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Development of New Intercalated Cathode Materials
for Use in Sodium Batteries

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Final Report

This report describes progress during the past six months, June-December 1981. In the June 1981 report, we observed that after cell cycling using $Na_xA_yTiS_2$ cathodes (where A = Cs, Rb or K), almost all the co-intercalant in these compounds is found in the auxiliary liquid electrolyte (1M NaI in triglyme). It was also observed that the amount of calcium lost to the triglyme-based liquid auxiliary electrolyte was much smaller ($\sim 4\%$) from a $Ca_{0.1}TiS_2$ cathode. Therefore further cycling studies with Ca_yTiS_2 (y = 0.1 and 0.2) cathodes have been undertaken.

Recently it was reported that more than 1 eq. Li^+ could reversibly intercalate into a $Na_{0.1}CrS_2$ cathode, with higher voltage for $Li/Li_xNa_{0.1}CrS_2$ cells ($\sim 0.67 - 0.25$ v higher when x = 0 - 0.75) than those obtained from Li/Li_xTiS_2 cells. Therefore, as part of our investigation of other cathode materials, potassium thiochromite, sodium thiochromite, and $Ti_{0.5}V_{0.5}S_2$ have been prepared and used in cycling studies. In addition, some electrochemical studies with polymer electrolyte (PEO-NaSCN) cells have also been attempted.

A. Preparation and Characterization of the Cathode Materials

Equimolar mixture of K_2S and Cr_2S_3 was sealed in an evacuated quartz tube and slowly heated ($\sim 50^\circ C/hr$) in a tubular furnace to $\sim 700^\circ C$ to prepare potassium thiochromite. After about 4 days at

this temperature, the quartz tube containing the sulfide mixture broke (in one experiment it exploded) when it was removed from the furnace. The $K_2S + Cr_2S_3$ mixture apparently reacts with the quartz tube. Subsequently, potassium thiochromite was prepared using the method described by Rüdorff and Stegemann[2]. Cr_2O_3 and KCNS (weight ratio 1:30) mixture was heated to $\sim 900^\circ C$ in an alumina crucible covered with a lid and maintained at this temperature for about one hour. The product was furnace cooled, washed with a 10% KOH solution in water, filtered and then washed with distilled water, ethyl alcohol and ether, in the given sequence. It was then dried at room temperature in vacuum ($\sim 20\text{-}30$ millitor) for about 4 hours.

Sodium thiochromite was prepared by heating a mixture of K_2CrO_4, Na_2CO_3 and sulfur in the weight ratio 1:15:15 to $\sim 800^\circ C$ and keeping it at this temperature for about one hour. After furnace cooling, the product was washed with a dilute NaOH solution in water, then with water and ethyl alcohol and finally with ether. It was then dried, at room temperature, in vacuum for about 4 hours.

$Ti_{0.5}V_{0.5}S_2$ was prepared by reacting titanium, vanadium and sulfur in required proportions, at $\sim 900^\circ C$ for 3-4 days, followed by annealing at $\sim 530^\circ C$ for about 3 days. The method of preparation of Ca_yTiS_2 compounds has already been described in the previous report.

The potassium - and sodium thiochromites were characterized using Debye-Scherrer technique, atomic absorption spectroscopy and X-ray fluorescence analysis. The Debye-Scherrer powder pattern of

"KCrS$_2$" shows the reported reflections[3] for KCrS$_2$ and many more. Some of these extra lines could be identified as KCr$_5$S$_8$. The additional phase(s) present in our compound could not be identified. Rüdorff has reported that KCrS$_2$ can decompose during washing of the powder and that there may exist other potassium thiochromites. Atomic absorption spectroscopic analysis for potassium determined the composition to be K$_{0.61}$CrS$_2$. However, the analysis done using X-ray fluorescence technique gave S = 58.59 at %, K = 22.39 at % and Cr = 19.02 at %. In view of our long experience of using atomic absorption spectroscopy, the composition determined by this technique may be more reliable.

All the lines on the Debye-Scherrer pattern for the "NaCrS$_2$" matched with those reported[4] and no extra lines were observed. The X-ray fluorescence technique gave its analysis as Na - 21.09 at %, Cr - 19.85 at % and S - 59.06 at %. The atomic absorption spectroscopic analysis for sodium gave the composition as Na$_{0.92}$CrS$_2$.

