

## SHORT COMMUNICATION

***Cyclic voltammetry test for the effectiveness of cathode additives in the sodium–sulphur battery***

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**1. Introduction**

The sodium–sulphur battery may have an important role in future electrochemical energy storage systems [1]. However, the recharging process has been found to be one of the critical factors among the technological problems that have still to be solved for the reliability of this high temperature (350°C) battery. During this process the battery capacity has often been found to suffer serious limitations because of deleterious local accumulation of the insulating liquid sulphur produced in the biphasic (polysulphide–sulphur) regime [2–4].

Several approaches have been adopted to avoid or reduce this phenomenon. For example, by an appropriate design of the sulphur electrode it has been found possible to effect suitable control of the spatial distribution of sulphur formation on the carbon graphite mat during battery recharging [5–7].

Fisher *et al.* attempted to increase the rechargability by decreasing the viscosity of the sulphur by adding small amounts of selenium and B<sub>2</sub>S<sub>3</sub> to the cathode [8] or by producing a charge-transfer complex for the native sulphur with tetracyanoethylene (TCNE) additive [9].

Several surface treatments of the current-collecting graphite felts have also been tested [10, 11] in an attempt to obtain preferential ionic polysulphide wetting at the electrode surface from which the native sulphur should be removed. Generally, the effectiveness of the additives or of the surface electrode treatments has been examined by statistical investigation of experimental sodium–sulphur single cell behaviour during operation under some definite discharge–recharge cycling process [8, 9, 11].

However, to evaluate a candidate additive such a procedure is expensive and time consum-

ing, at least for a ‘screening’ selection. This work deals with an approach giving a fast diagnosis of the depolarizing properties of additives by cyclic voltammetry (CV). In fact, this technique is a very powerful method of understanding the mechanisms of the electrode reactions [12] and has been successfully used for the molten polysulphide–sulphur redox system on graphite electrodes [4, 13, 14].

**2. Experimental procedure****2.1. Molten polysulphide electrolyte preparation**

The manipulation of the reagents and the assembly of the cell were performed in a stainless-steel glove box with an inert and dried atmosphere obtained by recirculating the argon cover gas through molecular sieves (moisture was maintained below 5 p.p.m.). Stoichiometric quantities of Na<sub>2</sub>S (Ventron Alpha Inorg. Div.) and precipitated sulphur (BDH lab. reagent) were mixed in a mortar.

TCNE is a typical electron ‘acceptor’, forming molecular complexes with ‘donor’ species. The electron is transferred to the  $\pi^*$  antibonding orbital of the ethylenic double bond, whose strength is then reduced (sacrificial-type acceptance). The TCNE used in this work was the Carlo Erba RPE grade reagent (98.5% purity).

**2.2. Electrochemical cell and instrumentation**

Fig. 1 shows the exploded view of the three-electrode cell assembly employed in this work. The molten polysulphides were contained in a vitreous carbon crucible (Atomergic Chementals) acting as counter electrode. It was possible to fill this crucible by melting the voluminous powder mixture placed both in the crucible and in an open

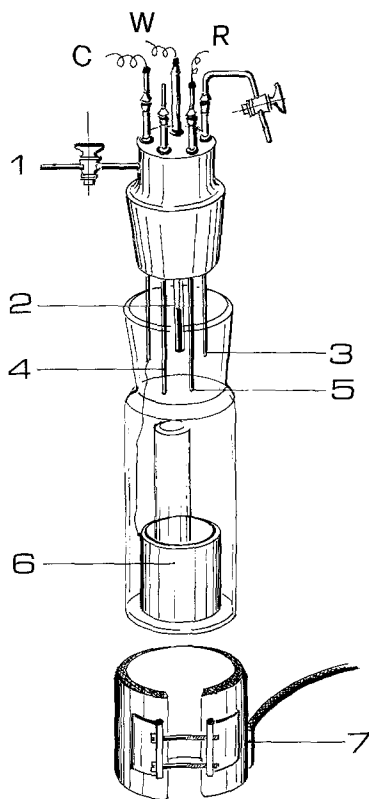


Fig. 1. The glassy carbon cell used for CV of molten polysulphides. 1, Inert gas inlet; 2, glassy carbon rod (working electrode W); 3, inert gas outlet tube; 4, temperature probe; 5, thin grafoil (flexible graphite) probe (reference electrode R); 6, glassy carbon crucible (counter electrode C); 7, heating element.

