the glovebox atmosphere was less than 50 ppm during electrochemical testing. The meter was calibrated with a documented mixture of 480 ppm O_2 in Ar. However, the lower limit of the meter for O_2 was not zero; even ultrahigh purity Ar gas which contained less than 10 ppm O_2 registered 25 ppm O_2 after 1 h flow through the O_2 meter.

Electrochemical Test Procedure

Electrochemical tests were initiated and controlled with a Bioanalytical Systems (BAS) 100W electrochemical workstation. This system utilizes a 486 IBM-compatible computer to control a potentiostat which can detect currents as small as 1 nA. The electrochemical behavior of Ti was usually studied using cyclic voltammetry, where the cell potential is swept from one predetermined voltage to another at a given rate (20). Other techniques utilized in this work were linear sweep voltammetry, rotating disk voltammetry, and bulk electrolysis.

The electrochemical cell consisted of a glass jar, with a resin lid that had been drilled to accommodate the electrodes. A three-electrode scheme was used. The reaction to be studied took place at the working electrode. The potential of the working electrode was determined by a reference electrode in close proximity to the working electrode. A counter electrode was required to complete the electrical circuit and to allow current to flow through the solution. Since the potential of the working electrode was measured from a stable reference, rather than the counter electrode, only the potential related to the electrochemical half reaction taking place at the working electrode was monitored. Therefore, this scheme allowed a given half reaction to be studied without concern for the other half reaction. The working electrode consisted of a disk of metal sealed in a polymer cylinder. Working electrodes of Pt and Ti were used. The area of the Pt working electrode was 0.020 cm^2 and the Ti electrode area was 0.317 cm^2. The counter electrode was either a C rod, or a coiled Pt wire. In many tests, the counter electrode was isolated from the remainder of the system by placing it in a tube with a glass frit bottom. This prevented cyclic oxidation and reduction of reactants. An aqueous solution could not be used in the nonaqueous environment because of contamination of the solvent. Therefore, a nonaqueous reference electrode consisting of an Ag wire immersed in a solution of 0.1M silver nitrate in AN was used. This was isolated from the test solution to prevent contamination with AN. The reference electrode was placed in a bridge tube containing 0.1M tetrabutyl ammonium perchlorate (TBAP) in the solvent being tested. Both the reference electrode and bridge tube contained a Vycor junction which maintained electrical contact without excessive flow of electrolyte. All potentials given in this work are versus the Ag nonaqueous electrode, which has a potential of 563 mV versus the standard hydrogen electrode. Also, unless otherwise noted, all voltammograms discussed here were generated at a Pt electrode, at a scan rate of 100 mV/s.

Preparation of Solutions

Test solutions were made up as follows: The required amount of supporting electrolyte, typically TBAP or tetrabutyl ammonium tetrafluoroborate (TBATFB), was weighed, transferred into the glovebox, placed in the test cell, and diluted to volume with solvent. Solvents were purchased in anhydrous form, with a septum seal on the container to prevent contamination. Solvent was forced from the bottle by piercing the septum with two hollow needles, one of which forced Ar into the bottle, and the other of which transferred solvent to the test cell. The Ti source was air sensitive and, therefore, had to be dispensed inside the glovebox. For solutions of $TiCl_4$, which is a liquid at room temperature, $TiCl_4$ was added by pipetting directly into the test cell, or by preparation of a stock solution in the solvent of interest. Solid materials such as $TiCl_3$ or TiI_4 were

dispensed from a vial inside the glovebox, then the vial was resealed and transferred out to obtain the weight by difference.

RESULTS AND DISCUSSION

Characterization Tests

Because of uncertainties in working with nonaqueous solvents, an initial series of characterization tests was carried out with the well known system of ferrocene (dicyclopentadienyliron) in acetonitrile. The oxidation of ferrocene is known to be rapid and highly reversible. The experimental cyclic voltammogram for a 0.01M solution of ferrocene with 0.1M TBAP as a supporting electrolyte is shown in figure 1. The potential sweep begins well negative of the ferrocene oxidation potential, sweeps through it, reverses at a potential well positive of the equilibrium potential, and returns to the initial value. For the ferrocene system under these conditions, the height of the anodic and cathodic waves should be equal, and the peak separation should be on the order of 57 mV (20). The experimental voltammogram gave a peak separation of 70 mV, and cathodic and anodic peak currents of 98 and 93 μA, respectively. The slight increase in peak separation is probably due to resistance effects but, generally, these results show that the electrochemical set up was satisfactory.

One of the first objectives of this work was to experimentally determine the equilibrium potential of the Ag/Ag$^+$ nonaqueous reference electrode. This was done by comparing voltammograms for the oxidation of ferrocene in AN using a Ag/AgCl aqueous reference electrode and the nonaqueous electrode. Using the average of the anodic and cathodic peak potentials to estimate the ferrocene equilibrium potential, values of 65 mV versus the nonaqueous electrode, and 431 mV versus the Ag/AgCl electrode were obtained. Using the manufacturer's value of 197 mV versus the standard hydrogen electrode (SHE) for the Ag/AgCl reference, the potential of the nonaqueous electrode is 563 mV versus the SHE. For a similar electrode, Mann gives 337 mV versus the saturated calomel electrode (SCE) (7, p. 64). This is 578 mV versus the SHE, which is in good agreement with the experimentally determined value. The experimentally determined potential for the oxidation of ferrocene is 628 mV versus the SHE, or 387 mV versus the SCE. Bard and Faulkner give 307 mV versus SCE for this reaction in AN (21), but using a lithium perchlorate electrolyte. The difference is probably due to junction potential errors. Junction potentials arise due to differences in the diffusivities of ions in the different media present at any junction in the solution, such as at the Vycor tip of the reference electrode. The junction potential is dependant on the composition of the test and electrode filling solutions. In most cases the junction potential will be less than 100 mV. In this study, the determination of the absolute voltage of a given reaction is not necessary, so this degree of error is acceptable.

Another source of error, which is generally more serious for nonaqueous applications, is that of the uncompensated resistance. In the three electrode geometry, the resistance between the counter and reference electrodes does not affect the potential at the working electrode, and is said to be compensated. However, the resistance between the reference electrode and the working electrode cannot be compensated in the same way. Therefore, this resistance is termed the uncompensated resistance. The error is usually minimized by placing the tip of the reference electrode as close as possible to the working electrode, and by addition of supporting electrolytes to increase conductivity. However, in nonaqueous systems, conductivities are often orders of magnitude less than in aqueous systems, and this can lead to distortion of test results, as shown in figure 2. Figure 2 shows a comparison of the voltammograms obtained for two different size Pt working electrodes for a solution of 0.01M ferrocene in AN. The ratio of electrode areas is about 20 to 1. The current has been normalized to current density in this figure. Since current is proportional to area, and uncompensated voltage drop is proportional to current, uncompensated resistances have caused the "widening" of the voltammogram obtained with the large electrode,

with a peak separation of 300 mV. This is not a true reflection of the chemistry of the system, but an experimental artifact that must be avoided whenever possible. All subsequent voltammograms shown in this work, with the exception of the Ti dissolution voltammogram, were obtained with electrodes no larger than that used in the generation of figure 1.

Reduction of Other Metals

Before Ti reduction tests were begun, the reduction of other, less active metals was done in order to become familiar with metal reduction processes in nonaqueous solutions. Silver was chosen for the first test, because only one oxidation state is stable, and silver ion is easily reducible to metal. A complication of this system is that silver chloride is not very soluble in DMSO. To increase silver chloride solubility, chloride was added as LiCl, which may have affected Ag speciation, and, therefore, the mechanism of electroreduction. A cyclic voltammogram for the reduction of Ag in DMSO is shown in figure 3. The voltammogram is very different in appearance than that of figure 1, where two soluble species were involved. When metal ions are deposited on an electrode surface, characteristics of the electrode change, and this gives rise to the different shape that is observed in figure 3. A common feature of the cathodic sweep where a metal is deposited is a nucleation loop, where the current trace is greater on the return sweep than on the outgoing sweep. This is due to an overpotential associated with nucleation of metal atoms on the electrode surface. Once the nucleation centers are formed, current readily flows, even after the scan direction is reversed, until the equilibrium potential is reached, where the trace crosses the axis. For Ag deposition in this system, the equilibrium potential was -0.86 V. The anodic sweep was also affected when metal deposition occurred. Anodic current increases very rapidly when the voltage drops below the equilibrium potential because the metal is already at the electrode surface, rather than diffusing to the surface under a concentration gradient. Once the supply of metal on the surface is exhausted, the anodic current decreases rapidly, as shown in figure 3. Although the height of the anodic peak is generally much greater than the cathodic peak, the total anodic charge, or the area under the anodic peak, should equal the total cathodic charge.