B.   Cycling Studies

The same cell design as described in our June 1981 report was used in the cycling studies. All cycling studies were carried out at 130 ± 5°C in a galvanostatic mode. The cell voltage during discharge or charge was continuously measured with the help of a Keithly 630 electrometer (input impedance $\sim 10^{14}$ ohms) hooked up to a chart recorder or with a Tigraph 100 (6 channel chart recorder, input impedance $\sim 10^7$ ohms).

The discharge and charge behaviour of a Ca$_{0.1}$TiS$_2$ cathode in a galvanostatic mode at a current density of 0.95 mA/cm^2 is

shown in Fig. 1. During the discharge, the cell voltage drops sharply by $\sim$ 0.2 V at the beginning of discharge and then drops gradually until about x $\simeq$ 0.8, after which it changes very slowly from 1.1 V at x = 0.8 to 1.02 V at x $\simeq$ 1.45 (the value of x in $Na_xCa_{0.1}TiS_2$ has been calculated from coulombs passed) when discharge was stopped and the charge cycle began. During recharge, the cell voltage remains almost unchanged when x < 0.4. A similar observation was made earlier with recharge of other co-intercalated electrodes (see June 1981 report).

Fig. 2 shows the discharge and charge behaviour of a $Ca_{0.2}TiS_2$ cathode in a galvanostatic mode. The features of discharge and charge curves in this figure are similar to those of the discharge and charge curves for a $Ca_{0.1}TiS_2$ cathode (Fig. 1). After an initial sharp drop of 0.1V at the beginning of the 1st discharge, the cell voltage drops gradually until x $\simeq$ 0.75. The cell voltage remains practically constant at $\sim$ 1 V from this point onwards until x $\simeq$ 1.5. During the first charge half cycle, the voltage remains practically unchanged at $\sim$ 2.5 V when x < 0.45. During the second and third discharge, the cell voltage changes very slowly from $\sim$ 1.3 V at x $\simeq$ 0.6 to $\sim$ 1.1 V at x $\simeq$ 1.4. During second recharge, the cell voltage remains unchanged at $\sim$ 2.5 V when x < 0.3. The cell voltages during the first discharge of $Ca_{0.1}TiS_2$ and $Ca_{0.2}TiS_2$ cathodes at x = 0.2, 0.4, 0.6, 0.8 id 1.0 are 1.76 and 1.81, 1.44 and 1.45, 1.33 and 1.22, 1.11 and 1.01, and 1.10 and 1.00 V, respectively. Thus, there is practically no difference in the discharge behaviours of these two cathodes.

Fig. 3 shows the cycling behaviour, in a galvanostatic mode of the $K_{0.61}CrS_2$ electrode. The initial cell voltage of 2.33 V

drops rapidly in the initial stages of discharge and reaches a value of $\sim 0.75V$ at $x \simeq 0.16$. After this the decrease in voltage is slow until about $x \simeq 0.85$, after which it drops sharply to zero and becomes even negative (~ -0.2 V). During the first charge, the cell voltage reaches a maximum (~ 2.6 V) when $x \simeq 0.8$ and then decreases slightly and remains almost unchanged at 2.5 V when $x < 0.4$. During the second discharge, the decrease in voltage is not as rapid, and the second recharge curve does not show a plateau towards the end of recharge. Analysis of the liquid electrolyte at the end of the second recharge showed that ~ 94 % of the potassium in $K_{0.61}CrS_2$ was present in the electrolyte. The color of the electrolyte at the end of the experiment was like that of red wine. During experiment, it was observed that the color becomes lighter during discharge and deeper during charge half cycle.

Fig. 4 shows the discharge and charge behaviour of $K_{0.61}CrS_2$ mixed with graphite (60 wt % $K_{0.61}CrS_2$ + 40 % graphite). The features of the first discharge and charge curves are similar to those of first discharge and charge curves in Fig. 3. But the discharge proceeds at a higher voltage, probably due to improved conductivity of the cathode.

Cycling studies with $Na_{0.92}CrS_2$ cathode were also attempted. It has been reported[1] that $NaCrS_2$ is not a good electronic conductor (specific resistivity $\simeq 10^5$ ohm.cm). The cathode in the cycling cell, therefore, consisted of 60 wt % $Na_{0.92}CrS_2$ and 40 wt % graphite. When the cell was charged in a galvanostatic mode at a current density of 0.63 mA/cm^2, the cell voltage

increased instantaneously from the initial value of $\sim$ 2.4 V to $\sim$ 2.75 V and then decreased to $\sim$ 2.62 V and remained almost unchanged for the remaining duration of the charge. The discharge of the cell was then attempted when the value of x in Na_xCrS_2 was $\simeq$ 0 (as calculated from the coulombs passed). On beginning the discharge of the cell, the voltage dropped to zero in less than one minute and then it became even negative. Similar behaviour was observed when the cathode pellet did not contain any graphite. The color of the electrolyte turned orange during the experiment, which indicates a reaction with the electrolyte.

