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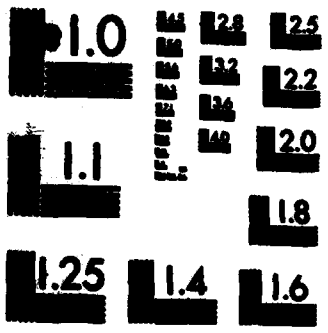
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Electrochemistry in Near-Critical and Supercritical Fluids. I. Ammonia.

By

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**Electrochemistry in Near-Critical and Supercritical Fluids. I. Ammonia.**

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(Abstract)

Cyclic voltammetric and chronocoulometric studies of  $\text{NH}_3$  containing 0.1 - 0.2 M KI at T and P up to  $160^\circ\text{C}$  and 272 atm are reported. Electrochemical generation of solvated electrons ( $e_s^-$ ) is possible even under supercritical conditions, but <sup>their</sup> the stability of  $e_s^-$  is lower at higher T. Reduction of m-chloronitrobenzene (MCNB) to the radical anion yields essentially Nernstian waves from  $55^\circ\text{C}$  to  $160^\circ\text{C}$ . The diffusion coefficient of MCNB at  $160^\circ\text{C}$  and 272 atm was  $3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ , in good agreement with the value calculated from measurements at lower temperatures via the Stokes-Einstein equation.

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## Electrochemistry in Near-Critical and Supercritical Fluids. I. Ammonia.

We report electrochemical studies in near- and supercritical ammonia and the behavior of solvated electrons and *m*-chloronitrobenzene in this medium. Thermodynamic and solubility studies of supercritical solutions have been an active area of research.<sup>1</sup> We are interested in applying electrochemical techniques to near- and supercritical fluids to obtain a better understanding of the thermodynamics and kinetics of reactions, particularly homogeneous and heterogeneous electron transfer reactions, that occur in these media and perhaps to utilize these solutions for electrosynthetic purposes. The high temperature and pressures necessarily associated with electrochemically useful supercritical solutions necessitate the use of highly specialized cells and electrodes. In addition, the increased reactivity of species and the highly corrosive environment of supercritical ammonia limits the types of useful electrolytes and redox couples that can be studied easily as test systems.

As the critical temperature of a liquid is approached, the gaseous and liquid phases merge into a single, space-filling phase called a supercritical fluid. For ammonia, the critical point occurs at 133° C and 112,5 atm; addition of low concentrations of electrolyte do not change these values appreciably. The characteristics which typify these fluids include: decreased viscosities, densities, and dielectric constants, unusual changes in inter- and intra-molecular forces and altered solvation characteristics. A primary question of interest is whether electrochemical studies can be carried out in a supercritical fluid containing an electrolyte. We show here that electrochemical techniques, such as cyclic voltammetry and chronocoulometry, with near- and supercritical ammonia can be used to probe

changes in redox potentials, electrogenerated product stability, and diffusion coefficients. Of the limited number of electrochemical studies that have been carried out on supercritical solutions, most have dealt with the corrosion of metals in contact with water.<sup>2</sup> To our knowledge, the only previous attempt at obtaining quantitative electrochemical information from supercritical  $\text{NH}_3$  involved a two electrode, constant current, electrodeposition of silver.<sup>3</sup>

There are two primary experimental difficulties associated with these types of experiments: containment of a high pressure, space filling, corrosive fluid and design of electrode feedthroughs which can withstand the supercritical environment and remain insulated from the walls of the cell. The base of the electrochemical cell we have fabricated is of 316 stainless steel; the interior is cylindrical and has an internal volume of 75 mL. A detachable lid of the same material is bolted to the base by means of a flange arrangement incorporating a diamond-shaped copper gasket. Three electrodes, supported by standard Swagelok fittings, pass through the lid. Provisions are also made for evacuation, filling, sample addition, and a rupture disk. All electrode feedthroughs consist of tungsten wire passed through a commercially available graded glass to Kovar seal. Construction of the feedthrough is completed by sealing the glass to the wire. The working electrode is a disk-shaped cross section of a tungsten wire, and the counter and quasi-reference (QRE) electrodes consist respectively of platinum and silver wires soldered onto the tungsten. These electrodes have withstood pressures of 340 atm at 160° C.

