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A study of semiconducting oxide-glass coatings on mild steel

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Preliminary attempts to develop inexpensive, protective conducting coatings on mild steel for use as insoluble anodes are described. From the consideration that a mixture of acid resistant semiconducting oxide and glass might form a satisfactory coating when heated on a steel substrate, Sb–SnO_2 and Ti–Fe_2O_3 were selected as conducting oxide materials for evaluation. With 3–30 wt.% glass added to the oxides, Sb–SnO_2 was found to be unsuitable as pellets of the glass-oxide mixture did not densify on heating up to 1400° C. 3% Ti–Fe_2O_3 plus 20% glass pellets fired at 1250° C showed low resistivity and porosity. An oxide-glass mixture of this composition fired on a mild steel substrate at 1250° C gave a coating with a porosity of ~ 0·5%, on which chlorine could be evolved in HCl solution. The Ti–Fe_2O_3 oxides were very acid resistant under conditions of chlorine evolution. A reduction in the porosity of the coating, or the use of an acid resistant metal substrate, would be required to make the oxide-glass coating a practicable proposition.

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1. Introduction

Inert electrodes operating at noble potentials are used for cathodic protection with an impressed current, for electrochemical oxidations, including the production of chlorine, for electroplating and other purposes [1, 2]. The materials presently used as inert electrodes at noble potentials in acid media include graphite, lead alloys, lead dioxide and platinum or ruthenium based coatings on titanium. Of these, the precious metal coated titanium electrodes, despite their very much higher cost, are finding extensive use in the chlor-alkali industry, since they are dimensionally stable, highly conducting, mechanically strong and possess a low overvoltage for chlorine evolution. This paper describes some preliminary attempts to develop inexpensive, protective conducting coatings on mild steel for use as chlorine electrodes.

2. Choice of materials

It is very difficult to find acid resistant and pore free semiconducting oxide coatings which have coefficients of thermal expansion which are sufficiently close to that of mild steel. On the other hand, enamelling and glass coating techniques have been used successfully for many years to provide a protective coating for mild steel vessels used in the handling of acidic media [3]. Thus it is possible that if acid resistant semiconducting oxide were mixed with glass powder, a conducting, protective coating could be formed on mild steel. The coating will be conducting if it consists of two continuous phases–a conducting oxide phase and a non-conducting glassy phase which fills up all the pores. This condition will be satisfied if the oxide has some solubility in the glassy phase to enable the liquid phase sintering [4] to take place.

Very few of the known semiconducting oxides possess adequate conductivity and corrosion resistance in acidic media [5–7]. Only two oxides have been chosen for initial evaluation in this study–Ti doped Fe_2O_3 [8] and Sb doped SnO_2. Ti doped Fe_2O_3 and Fe_2O_3 have been used in chlor-alkaline cells in the past but their resistivity is too high if they are used as solid electrodes [2].

3. Preparation and evaluation of the semiconducting oxides

All the starting materials were of Analar Grade (Hopkin and Williams). Unless otherwise stated,

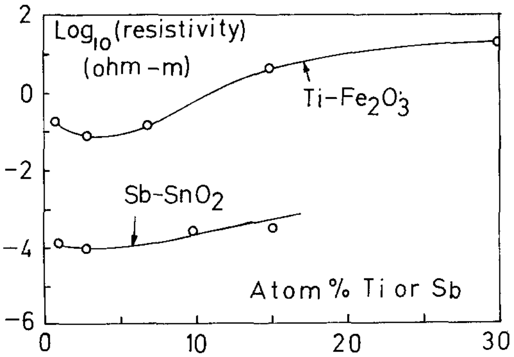

Fig. 1. Resistivity of semiconducting oxide pellets.