Fig. 5 shows a partial discharge of an $Na_xTi_{0.5}V_{0.5}S_2$ cathode. The cell voltage decreased to 0.86 V when the discharge was stopped at x $\simeq$ 0.7. No further studies have been made with this cathode.

The characteristics of the discharge and charge curves shown in Figs. 1-5, the coloration of the electrolyte and its chemical analysis after cell cycling, all indicate that reactions occur between the liquid triglyme-based electrolyte and the cathode material. A cyclic voltammetric study was performed using the 1M NaI solution in triglyme (vacuum distilled and then passed through neutral alumina) as the electrolyte, sodium reference and counter electrodes and platinum as the working electrode (area = 1.96 x 10^{-3} cm^2). The result is shown in Fig. 6. Peaks ($\sim$ 60 µA at 1.33V and 0.35 µA at 0.9 V) in the potential vs. current plot indicate reactions within the electrolyte. It is not possible to say what these reactions are. Fig. 6 also indicates that the electrolyte cannot be used above $\sim$ 2.65 V.

C. Other Electrochemical Cell Studies

Open circuit voltages using $Na_{0.86}TiS_2$, $Na_{0.36}TiS_2$, $Na_{0.32}TiS_2$, $Na_{0.2}TiS_2$ and $Na_{0.03}TiS_2$ cathodes were measured at 70-90°C using a PEO-NaSCN solid electrolyte. The results are in fair agreement (± 0.005 to 0.05 V) with those obtained with β''-Al_2O_3 cells at 120-130°C. Although the transference number of Na^+ in the PEO-NaSCN film has been reported[5] to be unity, the resistance of our cells, obtained using a complex impedance method, is $\sim 10^5$ ohms at 93°C. Therefore these cells cannot be used for cycling studies at current densities greater than $\sim$ 15-20 µA/cm^2.

Summary

Cycling studies with $K_{0.61}CrS_2$ electrodes showed that potassium is lost to the liquid, triglyme-based auxiliary electrolyte. The values of x in excess of unity in $Na_xCa_yTiS_2$ obtained during discharge of cells with $Ca_{0.1}TiS_2$ and $Ca_{0.2}TiS_2$ cathodes are most probably due to reactions with the liquid auxiliary electrolyte, as indicated by the results of cyclic voltammetry (Fig. 6). As this stage, it is unclear whether the loss of the co-intercalant, A, from an $AyTiS_2$ cathode (where A = Cs, Rb, K) or of potassium from a $KyCrS_2$ cathode to the liquid auxiliary electrolyte during cell cycling is due to some intrinsic factor related to the co-intercalated electrode material or to the triglyme-based auxiliary electrolyte. Further cycling studies with cells with another liquid auxiliary electrolyte or with cells with only a solid electrolyte, e.g. β''-Al_2O_3, may help clarify this.

