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SHORT COMMUNICATION

Photo-electrochemical energy conversion: electrocatalytic sulphur electrodes

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Electrodes for the sulphide/sulphur (polysulphide) redox system are described which show low polarization when operated under conditions to be expected in a practical photo-electrochemical cell (P. E. C.). These electrodes are composed of Teflon-bonded high surface area carbon, loaded with electrocatalysts, the best results having been obtained using cobalt as electrocatalyst.

The emergence of the photo-electrochemical cell (P. E. C.) based on the sulphur/sulphide redox couple [1–3] as a potential candidate for an economically feasible solar energy conversion and storage system has led to the need for a cheap, inert electrode with a minimal overpotential for sulphur or polysulphide reduction (in the case of an n-type photo-electrode) or for sulphide oxidation (for a p-type photo-electrode). Any overpotential at the counter-electrode in a P. E. C. is reflected in a decrease in output voltage of the cell under load and thus a decrease in efficiency of the cell. This has not been stressed in most published work up to now, because very small photo-electrodes were used together with counter-electrodes of much larger areas. In a practical cell however, the counter-electrode would preferably be of the same size as the photo-electrode and then its electrocatalytic properties become of the highest importance.

The effect of different electrode materials on the overpotential of sulphur/sulphide reduction and oxidation has been studied in the past [4], and typical overpotentials of 100–200 mV at ~ 10 mA cm^{-2} (a minimal current density which would typically be required in a practical P. E. C.), were reported. These overpotentials would lead to an intolerably high loss of efficiency in a practical P. E. C. Therefore, we studied and report here on Teflon-bonded carbon electrodes, loaded with electrocatalysts which, when cobalt is the electrocatalyst, yield overpotentials of less than 25 mV at current densities of 10 mA cm^{-2} for both the anodic and the cathodic reaction in an aqueous electrolyte of 1 M NaOH, S and Na_2S without stirring. With stirring, the results were better, particularly at higher current densities, due to the increased role of diffusion control at higher currents. Since in a P. E. C. however, we would obviously prefer a stationary system, we give results for a non-stirred system. The current densities shown in Fig. 1 are steady-state values, and do not vary by more than 10% over several days. The electrodes were prepared by impregnating high surface area carbon (B. D. H. decolouring carbon) with metal salts (17% w/w metal loading) and Teflon emulsion, sintering in an inert atmosphere at 300° C and subsequently electrolytically reducing in the S/S^{2-} solution at a current density of ~ 80 mA cm^{-2}. The Teflon used in bonding the electrodes was suspension 852/201 (Du Pont Teflon Finishel, Brussels, Belgium).

Fig. 1 shows the current/voltage characteristics, measured potentiostatically, of several electrodes, which compare the efficiencies of a simple Teflon-bonded carbon electrode to that of electrodes impregnated with different electrocatalysts. The current scale of the figure is a linear one and not logarithmic, as is usual for such measurements, since such a scale reflects directly the effect of

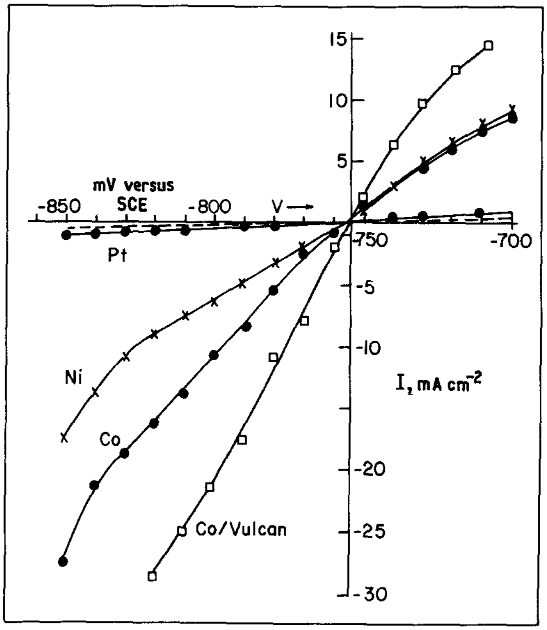

Fig. 1. Potentiostatic I–V plots of different sulphide electrodes. Electrode surface area: 4 cm^2; electrolyte: 1M NaOH, S, Na_2S at 27° C with Ar atmosphere, no stirring. Dashed line: without electrocatalyst.

overpotential on the efficiency of a P. E. C.

The results reported earlier for Pt, graphite and Au [4] seem to be of the same order as those we obtained without the use of electrocatalysts (although large variations in the true surface area of electrodes used in the earlier work make an accurate comparison impossible). The use of Pt as an electrocatalyst improves the electrode performance somewhat. However, when Co or Ni are used as electrocatalysts, the electrode efficiency increases up to an order of magnitude. Platinized Pt [4] seems to show behaviour in between that of our Ni and Pt impregnated electrodes. Cobalt is somewhat superior to nickel in the cathodic direction (at present the important direction, since up to now only n-type chalcogenide photo-electrodes have given good results in P. E. C.'s). The cobalt electrodes have another advantage over those with nickel in that, if a nickel electrode is exposed to air, after 30 min its activity drops to less than one tenth of its original value, while cobalt electrodes lose very little of their activity over such a period. It should be noted that, under working conditions, these electrodes should never be exposed to air, since then the S/S^{2-} solution itself is unstable, undergoing slow oxidation. With exclusion of air all these electrodes show excellent stability.

These results are still not the best ones obtainable. The use of Vulcan Carbon black XC 72R (Cabot Corp., Boston, Mass., USA) gives an appreciable improvement. Also the age of the Teflon suspension used in preparing the electrodes is of influence. Older suspensions can cause an ~ 35% drop in the activity of the electrodes, concurrent with a visible coagulation of the suspension, used in their preparation. The line in Fig. 1 (Co/Vulcan) shows results obtained with a cobalt-loaded Vulcan carbon electrode, using a fresh Teflon suspension. (The other curves are for electrodes using B. D. H. carbon and aged Teflon suspension, due to the temporary unavailability here of the required materials.)

The 17% metal loading was chosen somewhat arbitrarily. An increase in cobalt concentration above 17% also leads to an improvement in performance. This, and other optimizing factors, will be dealt with in a subsequent communication.

However, these preliminary results show that, when cobalt is used in these electrodes, results are obtained that are sufficiently good, so that such electrodes when used in presently described sulphide P. E. C.'s cause no more than a few percent of the total loss in such cells.

Acknowledgement

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Note added in proof. Recent experiments show that in the case of Co and Ni the electrocatalytically active species are the corresponding sulphides (probably CoS and NiS) which are formed upon immersing the electrode in the sulphide electrolyte.