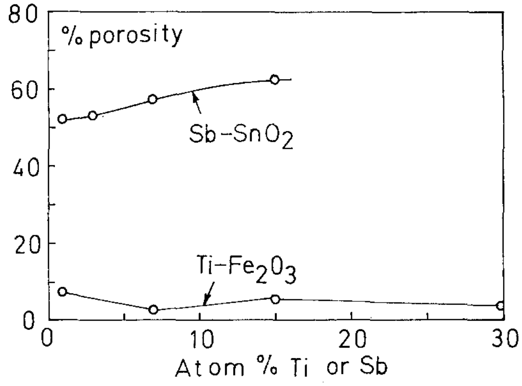

Fig. 2. Open porosity of semiconducting oxide pellets.

the atomic percentage of the doping element is quoted when giving the composition of the oxides.

The mixed oxides were prepared by co-precipitation of the hydroxides from solutions acidified with HCl, using excess ammonia. The precipitates were washed and heated to 1000° C for 2 h in air. 5 g of powder was then pressed in a 1 in steel die at 10 tons in^{-2} and fired in air – 3 h at 1400° C for Sb doped SnO_2 and 5 h at 1250° C for Ti doped Fe_2O_3.

The resistivity of the oxide pellets was measured by using a spring-loaded 4 point probe [10] with a probe spacing of 2·5 mm. A Wenking electrometer was used to measure the inner probe potential difference. The percentage open porosity of the pellets was determined by measuring their overall volume using a micrometer and measuring the volume of the non-porous part by weighing the pellets in air and in water. The results of the resistivity and porosity measurements are shown in Figs. 1 and 2.

Based on these results, 3% Sb–SnO_2 and 3% Ti–Fe_2O_3 samples were selected for further study as they corresponded approximately to minimum resistivity.

The electrochemical corrosion of the 3% Ti–Fe_2O_3 pellet was investigated in 2 N HCl and 5 N H_2SO_4 at 25° C. A glass cell, with a platinum counter and a platinized platinum hydrogen reference electrode was used for the investigation. The potential of the sample was controlled by a Chemical Electronics 0·5 A potentiostat. The current was measured by a Wenking electrometer connected across a series resistor.

The electrolyte solution was pre-electrolysed by the use of two platinum counter electrodes. The sample was placed in an electrode holder made up of platinum wire. Argon, nominally 4 ppm oxygen, was first de-oxygenated on red hot copper turnings and bubbled through the cell. Each corrosion test was preceded by a blank test on the electrode

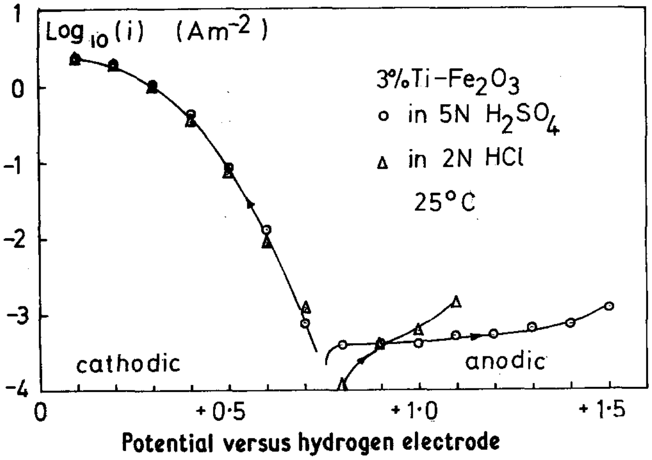

Fig. 3. Electrochemical corrosion of 3% Ti–Fe_2O_3. 0·1 V steps at 15 min intervals commencing from O.C.V.