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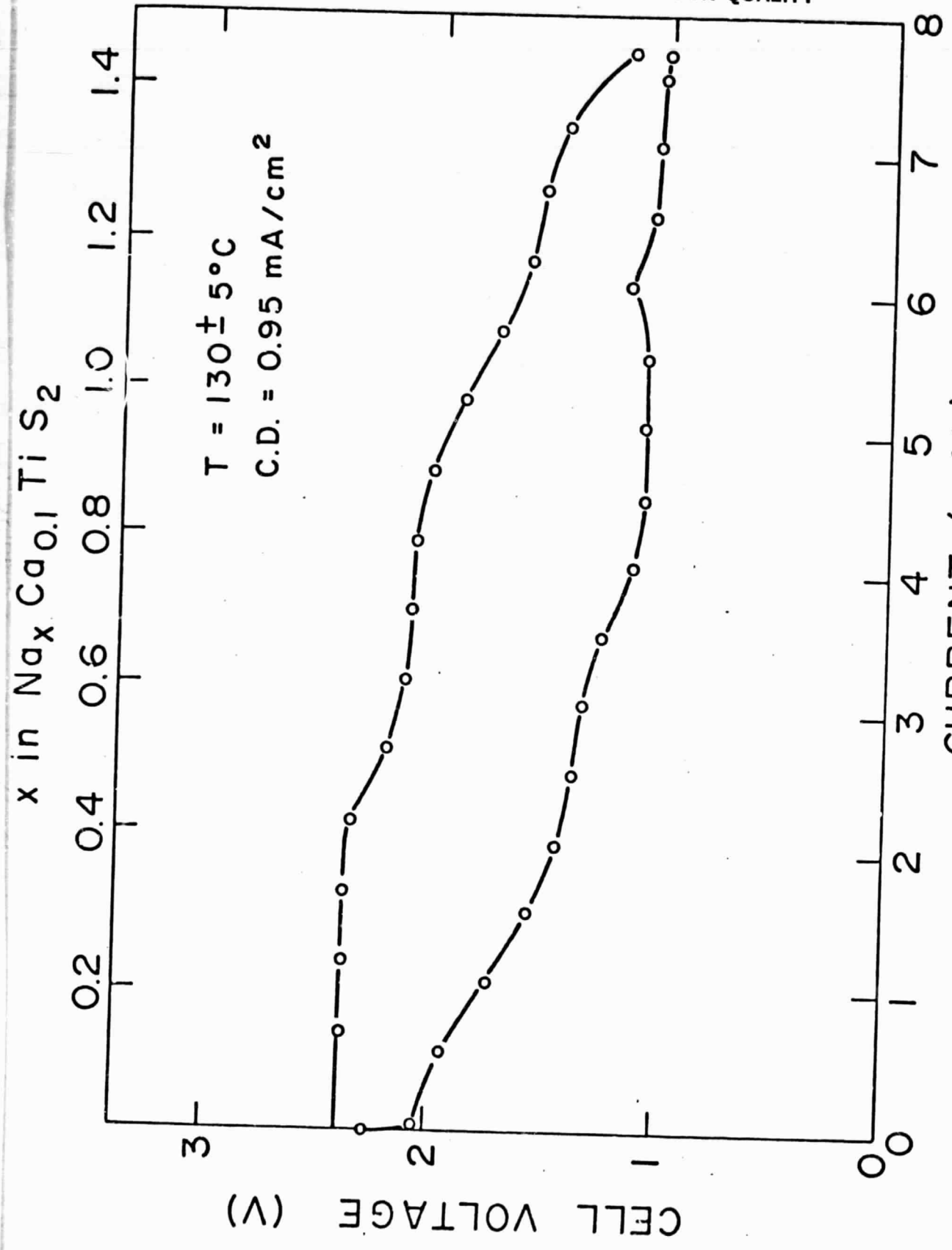
Fig. 1. Galvanostatic discharge and charge behaviour of a $Ca_{0.1}TiS_2$ Cathode.