Pyrex tube within the closed cell (Fig. 1) under controlled environmental conditions. The reference electrode was a thin flexible graphite strip probe following South *et al.* [13]. The working electrode was made by sealing a vitreous carbon rod (Atomergic Chemicals) into a Pyrex tube. The circular surface of this electrode of area  $0.075 \text{ cm}^2$  was polished with diamond paste.

The CV waves were obtained by an EGC/PAR Potentiostat mod. 173 modulated by a mod. 175 Universal Programmer. The signals were recorded by a mod. 4102 device and plotted on a X-Y Houston 2000 Recorder.

### 3. Cyclic voltammetry of the $\text{Na}_2\text{S}_4/\text{C}$ system

As mentioned above, much experimental and speculative work has been performed on the voltammetric behaviour of melt polysulphides on graphite working electrodes. We reproduced

the CV waves (Fig. 2A) already reported for the  $\text{Na}_2\text{S}_4$  melt on glassy carbon microelectrodes [4]. Clearly detected, in particular, was the 'blocking' of the anodic current during the positive potential scanning, which is due to elemental sulphur nucleation at the electrode surface [4].

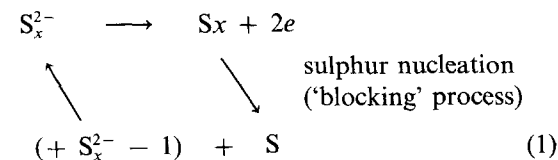
We also confirmed that after deep cathodic potential scanning a kinetic effect reduces the 'blocking effect' on the succeeding anodic potential scanning (Fig. 2B), probably the action of a catalytic process due to a reduced sulphide species adsorbed on the electrode surface [4]. We avoided such a situation by cycling the electrode potential within a few hundred microvolts versus  $\text{Na}_2\text{S}_4/\text{C}$  in the cathodic direction. In this range a reasonably constant ohmic drop ( $R = 5 \Omega$ ) was measured by means of an a.c. impedance bridge.

Since current ( $i$ ) variation with uncorrected electrode potential ( $E'$ ) is linear in this zone, both the corrected working electrode potential ( $E = E' - Ri$ ) and the potential scan rate ( $v = v' - Ri/t$ ) could be evaluated. Anodizing out of this range results in the 'blocking effect' being accompanied by a sudden ohmic drop producing a current signal which is not explicable by the CV theory.

By limiting to a small polarization field the CV diagnostic criteria could be employed using the current density values at given electrode potentials instead of the peak currents.

In Fig. 3 we have plotted the values of the parameter  $i/(Av^3)$  versus  $v^2$  for three corrected potential levels. The catalytic contribution is clearly occurring for potential scan rates below  $0.1 \text{ V s}^{-1}$ .

In spite of the complexity of the molten polysulphide oxidation mechanism, the oversimplified multistep anodic reaction path (1) should be assumed to occur [4], with  $x$  ranging from 3 to 5, and where the less oxidized sulphide species induce a regeneration of the electroactive species:



coupled catalytic reaction.