The deposition of Cu is a more complicated case, because two oxidation states are possible, yet the voltammogram more closely approximates the Ti system where at least two and possibly more solution oxidation states may exist. Figure 4 shows a voltammogram for $CuCl_2$ in a DMSO/$0.5M$ LiCl solution. Two reduction and two oxidation peaks are seen in this figure. The first set, centered at about -0.20 V, represents reduction of Cu^{2+} to Cu^+, both soluble species. The second set of peaks, centered at about -1.1 V, shows Cu deposition and stripping. A nucleation loop is not observed for the cathodic sweep in this voltammogram, but a strong anodic stripping peak is apparent.

Anodic Dissolution of Ti

It was expected that deposition of Ti would be more difficult than dissolution. Therefore, Ti dissolution tests were conducted prior to deposition tests. Anodic scans of a Ti working electrode in a solution of DMF containing TBAP were done but no significant dissolution of the Ti was observed to take place. Then, it was discovered that if Ti metal was added to a solution of $TiCl_4$ in DMF, the solution turned from yellow to violet, indicating that reduction of Ti^{4+} had taken place. This is only possible if Ti metal was oxidized. The probable reaction is:

$$Ti + 3Ti^{4+} = 4Ti^{3+}$$
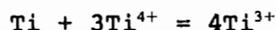
Additional electrochemical scans were generated for a Ti working electrode in a solution of DMF containing $TiCl_4$ in addition to TBAP. In this case, large anodic currents were obtained, as shown in figure 5, indicating significant

dissolution of Ti metal. In subsequent tests, a peak anodic current density of 26 mA/cm^2 was observed, which is comparable to that used in the commercial electrorefining of Cu. Tendrils of violet color formed around the Ti electrode. It appears that Ti^{4+} activates the metal surface, possibly by dissolving the TiO$_2$ passivation coating on the metal, allowing dissolution to take place.

Ti Reduction in DMF

Following characterization and dissolution tests, Ti reduction tests were begun. Initially, DMF was chosen as a solvent candidate because of its high solubility for TiCl$_4$ and supporting electrolytes, and its low vapor pressure and cost. Figure 6 shows the reduction of Ti on a Pt working electrode in a solution of TiCl$_4$ in DMF with 0.1M TBAP as the supporting electrolyte. On the initial cathodic sweep, reduction peaks were noted at about -0.6 V, -1.2 V, and -2.3 V. Only one anodic peak was observed on the reverse sweep, at about -0.3 V. However, if the anodic limit was increased slightly, two anodic peaks were observed, at -0.3 and -0.1 V. Experiments showed that both anodic peaks were observed even when the scan was reversed at -0.7 V. The effect of TiCl$_4$ concentration is also shown in figure 6, where the concentration of Ti was increased from 0.005 to 0.02 M. As the Ti concentration increased, the relative size of the peaks at -0.6 V and -1.2 V changed. This is believed to be due to the presence of two different Ti complexes of the +4 oxidation state, which are reduced to Ti^{3+} at slightly different potentials. It is apparent from figure 6 that as the Ti concentration increased, the relative heights of the peaks in this region changed. Evidently, as the concentration increases, the complex that is more easily reduced becomes more prevalent in solution.

As discussed in the introduction, several possible Ti^{4+} species could be present in solution. One possibility has been cited by Kolthoff and Thomas (*13*) who reported self dissociation of TiCl$_4$ in acetonitrile as follows:

$$2TiCl_4 = TiCl_5^+ + TiCl_3^-.$$

The extent of dissociation was calculated to be 2.6 pct. Another possibility is that two different isomers of the solvated Ti^{4+} complex are present, such as the cis and trans isomers of the complex TiCl$_4$(DMF)$_2$. Still other researchers (*16*) have hypothesized that the TiCl$_4$ loses some of its chloride ligands upon addition to the solvent (in this case DMSO) as follows:

$$TiCl_4 = TiCl(DMSO)_2^{3+} + 3Cl^-$$
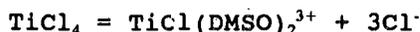
However, this hypothesis is hard to accept in view of the fact that both DMF and DMSO are poor solvating agents for anions. Without definitive speciation studies, it is not possible to identify the complexes participating in electroreduction.

Upon prolonged electrolysis of the DMF/TBAP/TiCl$_4$ solution, the color changed from yellow, to green, to violet. Greenwood and Earnshaw have documented hydrate isomerism as responsible for a similar color change for hydrated Ti salts (*22*). The violet solution was stable if kept from contact with air and moisture, while the green color appeared only as an intermediate in the reduction process. The violet solution could be reoxidized to yellow by sparging with air. No deposits were obtained upon extended electrolysis of these solutions, nor was a further color change noted that might have signaled production of a different complex.

The reverse peak associated with the cathodic peak for the reduction of Ti^{4+} to Ti^{3+} indicates chemical reversibility of the system. The minimum peak separation observed in this work was 200 mV, which is much greater than the

57 mV separation observed in the ideal ferrocene system. This indicates electrochemical irreversibility, which is to say that the rate of electron transfer is not rapid enough to keep up with diffusion of reactants to the electrode surface. An indication of slow electron transfer kinetics is not a good sign for commercialization. This phenomenon has also been observed for Fe oxidation in DMSO (23). Those researchers claimed that adsorption of S from the solvent was responsible for the decrease in electron transfer kinetics.

Since the first two cathodic peaks on the voltammogram in figure 6 appeared to be associated with reduction of Ti^{4+} complexes to Ti^{3+}, the third peak could represent reduction of the Ti^{3+} complexes to lower oxidation states, possibly Ti^{2+} or metal. Alternatively, this peak could be a solvent or electrolyte decomposition reaction. These hypotheses were tested by preparing a solution of $TiCl_3$ in DMF and running the voltammogram. Figure 7 shows the voltammograms for the $TiCl_3$/TBATFB/DMF system. Note that a different electrolyte was used in this experiment. The tetrafluoroborate salt was used in this case because it had been suggested that the perchlorate species could act as an oxidant which might react with any reduced Ti species. The voltammograms show a small cathodic peak at about -1.2 V, which is the same potential observed for reduction of Ti^{4+} to Ti^{3+}. This suggests the presence of oxidized Ti in the $TiCl_3$ reagent. A much larger cathodic peak appeared at -2.3 V that was sensitive to Ti concentration. This peak correlates well with that observed on the $TiCl_4$ voltammogram, and suggests that the peak represents a reduced Ti compound of oxidation state +2 or less. The fact that the peak height was proportional to $TiCl_3$ concentration indicated that solvent or electrolyte decomposition was not involved.

The lack of a reverse (anodic) peak for the cathodic peak at about -2.3 V indicates that this is not a reversible reaction. Further information about an electrochemically active species can often be obtained by studying the effect of scan rate during the voltammogram, in essence, the time window of the experiment. Figure 8 shows the effect of increasing scan rate on the cathodic peak at -2.3 V. This voltammogram was generated using the same solution as was used in figure 7. Under no conditions was a reverse anodic peak observed in these experiments. There are several possible explanations for this behavior. The reaction could be chemically irreversible, so that the products simply cannot recombine to form the reactant. An example of this case would be that the reduced Ti compound acts as a polymerization catalyst for the solvent, instantly becoming coated or encapsulated with an inert coating. Another example would be that the reduced compound precipitates (perhaps as $TiCl_2$) as an insoluble coating on the electrode. However, the results from the Ti dissolution test in figure 5 show that this can not be the case, since the result of either postulated reaction (polymerization or $TiCl_2$ formation) would be an insoluble coating on the electrode which would prevent dissolution of Ti from the electrode surface. Also, in either of these cases, one would expect the reduction current to be significantly decreased on subsequent sweeps after the formation of these coatings on the working electrode, but this behavior was not observed.

An alternative explanation is that the reduced Ti species were consumed, for example, by a subsequent homogenous chemical reaction, before the reverse reaction could take place. Two possibilities of this type would be oxidation of the deposit by perchlorate supplied by the TBAP or by Ti^{4+} present at the electrode surface. However, the voltammogram in figure 8 shows that even in the absence of either Ti^{4+} or perchlorate, no reverse peak was seen. It is possible that another species is responsible for consumption of the reduced Ti species, but if so, the reaction is very fast, because even at a scan rate of 500 mV/s, no reverse peak was seen. A further possibility would be water. Even though the nonaqueous solvents were purchased in the anhydrous form, some remnant of water was present. The specification for anhydrous DMF from the

manufacturer is less than 0.005 pct water, but this translates to about 0.003M. The fact that the working electrode was not passivated in this case shows that the reduced Ti species was soluble, suggesting Ti^{2+}. It may be that the Ti^{2+} reacts with water to give a titanium oxychloride. This explanation would not conflict with the Ti dissolution results reported earlier, since a soluble species would not passivate the Ti electrode surface.

Ti Reduction in DMSO

Many Li salts are soluble in polar aprotic solvents, and Li salts have been used as electrolytes in Ti reduction tests. However, it is possible that Li could be reduced preferentially to Ti. In fact, some researchers have speculated that electrodeposited Li reacts with Ti complexes in solution in a cementation type reaction (18-19).