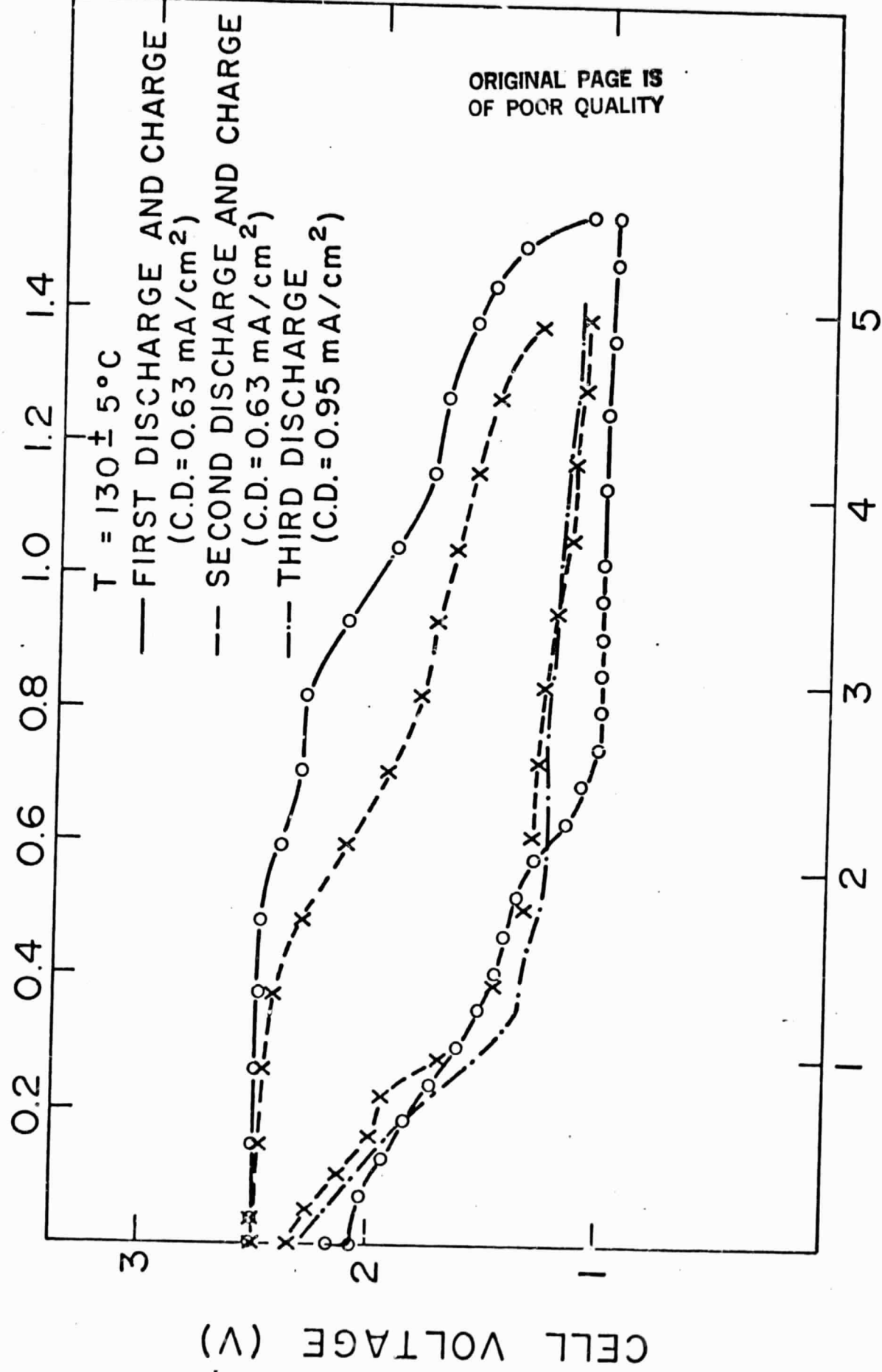
Fig. 2. Cycling behaviour of a $Ca_{0.2}TiS_2$ cathode
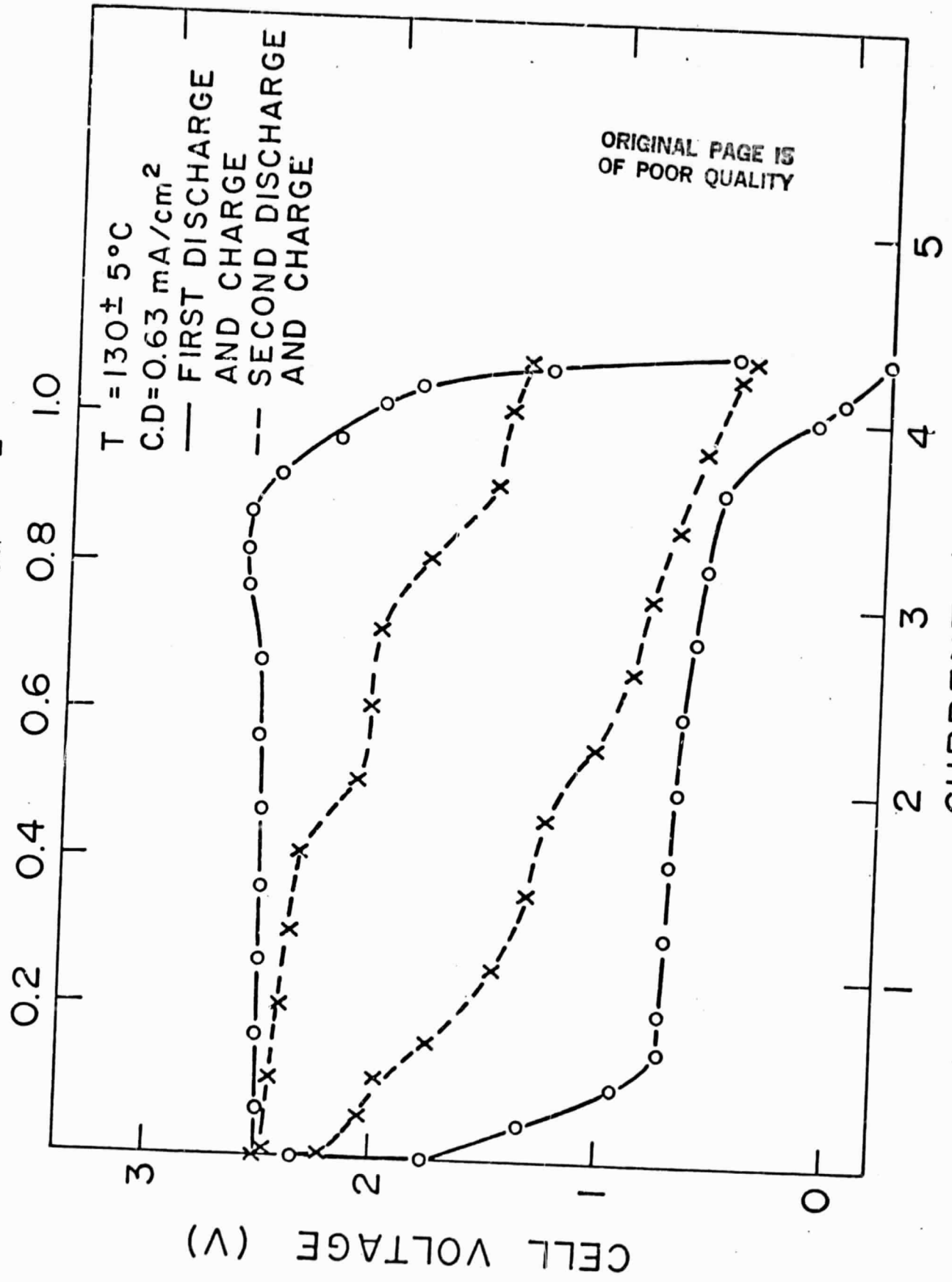
