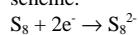


The Electrochemical Reduction of Sulfur in Dimethylformamide

A.Evans^a, M.I.Montenegro^a and D.Pletcher^b

^a IBQF – Centro de Química, Universidade do Minho, Braga, Portugal
^b University of Southampton, Dept of Chemistry, Southampton, England

The electrochemical reduction of sulfur has attracted much interest over the past few decades^{1,2,3}. However, to this day uncertainty still remains as to the exact reduction mechanism and identity of species produced in this system. Work carried out by Martin *et al*¹ at the beginning of the 1970's gave some insight into the reduction process. The cyclic voltammograms that they obtained at a gold electrode in dimethylsulfoxide exhibited a first irreversible reduction peak at -0.6 V followed by a reversible second reduction peak at -1.17 V. It was concluded from this work that the irreversibility of the 1st reduction peak was due to a change in structure from cyclic sulfur to linear chain sulfur. This conformation change was envisaged as enabling greater stabilization of the negative charge. The reduction followed the general scheme:



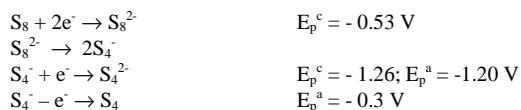
In order to get further information on the reduction mechanism cyclic voltammetry, square wave voltammetry, steady state voltammetry and controlled potential bulk electrolysis were used.

A typical cyclic voltammogram obtained at a vitreous carbon electrode can be seen in figure 1. Cathodic peaks are observed at potentials of -0.53 V and -1.26 V, anodic peaks are seen at potentials of -1.20 V, -0.76 V and -0.3 V. The irreversible cathodic peak at -0.53 V is associated with the anodic peak at -0.3 V (as shown by wave clipping) and is a two-electron system. The reversible cathodic peak at -1.26 V has its counterpart at -1.20 V and, contrary to previous thinking, the present work suggests that it is a one-electron system. The small anodic peak at -0.76 V is only seen when the scan is reversed at potentials more negative than -2.1 V.

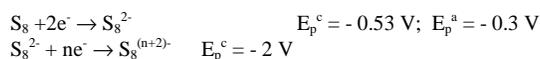
When the solution of sulfur in DMF is cooled to sub-zero temperatures, the shape of the voltammograms changes as can be seen in figure 2. As the temperature decreases the second reduction peak at -1.50 V (vs. a Pt wire reference) diminishes in size and a new peak at -2 V appears. This decrease in the peak size at low temperatures surely indicates the presence of a kinetic step between the two reduction processes. Microelectrode experiments at high sweep rates (200 – 1000 V/s) concur with these results.

Figure 3 shows the effect of scan rate on the reduction of sulfur at 0°C. Bulk electrolysis of a sulfur solution shows different colours throughout the duration of the electrolysis. This variation in colours in most probably due to the changing concentration of different sulfur species during the electrolysis.

With the results gathered so far the following mechanism for the reduction of elemental sulfur in DMF at room temperature can be postulated:



However at low temperatures the kinetic step does not occur and the mechanism can be written as:



Future work includes environmentally clean synthesis of polysulfide molecules using intermediates formed in this reduction process.

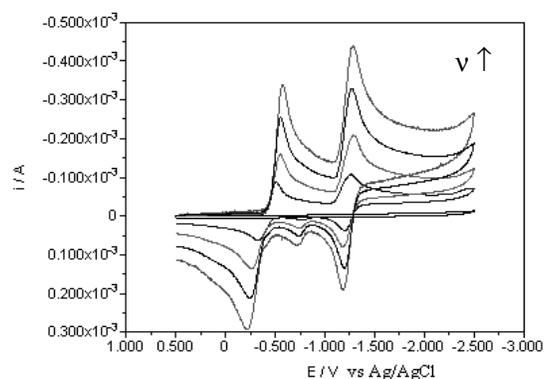


Figure 1. Cyclic voltammogram of a solution of 2mM sulfur in DMF (0.1M TBAB) at four scan rates between 0.05 and 1 V/s at a vitreous carbon electrode. Blank also shown.

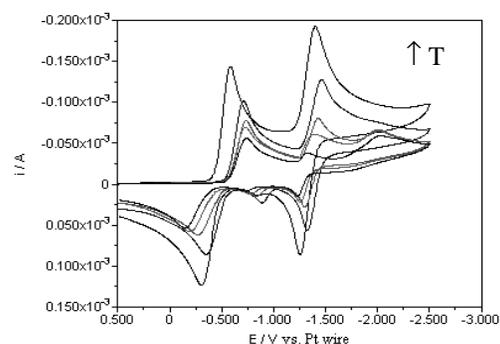


Figure 2. Cyclic voltammograms of a solution of 2mM sulfur in DMF (0.1M TBAB) upon a vitreous carbon electrode at five temperatures between +50°C and -25°C at a scan rate of 0.1 V/s.

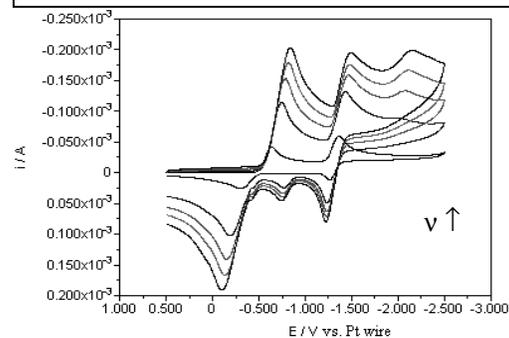


Figure 3 Cyclic voltammograms of a solution of 2mM; sulfur in DMF (0.1M TBAB) at a vitreous carbon electrode at a temperature of 0°C at five scan rates between 0.05 and 2V/s

1. R.P.Martin *et al.*, *Inorg.Chem.* **12**, 1921 (1973)
2. E.Levillain, F.Gaillard, *J.Electroanal.Chem.*, **420**, 167, (1997)
3. Shin-Ichi Tobishima, Hideo Yamamoto, *E.Chim.Acta.*, **42 (6)**, 1019, (1997)