In the present study, several tests were performed using Li salts as the supporting electrolyte. Tests showed that DMSO was stable and that DMF and AN were unstable in the presence of metallic Li. Therefore, electrochemical tests were run using Li salts in DMSO solution. Figure 9 shows a voltammogram for the reduction of Li from a solution of 0.1M LiCl in DMSO. This voltammogram shows an anodic stripping peak at -3.2 V, which indicates that Li was deposited on the electrode surface. However, with the addition of $TiCl_4$ to the solution, the voltammogram, which is shown in figure 10, changes significantly. Neither the Li deposition or stripping peaks are observed, and after about the third sweep, the Ti peak currents had decreased to less than one quarter of their original value. These results indicate some reaction between the Ti and Li which results in passivation of the electrode. Clearly, it will not be possible to produce Ti in a DMSO/LiCl/$TiCl_4$ bath.

Ti Reduction in Other Solvents

It is possible that polar solvents are not suitable for Ti reduction because the solvent stabilizes the Ti in solution, preventing decomposition at the electrode. If this were the case, solvents with less polarity than DMF and DMSO may support Ti reduction. Most inorganic salts have lower solubility in less polar solvents, and as a result, lower conductivity. Lithium battery research has shown that Li can be deposited from solutions of ethers such as dimethoxyethane (DME); therefore, this solvent was chosen for Ti reduction studies. Figure 11 shows a voltammogram for the reduction of $TiCl_4$ in a DME solution, with a supporting electrolyte of TBATFB. A set of oxidation and reduction peaks are observed at about -1 V, which is probably due to the Ti^{4+}/Ti^{3+} couple. Another peak appears to be present at higher $TiCl_4$ concentration at -3.2 V, but no stripping peak was apparent. Ti dissolution tests were run in the same solution, but anodic currents were negligible. This is reasonable, since the low polarity of the solvent means that solution complexes are less stable.

Another possibility is that since some of the solvents tested in this study, particularly DMF and DMSO, were strongly associative, the reduced Ti species were stabilized in solution, thus preventing deposition. Sawyer and Roberts (24) list propylene carbonate (PC) as a much weaker associative solvent than either DMF or DMSO. Therefore, several tests were conducted using PC. Also, the Ti source was changed to TiI_4 in these tests with the thought that the softer more polarizable I^- ions would be less likely to complex and stabilize Ti. The background electrolyte in these tests was TBATFB. A typical voltammogram for this system is shown in figure 12. Reversible peaks appear centered at +0.25 and -0.25 V, which are probably due to the I^-/I_2 and Ti^{3+}/Ti^{4+} couples, respectively. The presence of the iodine species in the voltammogram suggests that the TiI_4 complex does indeed dissociate to some extent in PC. As with DME, a cathodic peak appears in the voltammogram at about -3.2 V, but no associated reverse peak was present.

These results indicate that neither DME nor PC are suitable solvents for reduction of Ti to the metallic state.

CONCLUSIONS

Deposition of Ag and Cu was readily accomplished from solutions of DMSO. The deposition of metal ions changes the electrode surface, and therefore significantly affects the shape of the cyclic voltammogram.

In DMF and DMSO solutions, Ti metal reacted with Ti^{4+} to give Ti^{3+}, thus raising the possibility of chemical dissolution of Ti metal. The Ti^{3+} so produced could be electrochemically regenerated by an anodic reaction and recycled.

Titanium electrodissolution was observed in DMF solutions containing Ti^{4+}. Current densities of up to 26 mA/cm^2 were observed, which is comparable to conditions in commercial Cu electrorefining. Much lower currents were observed in the absence of Ti^{4+}, indicating that the Ti^{4+} may clean the electrode surface, thus allowing the dissolution reaction to proceed.

In DMF solutions, at least two different isomers are involved in the reduction of Ti^{4+} to Ti^{3+}. These could be geometrical isomers, or completely different complexes. The relative concentrations of these complexes varied with the total Ti concentration in solution. Further study would be required to identify these species.

In DMF solutions, reduction of Ti to oxidation states below Ti^{3+} was observed. However, no solid deposits were obtained, and no reverse stripping peaks were observed that could have indicated the presence of reduced Ti complexes. Several possible mechanisms were discussed that could account for this behavior, but no specific mechanism could be identified that was responsible for preventing Ti deposition.

Lithium salts are often used as electrolytes in nonaqueous solvent systems. However, it is possible that Li metal can be deposited from these solutions. Contact studies between solvents and Li metal showed that DMF and AN were not stable in the presence of Li metal. This demonstrates that Li salts would not be appropriate for these solvents if large cathodic voltages were to be applied.

As demonstrated by stripping peaks on the voltammogram, Li metal was deposited from a solution of LiCl in DMSO. When TiCl$_4$ was added to solution, Li peaks were no longer observed, and the electrode passivated within three cycles. This demonstrated that the DMSO/LiCl system is unsuitable for Ti deposition.

Other solvents tested in this study were DME and PC. Although reduction of Ti^{4+} to Ti^{3+} was observed for these systems, further reduction of the Ti was not observed.

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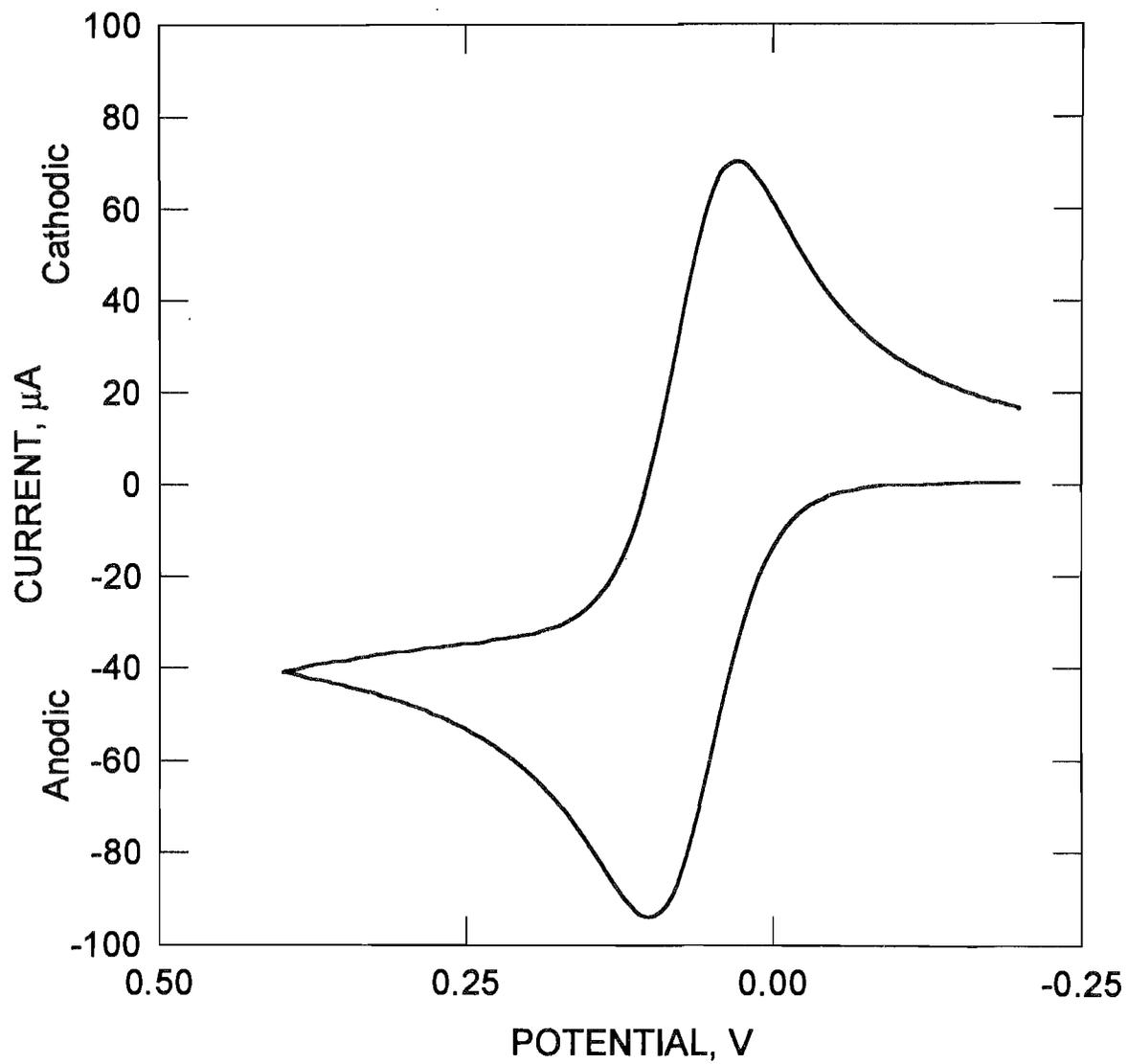
Figure 1
Cyclic voltammogram for ferrocene in AN. Test conditions: 0.01M ferrocene,
0.1M TBAP in AN. IR compensation.