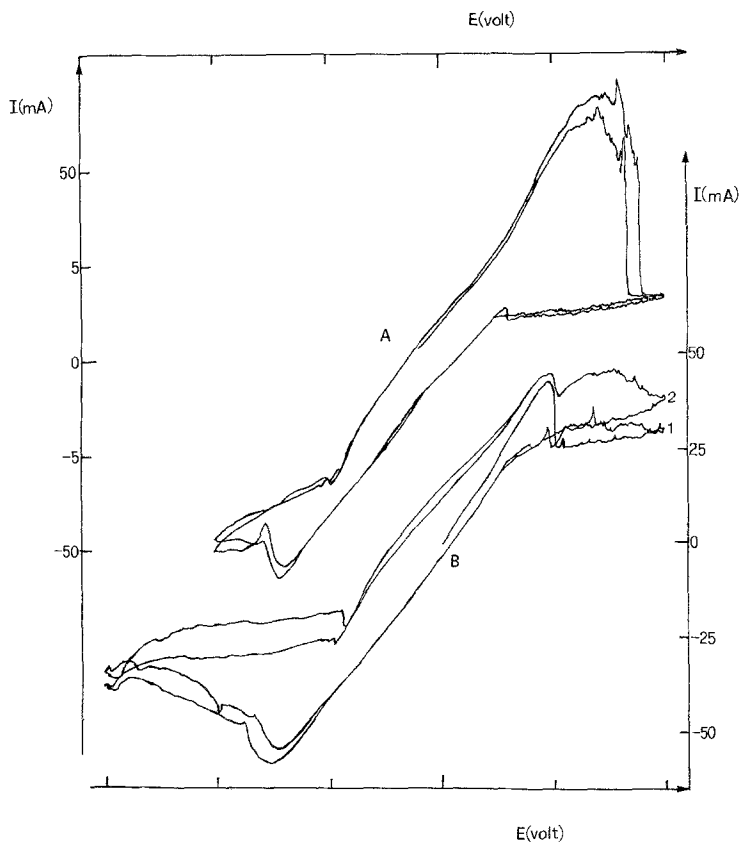


Fig. 2. (A) CV signals for  $\text{Na}_2\text{S}_4$  at  $350^\circ\text{C}$ ,  $\nu = 0.1 \text{ V s}^{-1}$ , (B) CV signals under the same conditions as (A), but with a cathodic potential limit of  $-1.5 \text{ V}$  versus  $\text{Na}_2\text{S}_4/\text{C}$  reference electrode.

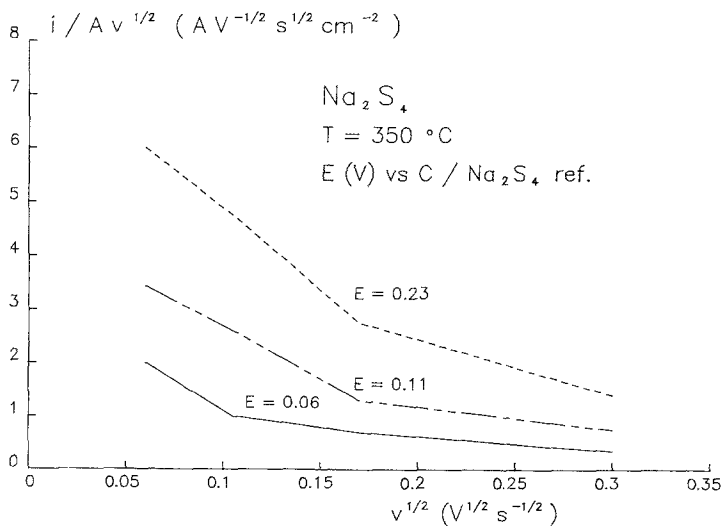


Fig. 3. CV-working curves showing the catalytic current contribution at three electrode potentials on the anodic step for  $\text{Na}_2\text{S}_4$  oxidation at a vitreous carbon electrode ( $350^\circ\text{C}$ ).

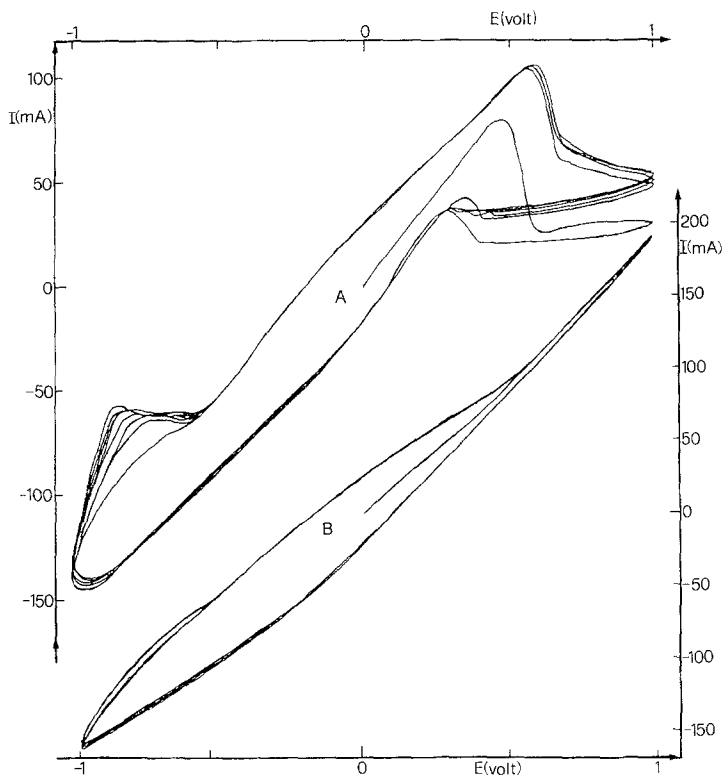


Fig. 4. (A) CV signals for pure  $\text{Na}_2\text{S}_4$  at  $350^\circ\text{C}$ ,  $v = 1 \text{ V s}^{-1}$ . First potential scan (1) in the anodic direction. (B) CV signals under the same conditions as (A), but with 1% TCNE added to the melt.