Fig. 3. Cycling behaviour of a $K_{0.6}CrS_2$ cathode
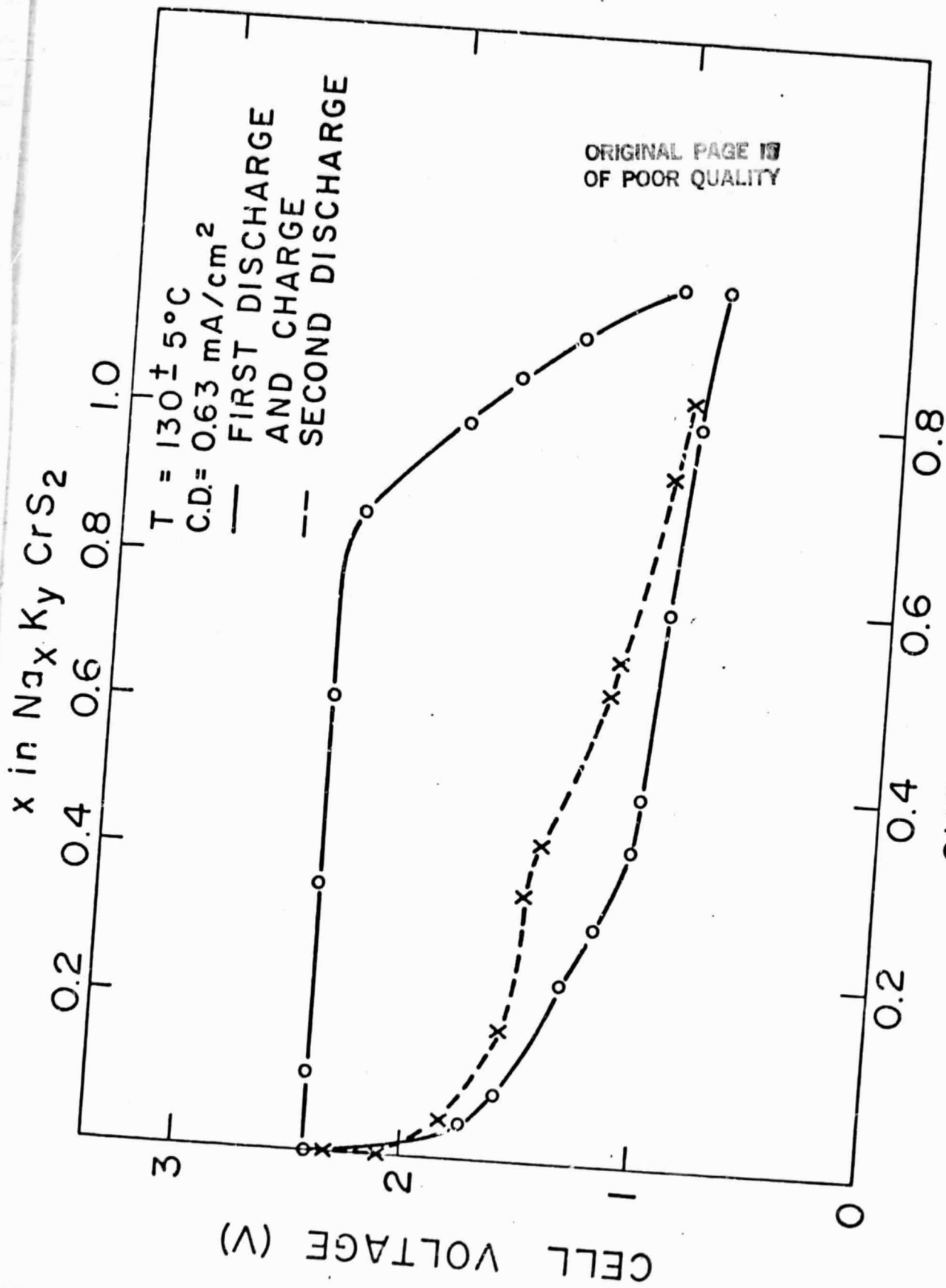
Fig. 4. Cycling behaviour a $K_{0.61}CrS_2$ (+ graphite) cathode