A typical experiment involved evacuating the cell, to which electrolyte had previously been added, followed by the addition of sufficient dry ammonia under vacuum line conditions to generate the desired pressure and density at a specified temperature. The cell was isolated from the vacuum

line by means of a high pressure valve, and removed to an armored autoclave for heating above the critical temperature ( $\sim 140^\circ\text{C}$ ) of the electrolytic solution. To probe changes in the available potential range of  $\text{NH}_3$  and the stability of solvated electrons ( $e_s^-$ ) as a function of temperature, cyclic voltammetric scans were employed (Figure 1).<sup>4</sup>

As the temperature increased, the polarizable range of the ammonia solution decreases as evidenced by a positive shift of the solvated electron peak and a negative shift of the anodic background (vs. QRE). A small shoulder preceded the onset of solvated electron production at higher temperatures which persisted when the solution was cooled back to  $-77^\circ\text{C}$  (curve D). A similar wave was observed at  $-77^\circ\text{C}$  in single compartment glass cells and thus is probably associated with the reduction of a species generated at the counter electrode. Above the critical temperature (curve C) generation of solvated electrons is still observed, although on the voltammetric time scale little, if any, oxidation is seen upon scan reversal. This can be attributed to a decrease in the stability of the solvated electrons, probably by reaction with  $\text{NH}_3$  at the higher temperatures.<sup>5</sup> Upon cooling the solution to  $77^\circ\text{C}$ , the system returns to essentially its initial condition, demonstrating no extensive contamination or irreversible changes in the solution. The apparent shift in potential of the solvated electron peak (between curves A and D) is probably caused by a change in potential of the silver wire (QRE).

To study changes in reversibility and diffusion coefficient ( $D$ ) with  $T$  and  $P$ , the reduction of *m*-chloronitrobenzene<sup>6</sup> (MCNB) was investigated; typical voltammograms are shown in Figure 2. The behavior remains essentially Nernstian as  $T$  is raised; for example, at  $160^\circ\text{C}$  a  $\Delta E_p$ -value<sup>7</sup> of 90 mV was found with a fresh solution (compared to the Nernstian value of 85 mV). However, replicate experiments at  $160^\circ\text{C}$  sometimes showed  $\Delta E_p$ -values

up to 160 mV, perhaps because of some, yet undefined, electrode surface effect. As the critical temperature is approached, the voltammograms show convective features such as an unusually shallow drop off of current past the cathodic peak current. The onset of natural convection is promoted by the low viscosity of the solution (0.024 cp at 160° C). These convective effects probably also account for the  $i_{pa}/i_{pc}$  ratio being 0.7 (rather than 1). However, normal and nearly reversible behavior is restored upon decrease in T and condensation of the solvent. Chronocoulometric experiments<sup>8</sup> involving potential steps and acquisition of data at short times (50 to 250 ms) to avoid convective problems were used to determine D as a function of T and P. The value found at 160° C and 272 atm (density, 0.40 g cm<sup>-3</sup>) was  $3 \times 10^{-4}$  cm<sup>2</sup> s<sup>-1</sup>. This value can be compared with that calculated from the D-value at -40° C ( $2.8 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>) and the change in viscosity via the Stokes-Einstein equation ( $6 \times 10^{-4}$  cm<sup>2</sup> s<sup>-1</sup>) and appears to be consistent with values of aromatic hydrocarbons in CO<sub>2</sub> at similar viscosities.<sup>9</sup> The results demonstrate the stability of the MCNB radical anion and the enhanced mass transport under supercritical conditions. Further investigations of electrochemistry of NH<sub>3</sub>, water and other fluids at near- and supercritical conditions are in progress<sup>10</sup>.

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5. (a) Jolly, W. L. "Metal-Ammonia Solutions," Lagowski, J. J.; Sienko, M. J. (eds.) Butterworths:London, 1970, p. 168; (b) The lifetime of  $e_s^-$  in supercritical metal-ammonia solutions has been estimated to be  $\sim 1$  h in glass cells. Transition metals catalyze the reaction  $e_s^- + NH_3 \rightleftharpoons NH_2^- + 1/2 H_2$  (Excess  $NH_2^-$  and  $H_2$  will form  $e_s^-$  in supercritical  $NH_3$ ). Naiditch, S. "Solutions Métal-Ammoniac, Propriétés Physicochimiques," Lepoutre, G.; Sienko, M. J. (eds.) W. A. Benjamin:New York, 1964, pp. 113-136; Schindewolf, U.; Vogelsgesang, R. Böddeker, K. W. Angew. Chem. Int. Ed. Engl. 1967, 6, 1076-1077.

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7.  $\Delta E_p$  is the difference between the anodic and cathodic peak potentials and equals about  $2.3 RT/F$  for a Nernstian process. Cathodic and anodic peak currents are  $i_{pc}$  and  $i_{pa}$ , respectively.
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10. We would like to thank David Campbell for helpful discussions. The support of this research by the National Science Foundation (CHE 8402135) and the Office of Naval Research is gratefully acknowledged.