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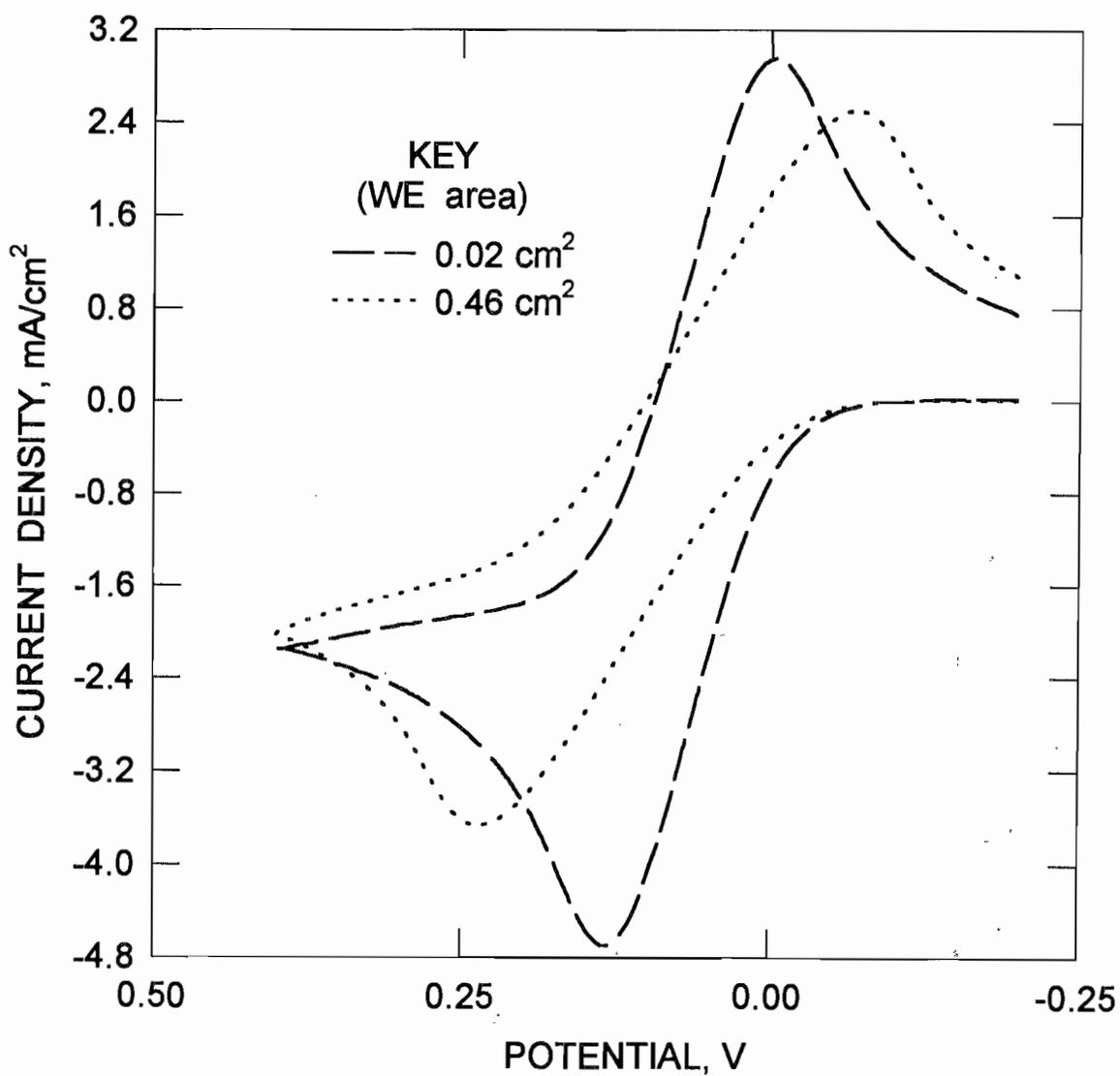
Figure 2
Cyclic voltammograms for ferrocene in AN. Effect of electrode area
(uncompensated resistance). Test conditions: 0.01M ferrocene, 0.1M TBAP in
AN. Currents normalized to current density.
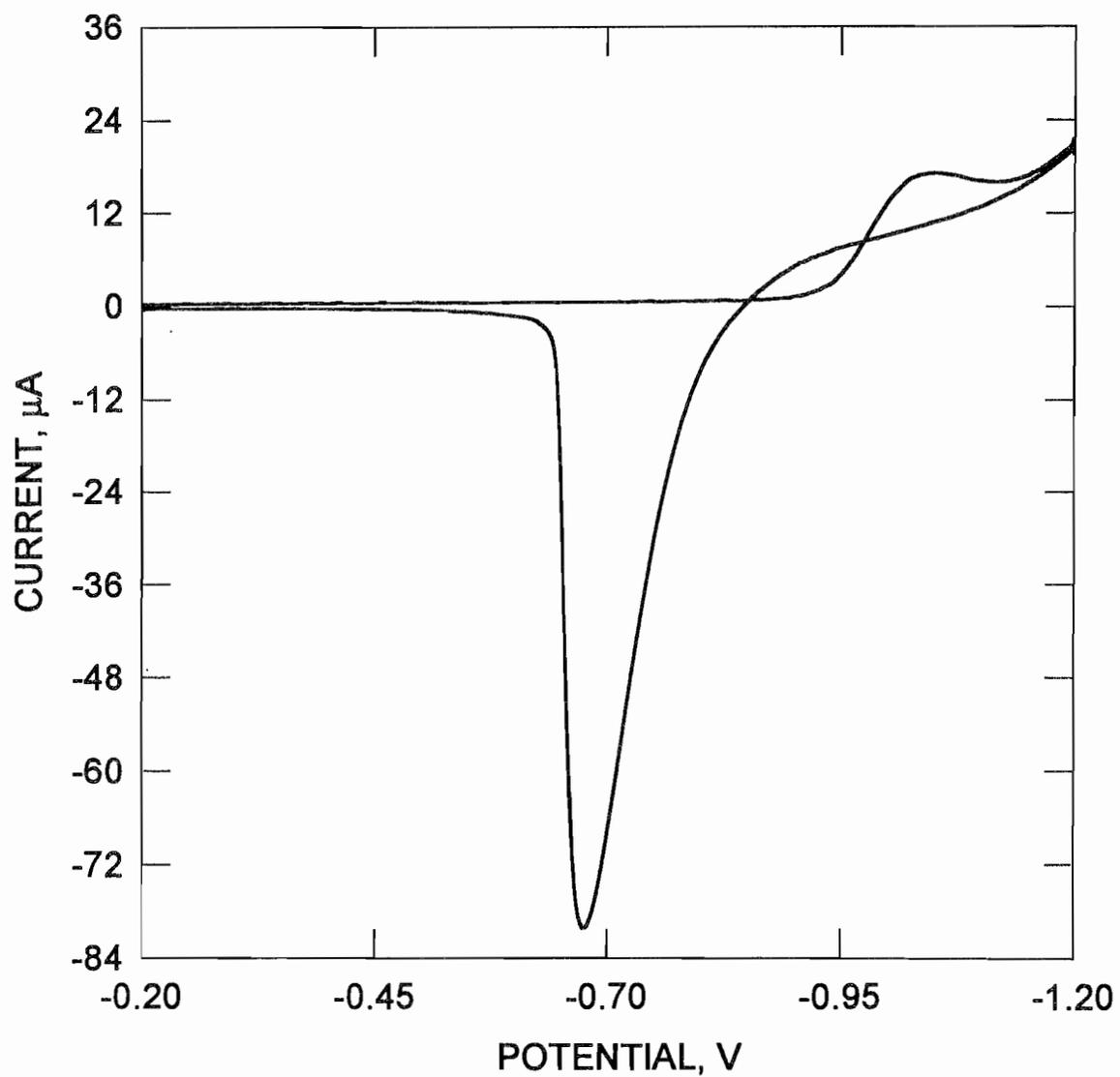
Figure 3
Cyclic voltammogram for Ag in DMSO. Deposition and stripping of Ag. Test conditions: 0.01M AgCl, 0.5M LiCl in DMSO.