The results reported in Fig. 3 show, on a quantitative basis that only for electrode scan rates greater than  $0.2 \text{ V s}^{-1}$  does the autocatalytic coupled process not affect the CV signal of the  $\text{Na}_2\text{S}_4$  oxidation process. In these conditions the CV waves were found to be reproducible within  $\sim 10\%$  by using several working electrodes. By repetitive triangular scanning of the electrode potential more reliable and clearer CV signals were obtained.

#### 4. The TCNE effect

Spectacular evidence of the presence of TCNE in the polysulphide bath is shown in Fig. 4, in which repeated CV signals for pure  $\text{Na}_2\text{S}_4$  (A) and for  $\text{Na}_2\text{S}_4 + 1\%$  TCNE (B) systems are plotted. The CV waves were obtained using the conditions described in Section 3 to avoid coupled chemical effects.

The anodic blocking process disappears for electrode scan rates greater than  $0.1 \text{ V s}^{-1}$ , even for deep anodic polarizations to  $+1.7 \text{ V}$  versus

$\text{Na}_2\text{S}_4/\text{C}$  (graphite) reference electrode (with no ohmic correction). At lower scan rates the blocking effect still occurs but at measured anodic current densities much higher than the typical ones for the pure  $\text{Na}_2\text{S}_4$  melt.

With repetitive scanning of electrode potential in a deeper cathodic direction, where the  $\text{Na}_2\text{S}_2$  film is produced on the vitreous carbon microelectrode surface [4], the polarizing effectiveness of the TCNE slowly decreases, as is shown in Fig. 5 where a typical CV signal is reported whose qualitative features were reproducibly obtained. It is well known that TCNE may be easily reduced to tetracyanoethane in a protonating medium [15].

Our observations give an indication that some irreversible reduction of TCNE could be occurring in  $\text{Na}_2\text{S}_4$ , inducing a decrease of the depolarizing effectiveness. This point is of technological interest and a quantitative evaluation of the TCNE degrading performance in service-simulating conditions is under investigation.

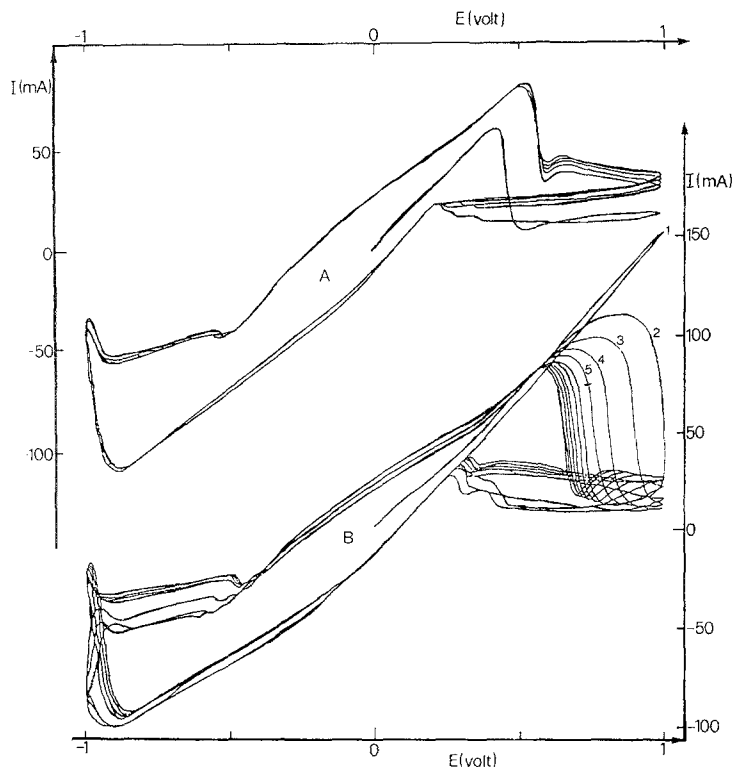


Fig. 5. (A) CV signals for pure  $\text{Na}_2\text{S}_4$  at  $350^\circ\text{C}$ ,  $v = 0.5 \text{ V s}^{-1}$ . First potential scan (1) in the anodic direction, (B) CV signals under the same conditions as (A), but with 1% TCNE added to the melt. The TCNE effect disappears after about 10 triangular potential scanning cycles.

## 5. Conclusion

In this preliminary note we demonstrate the effectiveness of the simple CV technique to examine the depolarizing process of candidate additives for the sulphur electrode of the Na/S (beta) battery.

In spite of the complexity of the actual electrochemical process in polysulphide melt redox systems, use of CV on a stationary vitreous carbon microelectrode leads to significant qualitative information and semiquantitative evaluation may be possible using comparative analysis.

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