

Sulphur Electrochemistry and Large Scale, Fuel Cell-type, Energy Storage Systems

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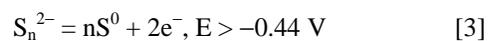
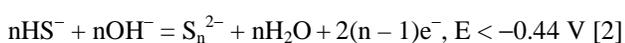
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The use of energy storage facilities in large-scale power networks has been limited by the availability of suitable cost effective technology. Regenesys[®] (1), a new energy storage technology developed by the UK company Innogy Technology Ventures Limited (ITVL), uses regenerative fuel cells to store and release large quantities of electrical energy by means of a reversible electrochemical reaction which, in simple terms, may be represented by the equation



The open-circuit voltage of the polysulphide/bromine cell, in its charged state, is ca. 1.5 V. The technology involved is environmentally benign, comparatively easy to site and separates the power rating from the energy storage capacity. A 100 MWh electrochemical energy storage plant, on a compact site of less than 0.5 hectare, is currently being commissioned at Didcot power station in the UK (1). The Regenesys system uses concentrated solutions of sodium bromide and sodium polysulphides as electrolytes. These salts, which are plentiful and available at low cost, are readily soluble in aqueous media and relatively safe. However, full optimisation of the chemistry/electrochemistry has yet to be completed. During the discharge process polysulphide species are oxidised to elemental sulphur, which precipitates onto the electrode before dissolving to form longer chained polysulphide species. This process passivates the electrode at high discharge current densities. It was decided to investigate the basic electrochemical response of polysulphide ions in base and in particular to monitor the formation and removal of this deactivating film in order to gain a better understanding of the mechanism of its formation.

The electrochemical behaviour of sulphur on metals is of interest in several areas, e.g. the processing of crude oil and natural gas, and in the field of electrocatalysis (2). The electrochemistry of aqueous sulphide and polysulphide solutions is quite complex due to a number of factors, viz. (i) the various polysulphide equilibria which exist in solution, (ii) the deposition of a passivating sulphur layer during electro-oxidation and (iii) the sensitivity of the solutions to temperature and pH changes. In this study, cyclic voltammetry and an electrochemical quartz crystal microbalance (EQCM) were utilised to investigate the sulphur deposition process at gold electrodes in 0.012 M Na₂S_x in alkaline solution at ambient temperature. Oxidation commenced in the positive sweep at ca. -0.65 V (SCE), the anodic current increasing (Fig. 1) first to a plateau and later to a peak at ca. -0.33 V; the reactions involved are assumed to be as follows:



i.e. oxidation is assumed to occur via a polysulphide ion intermediate in alkaline solution as suggested by Allen and Hickling (3); however, other authors have concluded that polysulphide ions are not produced when a layer of sulphur is deposited on gold (4). EQCM data confirmed that sulphur deposition onto the gold surface commenced only above ca. -0.4 V, i.e. in the region of the second anodic feature. Superficially it may appear that the anodic maximum at ca. -0.33 V is due to accumulation of sulphur at the anode surface. However, the process involved is not simple, e.g. much heavier deposits of sulphur were formed on holding the potential at -0.4 V than at -0.33 V. Passivation obviously occurs in the sulphur deposition region but it may not be due to the thick layer of sulphur. There may be duplex film formation, e.g. an inner, highly passivating, film may be produced at ca. -0.33 V, giving rise to the decay in anodic current at more positive potentials. The sulphur film formed at -0.4 V is less inhibiting, either due to the absence of the inner passivating layer or to a difference in the texture, density or blocking capability of the thick sulphur deposit. Further aspects of the sulphur formation and removal reactions at this electrode system will be discussed.

ACKNOWLEDGEMENTS

We would like to thank ITVL for financial and technical support for this project.

REFERENCES

1. A. Price, S. Bartley, S. Male and G. Cooley, *Power Eng. J.*, **13**, 122 (1999).
2. R. Jayaram, A.Q. Contractor and H. Lal, *J. Electroanal. Chem.*, **87**, 225 (1978).
3. P.L. Allen and A. Hickling, *Trans. Faraday Soc.*, **53**, 1626 (1957).
4. D.G. Wierse, M.M. Lohrengel and J.W. Schultze, *J. Electroanal. Chem.*, **92**, 121 (1978).

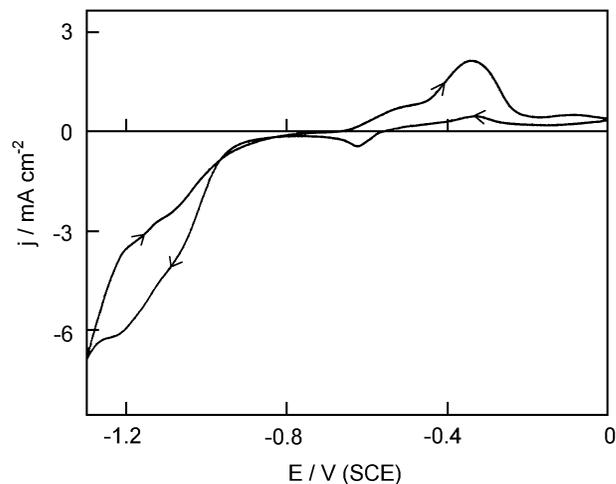


Fig. 1 Cyclic voltammogram (-1.3 → 0.0 V, 5 mV s⁻¹) for Au wire in 0.012 M Na₂S_x (half-charged) in 0.5 M NaOH + 0.5 M KOH at 35°C.