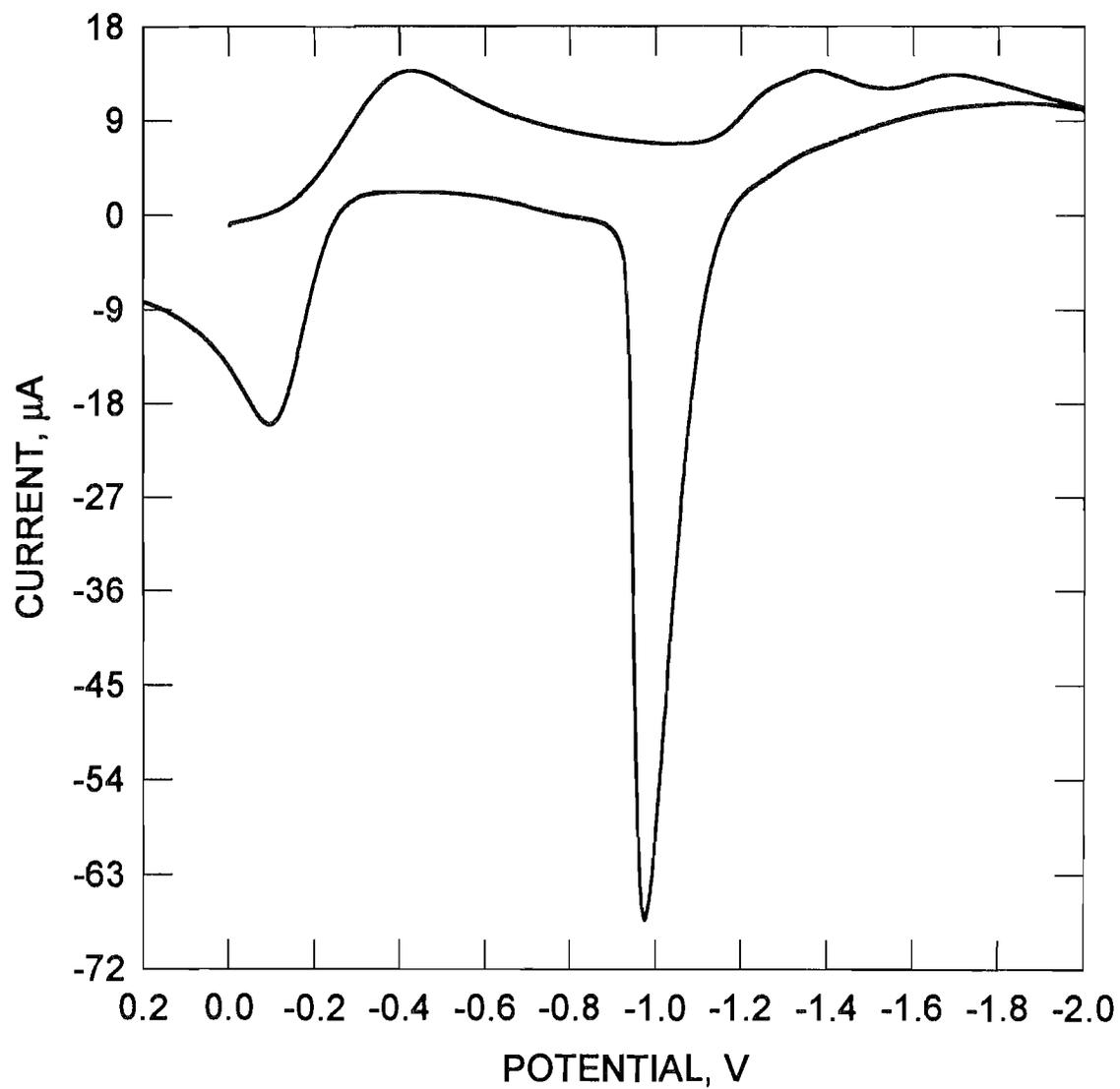
Figure 4
Cyclic voltammogram for Cu in DMSO. Deposition and stripping of Cu. Test
conditions: 0.01M CuCl$_2$, 0.5M LiCl in DMSO.
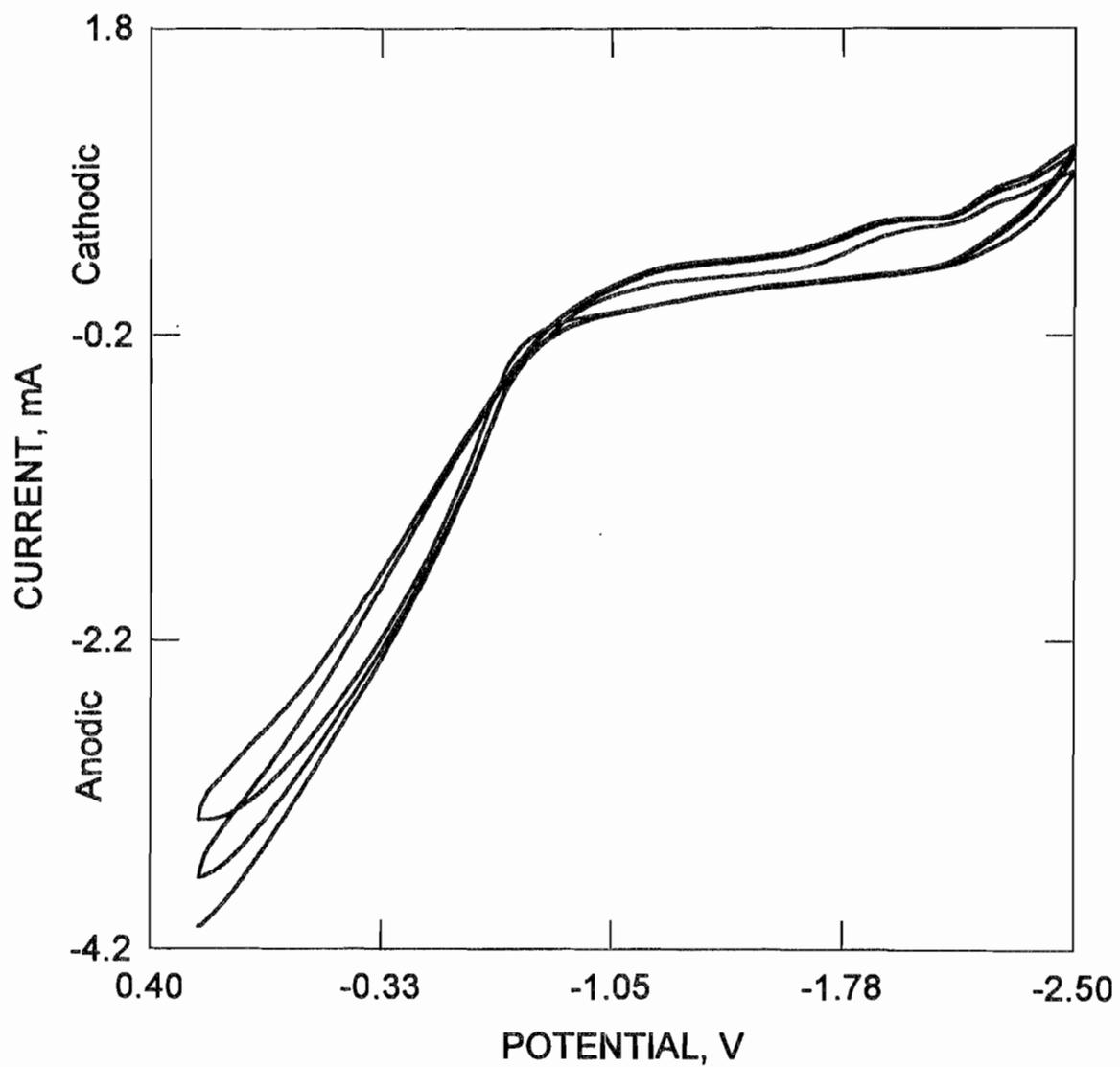
Figure 5
Cyclic voltammogram for Ti WE in DMF. Anodic dissolution of Ti. Test
conditions: 0.02M TiCl$_4$, 0.1M TBAP in DMF. WE area = 0.317 cm^2.