**FIGURE CAPTIONS**

**Figure 1** Cyclic voltammograms for generation and oxidation of solvated electrons in  $\text{NH}_3$ . (a)  $-77^\circ \text{C}$ ,  $0.2 \text{ M KI}$ ; (b)  $50^\circ \text{C}$ ,  $20 \text{ atm}$ ,  $0.2 \text{ M KI}$ ; (c)  $160^\circ \text{C}$ ,  $252 \text{ atm}$ ,  $0.1 \text{ M KI}$  (supercritical); (d)  $-77^\circ \text{C}$  (after cooling from  $160^\circ \text{C}$ ),  $0.2 \text{ M KI}$ . Scan rate,  $200 \text{ mV s}^{-1}$ .

**Figure 2** Cyclic voltammograms for reduction of *m*-chloronitrobenzene (MCNB) in  $\text{NH}_3$ . (a)  $55^\circ \text{C}$ ,  $10 \text{ atm}$ ,  $8 \text{ mM MCNB}$ ,  $0.2 \text{ M KI}$  ( $\Delta E_p = 130 \text{ mV}$ ), (b)  $115^\circ \text{C}$ ,  $82 \text{ atm}$ ,  $6 \text{ mM MCNB}$ ,  $0.2 \text{ M KI}$  ( $\Delta E_p = 180 \text{ mV}$ ); (c)  $160^\circ \text{C}$ ,  $265 \text{ atm}$ ,  $5 \text{ mM MCNB}$ ,  $0.1 \text{ M KI}$  ( $\Delta E_p = 160 \text{ mV}$ ); (d)  $25^\circ \text{C}$  (after cooling from  $160^\circ \text{C}$ ),  $10 \text{ atm}$ ,  $8 \text{ mM MCNB}$ ,  $0.2 \text{ M KI}$  ( $\Delta E_p = 120 \text{ mV}$ ). Scan rate,  $500 \text{ mV s}^{-1}$ .