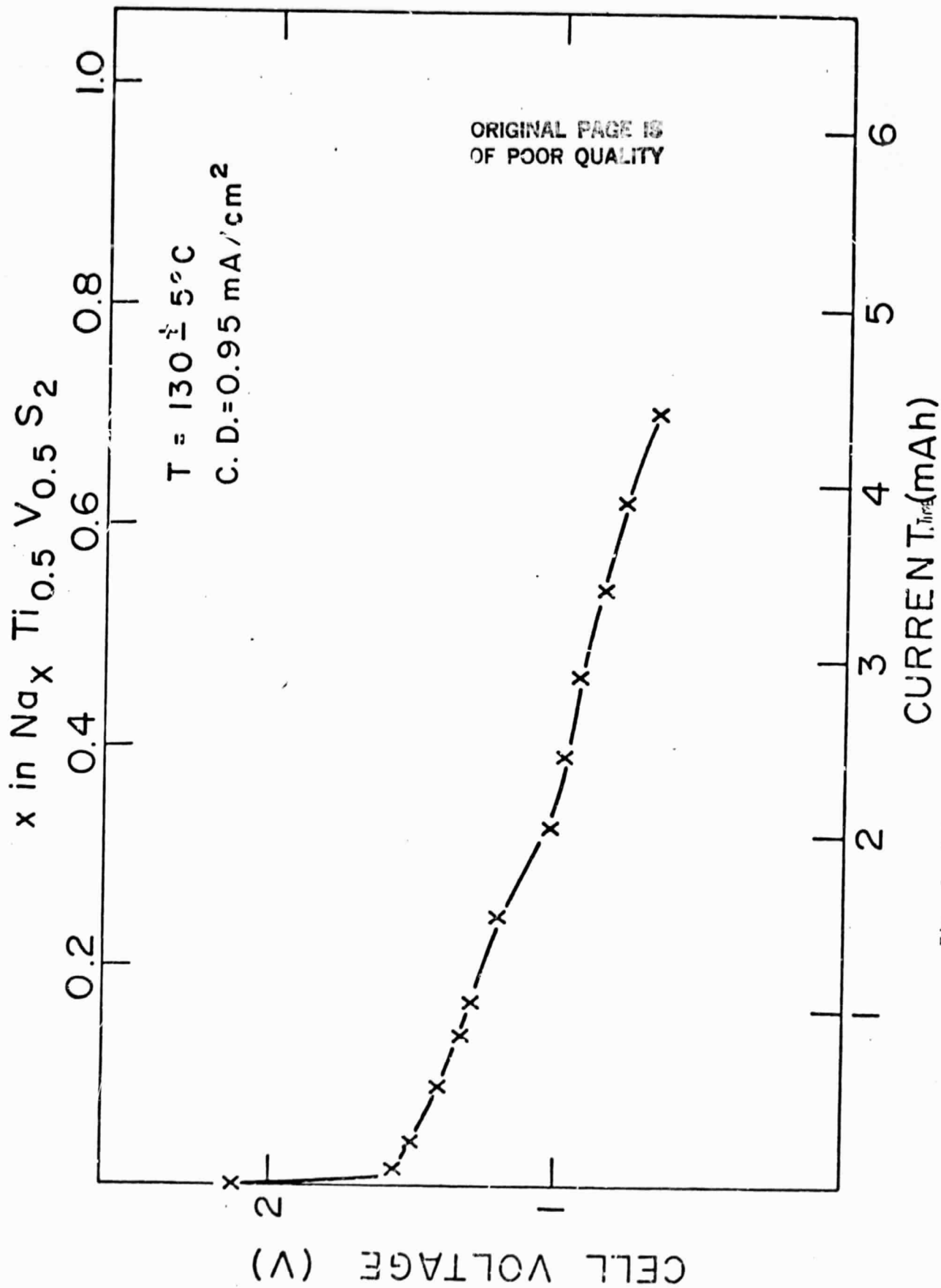Fig. 5. Galvanostatic discharge behaviour of a $Ti_{0.5}V_{0.5}S_2$ cathode
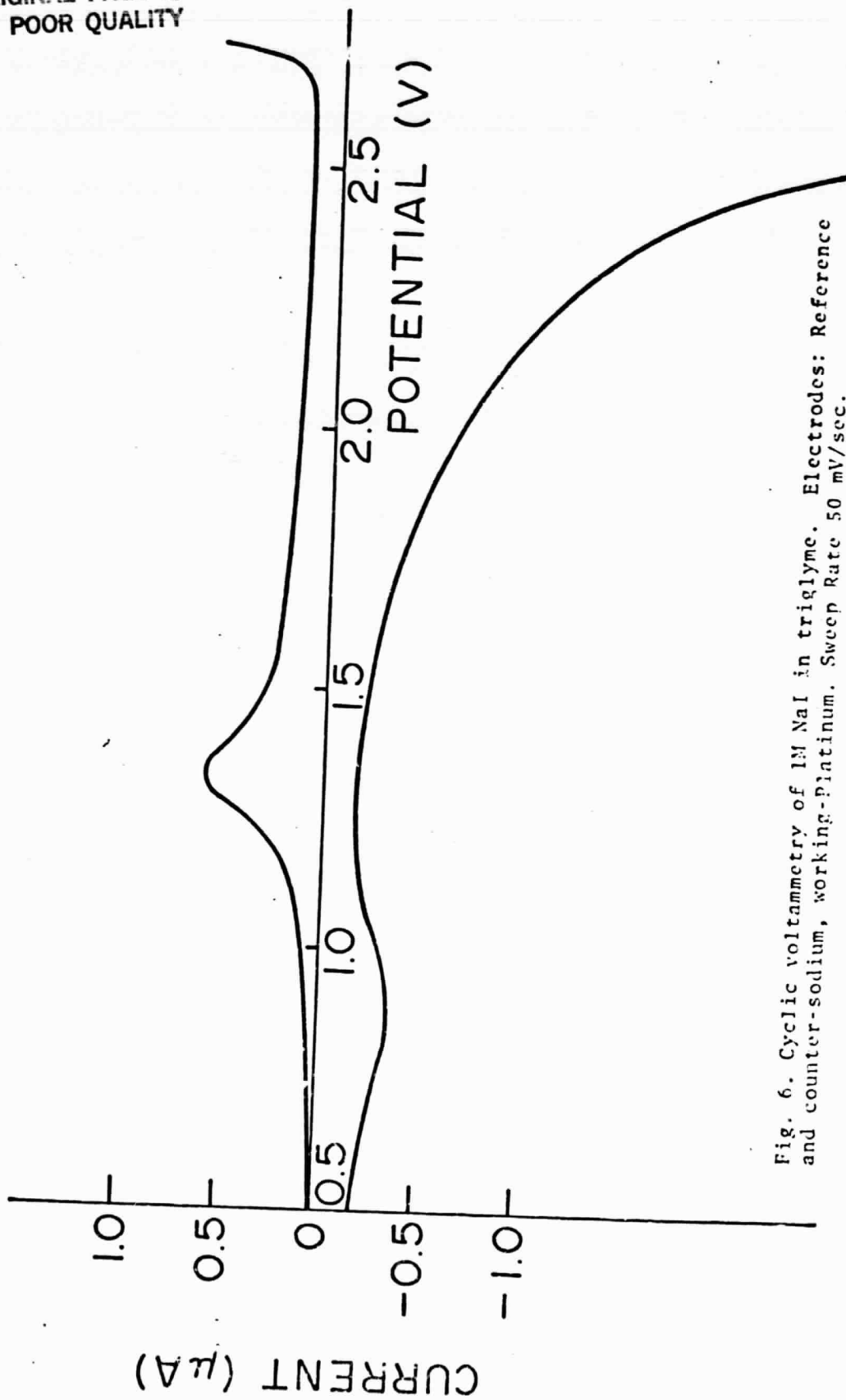
Fig. 6. Cyclic voltammetry of 1M NaI in triglyme. Electrodes: Reference and counter-sodium, working-platinum. Sweep Rate 50 mV/sec.