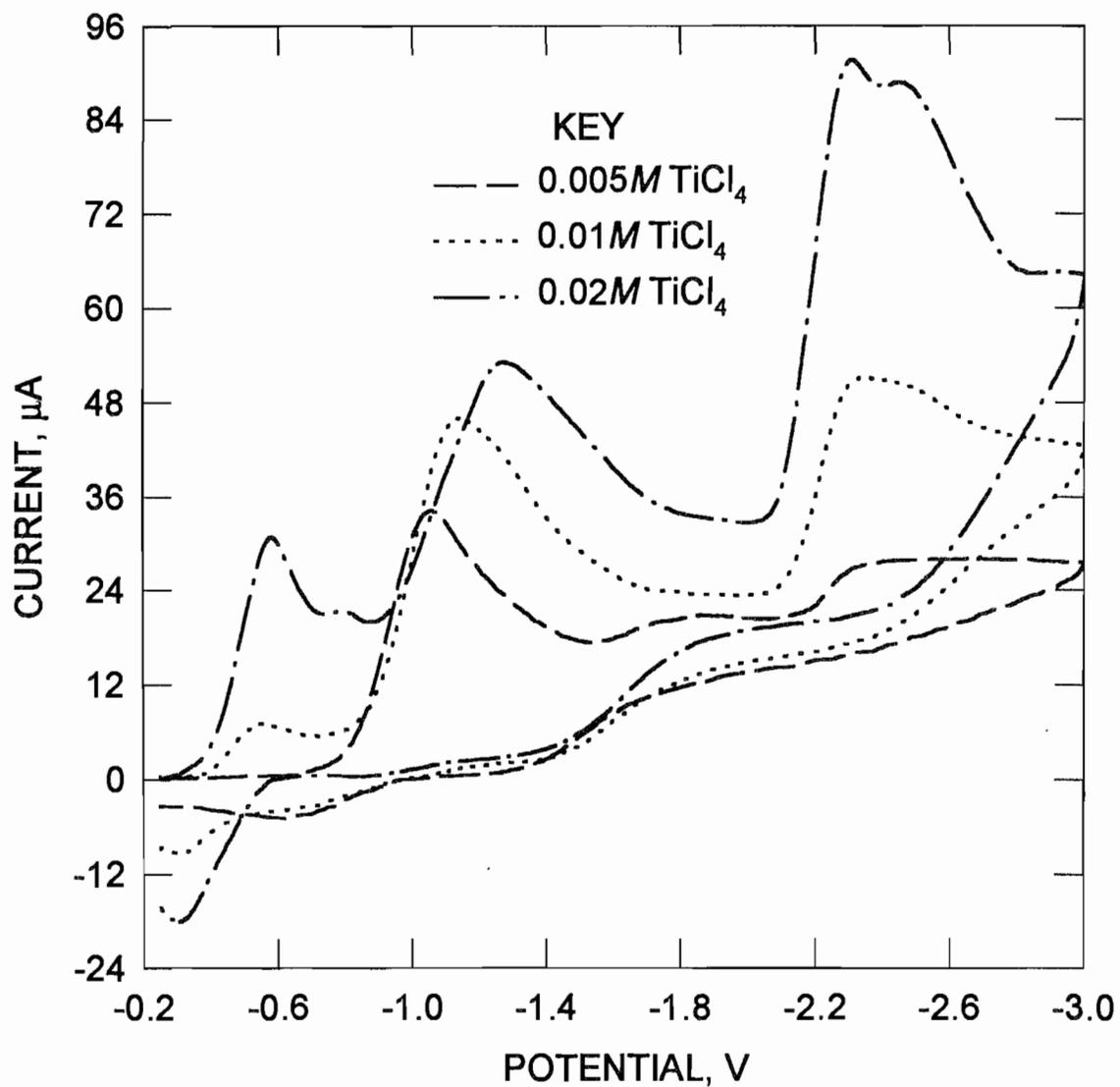
Figure 6
Cyclic voltammograms for TiCl₄ in DMF. Effect of Ti concentration. Test
conditions: 0.005, 0.01, and 0.02 *M* TiCl₄, 0.1*M* TBAP in DMF.
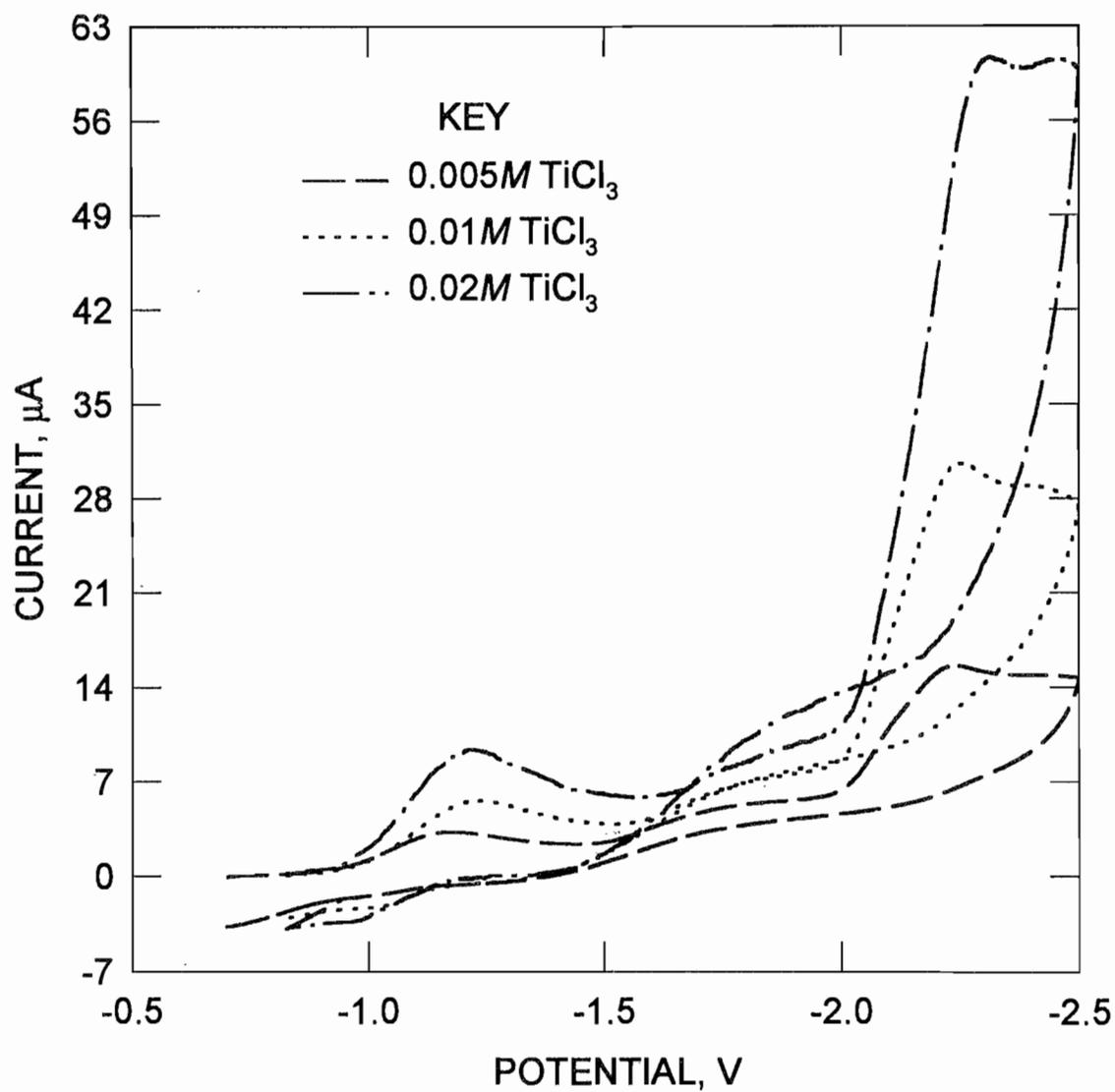
Figure 7
Cyclic voltammograms for TiCl₃ in DMF. Effect of TiCl₃ concentration. Test conditions: 0.005, 0.01, and 0.02 M TiCl₃, 0.1M TBATFB in DMF.