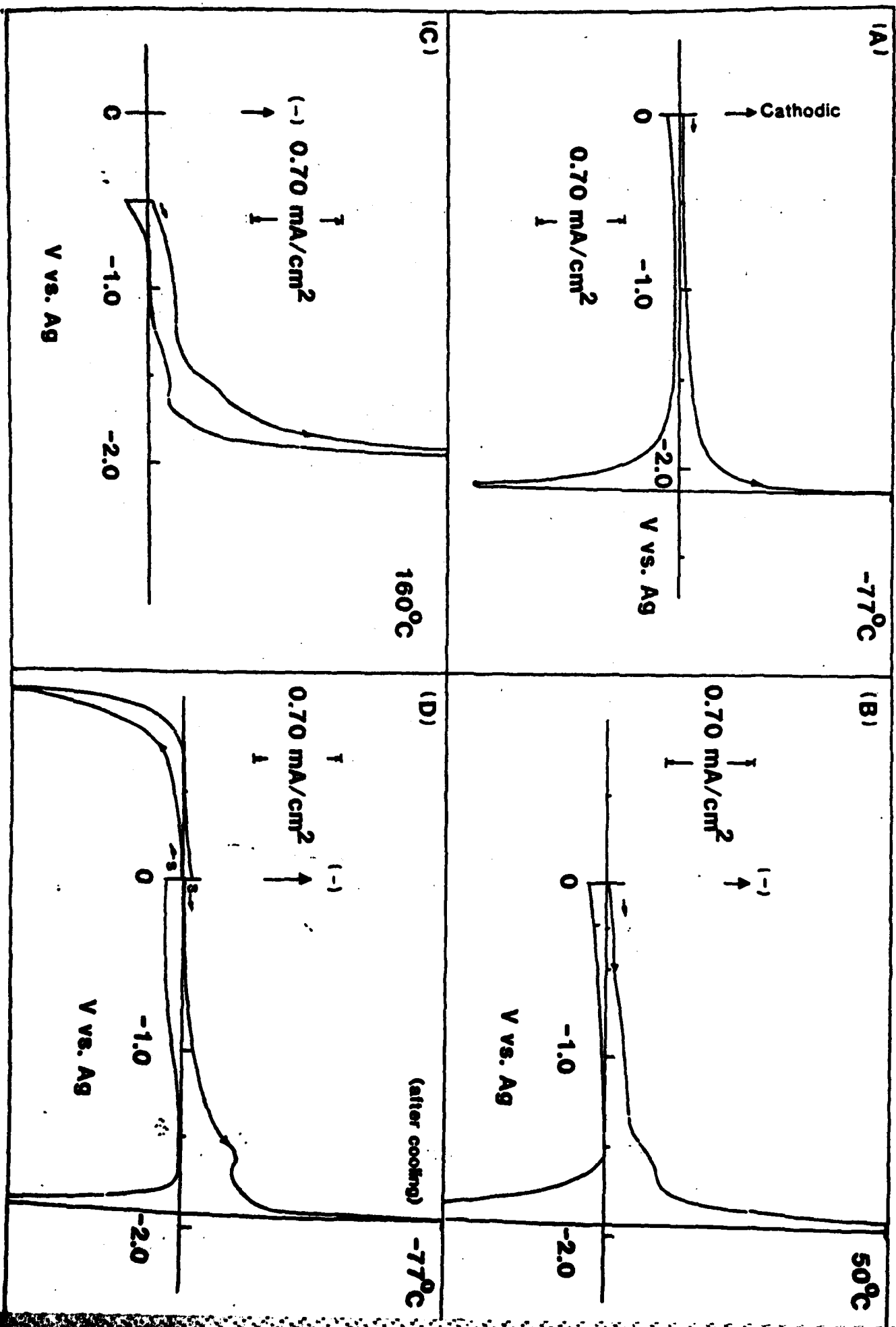


Fig. 1

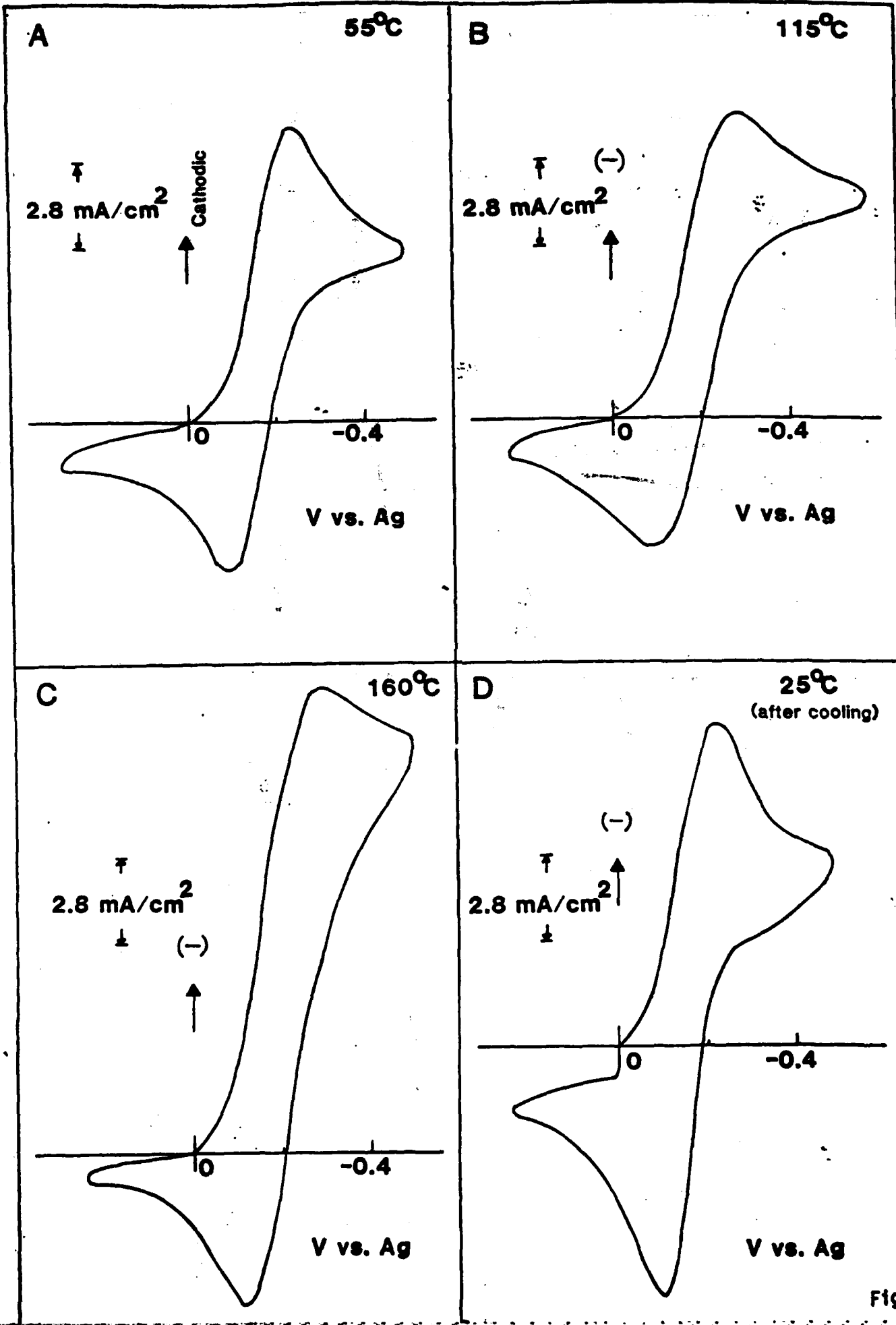


Fig. 2