# Mechanical Removal of the Diffusion Layer in the Electrolytic Production of Sodium Dithionite[1]

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PREVIOUS work[2,3] on the cathodic reduction of aqueous sodium hydrogen sulphite showed that under normal laboratory conditions high yields of sodium dithionite could be obtained only with mercury cathodes at low current density. We have now shown that dithionite yields are normally diffusion limited and if the boundary layer is mixed mechanically, high yields are obtained at high current densities with mercury and also with various solid metal cathodes. The wiped-electrode technique described here, unlike the rotating disc electrode, can be used at the high currents required for electrochemical preparations and so should have use in organic and inorganic electrosynthesis.

Two-compartment cells were used, with either porous ceramics or cation-exchange membranes as diaphragms. The anode compartment contained a graphite anode and saturated brine electrolyte. The catholyte used in most runs was $2\cdot38\text{M-NaHSO}_3\text{–}0\cdot25\text{M-Na}_2\text{SO}_3\text{–}3\cdot42\text{M-NaCl}$, giving a measured pH of 5·2. Aqueous sodium dithionite decomposes homogeneously,[4] but losses can be minimised by the use of a large current/unit volume of catholyte. The cells were operated as flow reactors and the observed current efficiencies were corrected (usually by $< 5\%$) to allow for the known[4] rate of decomposition in these solutions.

Conventional paddle stirrers were of only limited efficacy with mercury-pool cathodes of about 50 cm.$^2$ area. A Perspex cross, floating freely on the cathode surface and rotated by a glass fork on a stirrer shaft, was much more satisfactory. Sodium dithionite was formed at 90% current efficiency at current densities up to 0·7 A/cm.$^2$ with a stirrer speed of 100 r.p.m. even when solid sodium dithionite dihydrate was present in suspension. With less effective mixing of the diffusion layer dithionite formation was followed by further reactions, giving ultimately sodium thiosulphate.

The current efficiency of dithionite formation was then much lower, less than 50% under some conditions even at current densities below 0·1 A/cm.[2]. Clearly the further reduction of dithionite is significant only when diffusional mass transport leads to a much higher value of the ratio $[S_2O_4^{2-}]:[HSO_3^-]$ next to the cathode surface than in the bulk catholyte. It is noteworthy that the yield of intermediate is affected by diffusion limitations at current densities well below the limiting current density set by diffusion of the hydrogen sulphite ion to the cathode surface.

Dithionite formation in these solutions occurs at a comparatively small cathode potential, *e.g.* about −0·7v against normal hydrogen electrode at 0·1 A/cm.[2]. The reaction cannot, therefore, involve intermediate formation of sodium amalgam[3,5] or chemisorbed hydrogen atoms. In view of this we re-examined the reduction of the hydrogen sulphite ion at solid metal cathodes under conditions of minimal diffusion limitation. Cells were built with a 7·6 cm. diam. metal disc in the base. The diffusion layer was mixed by a rotating rubber wiper pressed against the disc. Typical results are shown in the Table for a wiper speed of 250 r.p.m. The effect of diffusion limitation on yield is again most marked, and accounts for earlier failures to obtain high yields with solid cathodes. Cadmium, lead, graphite, nickel, titanium, and various stainless steels also gave sodium dithionite at current efficiencies of ⩾90%.

TABLE

*Sodium dithionite formation at bismuth cathode*

| Nominal cathode/wiper clearance (cm.) | Boundary layer thickness (cm.) | Current efficiency (%) |
|---|---|---|
| 0 | $10^{-4}$ | 96 |
| 0·012 | $10^{-3}$—$10^{-2}$ | 33 |
| 0·062 | $10^{-3}$—$10^{-2}$ | 26 |

A cell in which a metal cylindrical cathode rotated against fixed wipers gave better control of experimental parameters. The anode compartments were arranged circumferentially round the cathode compartment. With the more effective wiping in this cell the further reduction of dithionite to thiosulphate is not significant with any of the metals tested (Pb, Bi, Ni, Cr, and stainless steels). The maximum current density at which high yields of dithionite could be obtained was now fixed by the onset of hydrogen evolution, except on lead where a sulphide film was formed. On the other metals current efficiencies of ⩾90% were attained at current densities of 0·2—0·3 A/cm.[2].

The mechanical removal of the diffusion layer has given order of magnitude improvements in the performance of dithionite cells. It is clear that the apparent uniqueness[3] of mercury lay in its fluidity, which allowed boundary layer mixing, rather than in any electrochemical properties. The dominance of mercury in other cathodic reductions[6] may arise at least partly in the same way. Use of the wiped-electrode cell, possibly in combination with potentiostatic control of electrode potential, should give much better yields of intermediate products than have been attained so far.

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