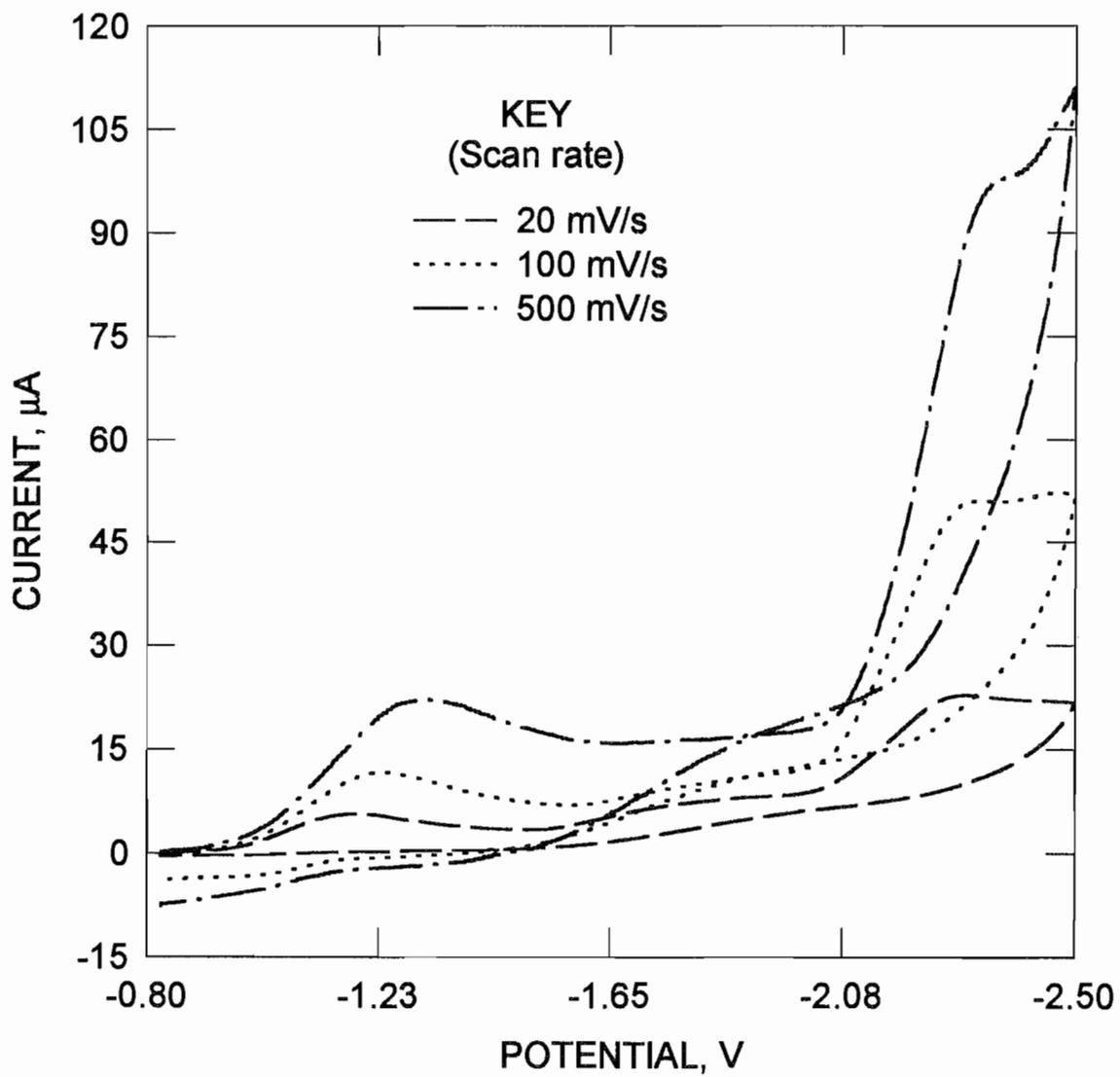
Figure 8
Cyclic voltammograms for TiCl₃ in DMF. Effect of scan rate. Test conditions: 0.02*M* TiCl₃, 0.1*M* TBATFB in DMF. Scan rates 20, 100, and 500 mV/s.
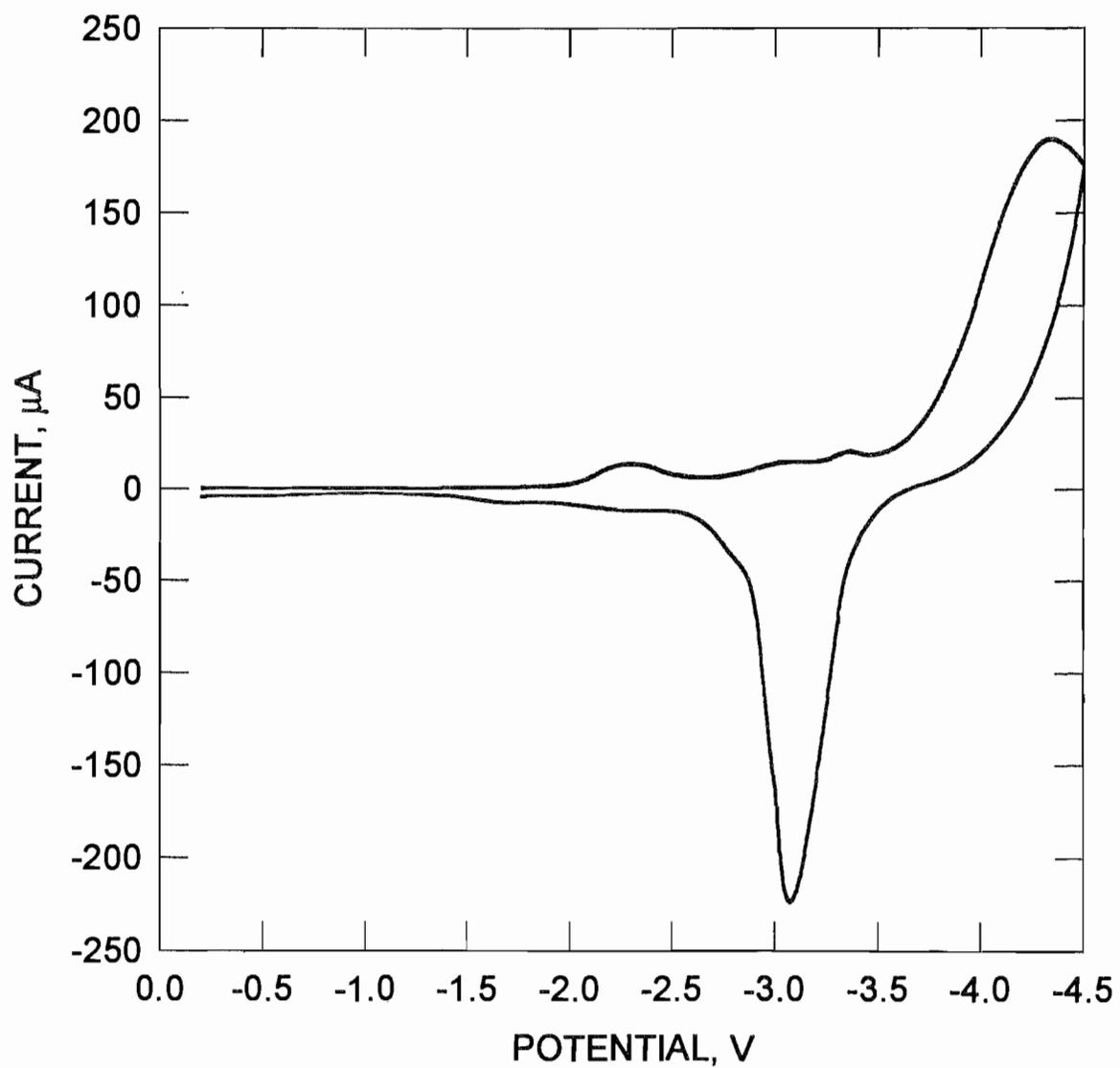
Figure 9
Cyclic voltammogram for LiCl in DMSO. Li deposition and stripping. Test
conditions: 0.1*M* LiCl in DMSO.
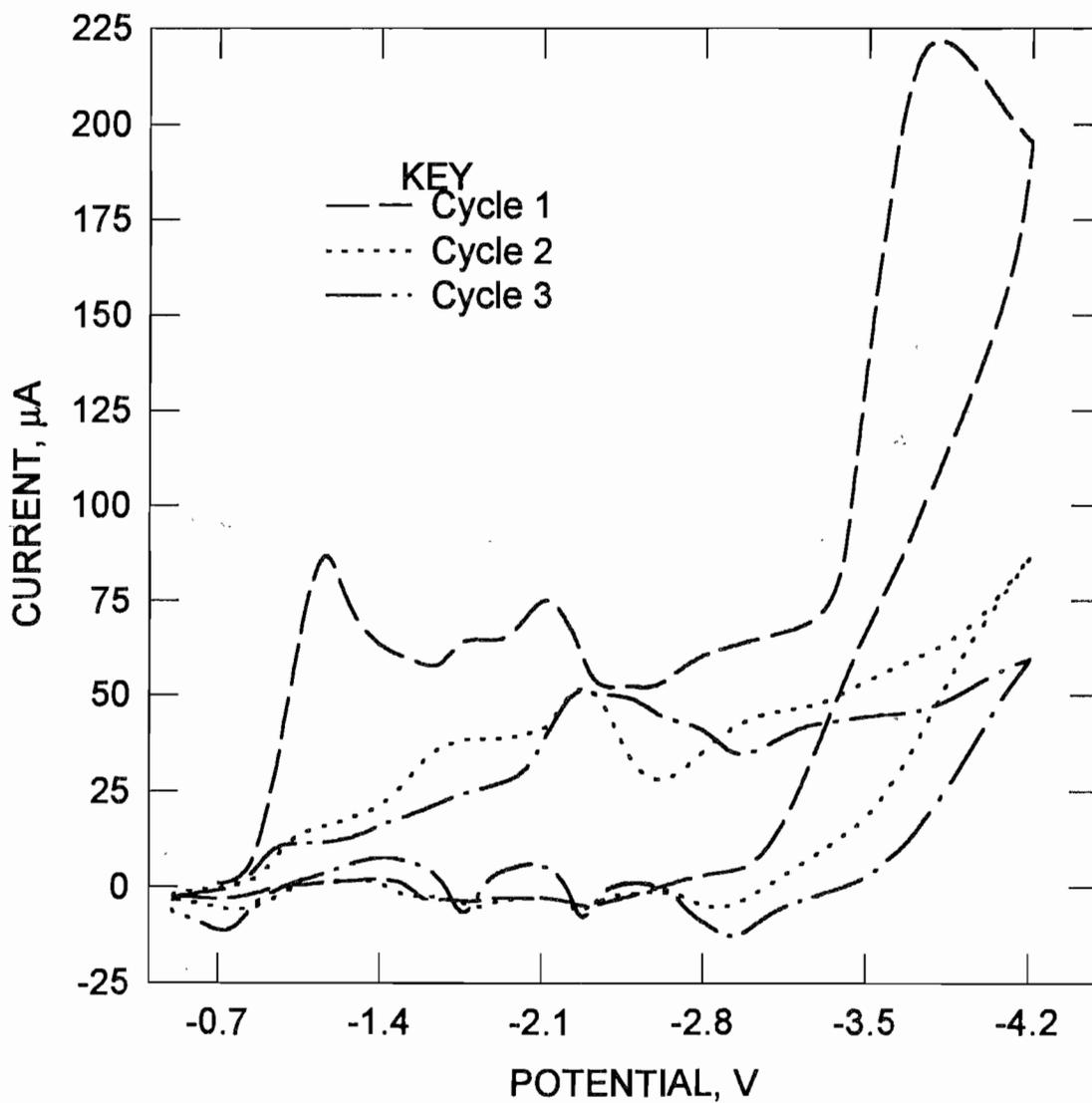
Figure 10
Cyclic voltammogram for TiCl₄ in DMSO. Passivation of WE. Test conditions:
0.03*M* TiCl₄, 0.1*M* LiCl in DMSO.
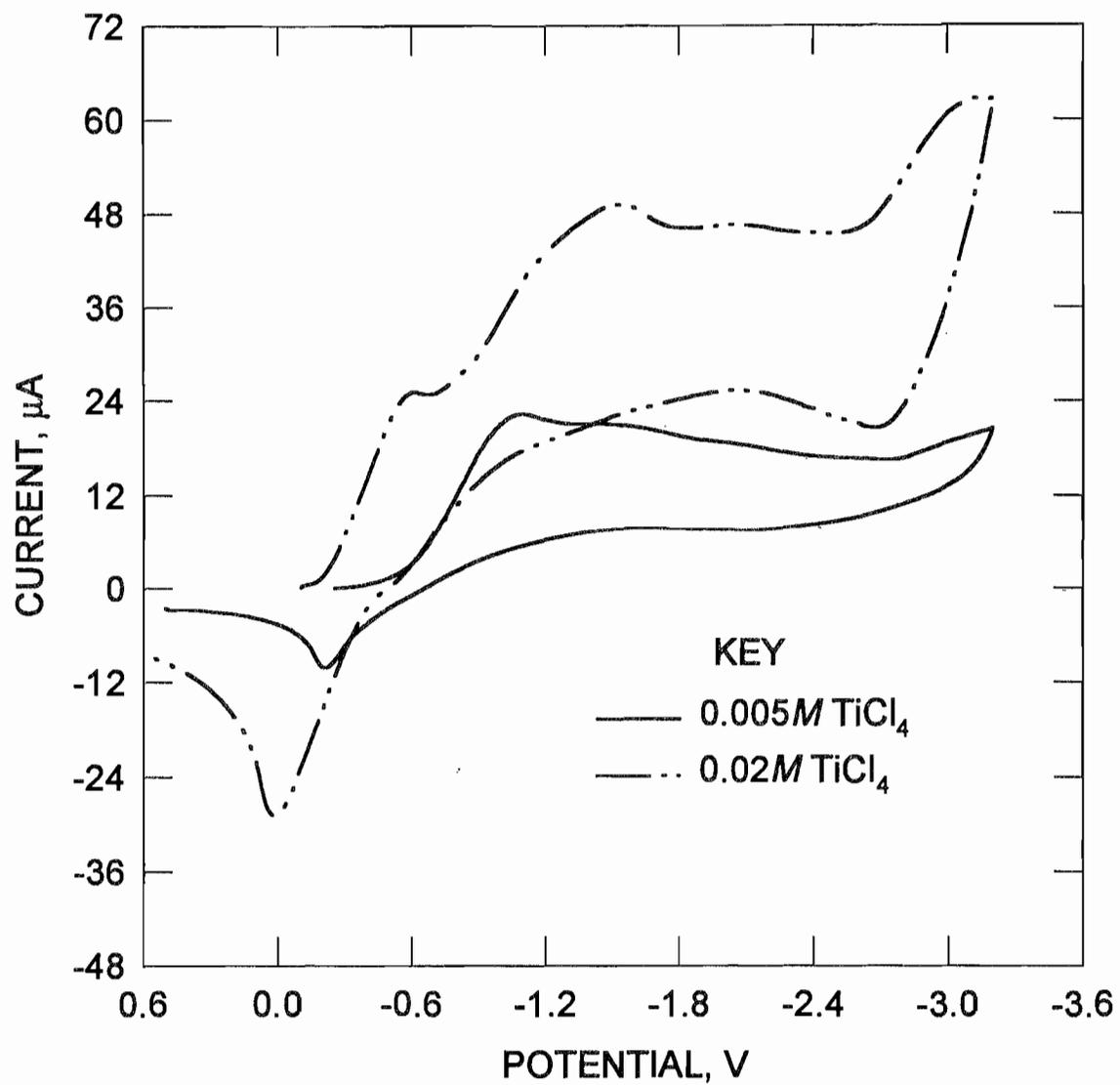
Figure 11
Cyclic voltammogram for TiCl₄ in DME. Test conditions: 0.005 and 0.02 *M*
TiCl₄, 0.1*M* TBATFB in DME.
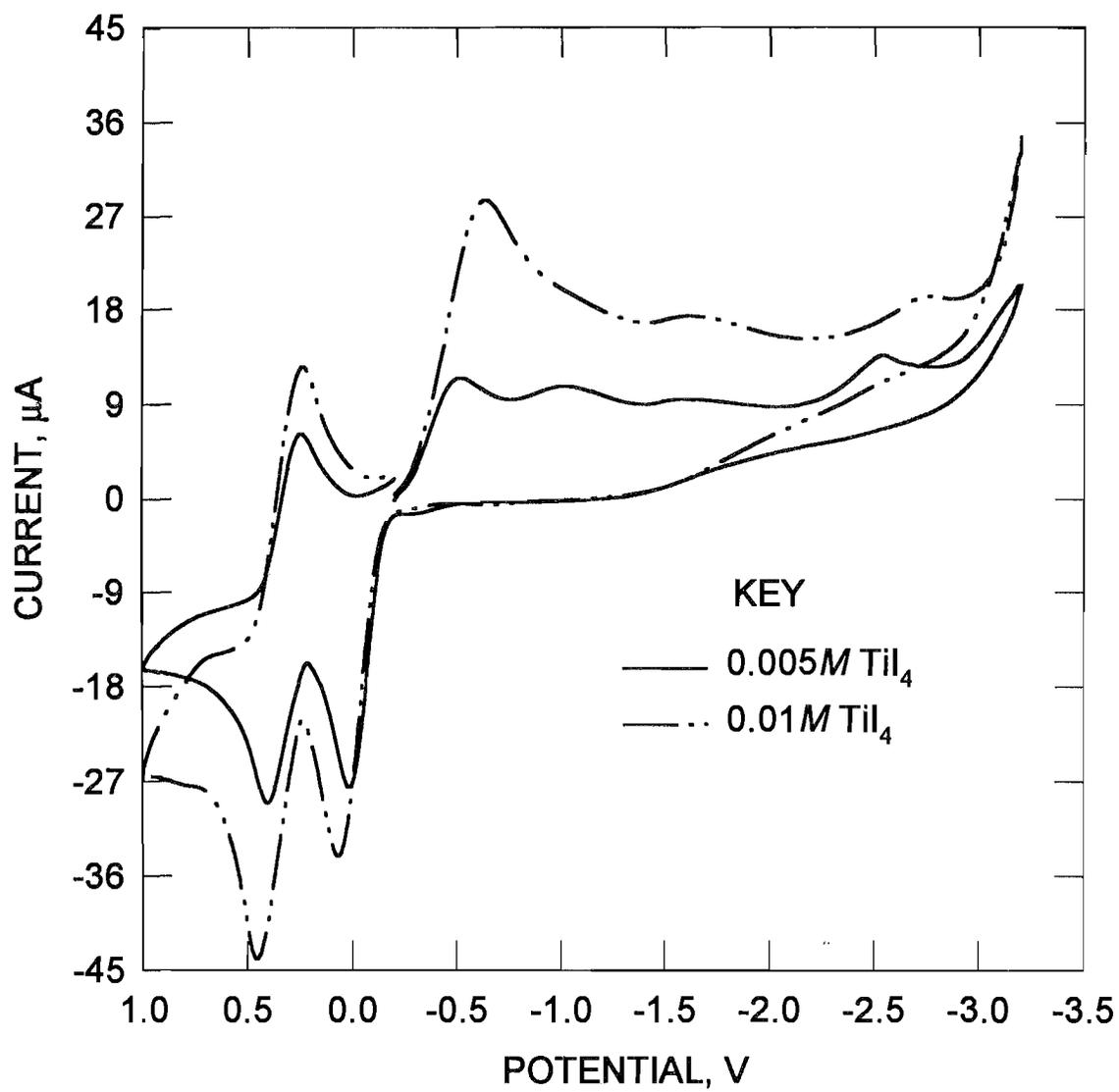
Figure 12
Cyclic voltammogram for TiI$_4$ in PC. Test conditions: 0.005 and 0.01 M TiI$_4$, 0.1M TBATFB in PC.