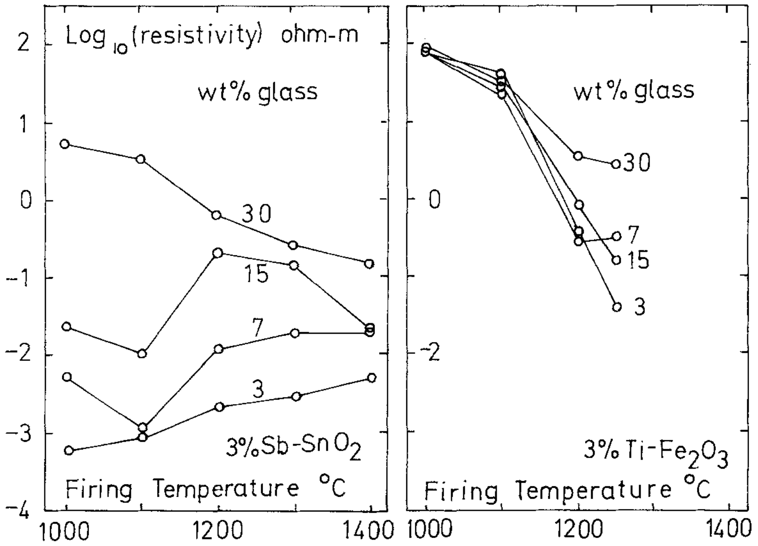

Fig. 4. Resistivity of glass-semiconducting oxide mixtures after successive 3 h firings in air.

holder under identical conditions and the corrosion rate was plotted as the difference between the two sets of experiments. Corrosion scans on the tin oxide pellet could not be distinguished from the scans on the platinum electrode holder ($< 0{\cdot}1$ $\mu A\ cm^{-2}$).

The above results indicate that Ti–Fe_2O_3, although unsuitable for use below 900 mV versus RHE, possesses adequate corrosion resistance in H_2SO_4 and HCl at more anodic potentials (Fig. 3).

3. Preparation and characterization of glass-semiconducting oxide pellets

5 g pellets of 3% Sb–SnO_2 and 3% Ti–Fe_2O_3, containing 3%, 7%, 15% and 30% by weight of soda-lime glass powder were prepared by pressing 5 g of the mixture in a die at 10 tons in^{-2}. The pellets were then sintered in air at 1000° C for 3 h, after which the resistivity and open porosity were determined as described previously. The same pellets were then heated to progressively higher temperatures for 3 h at each temperature. At and above 1200°C, the 3% Ti–Fe_2O_3 glass pellets attacked platinum, alumina or mullite refractory supports. By supporting them on powdered TiO_2 instead it was possible to carry the sintering investigation up to 1250°C. The results are shown in Figs. 4 and 5. The 3% Sb–SnO_2 glass compacts did not become sufficiently dense to warrant further study, but the 3% Ti–Fe_2O_3 glass pellets showed significant densification when they were heated above 1200° C. The results for the percentage of open porosity for the 3% Ti–Fe_2O_3 glass pellets are still relatively high, but these results may be on the pessimistic side. On firing at 1200° C or above, the bottoms of the pellets adhered to the TiO_2 powder and, as a result, there were always a number of pores at the bottoms of the pellets. Again, it shows that the 3% Ti–Fe_2O_3 glass pellet containing 20% soda-lime glass or less would possess adequate conductivity for our requirements.

5. Preparation and electrochemical evaluation of 3% Ti–Fe_2O_3 glass coated mild steel anode

A 1 in diameter, 1·5 g, 3% Ti–Fe_2O_3 glass pellet (20% by weight of glass) was placed on a piece of mild steel and heated to 1250° C in an argon atmosphere. The temperature cycle of firing is shown by the curve marked 1250° in Fig. 6. The resultant black coating was 0·45 mm thick and the resistivity of the coating was about 5×10^{-2} Ω m. Three different electrodes were then mounted: an oxide-glass coated electrode; a mild steel electrode; a 3% Ti–Fe_2O_3 electrode. The uncoated side of the glass coated electrode was first cleaned with emery paper and then coated with silver paste–epoxy resin adhesive (Johnson Matthey Ltd). A platinum screen, attached to a Teflon covered platinum wire, was pressed on to the

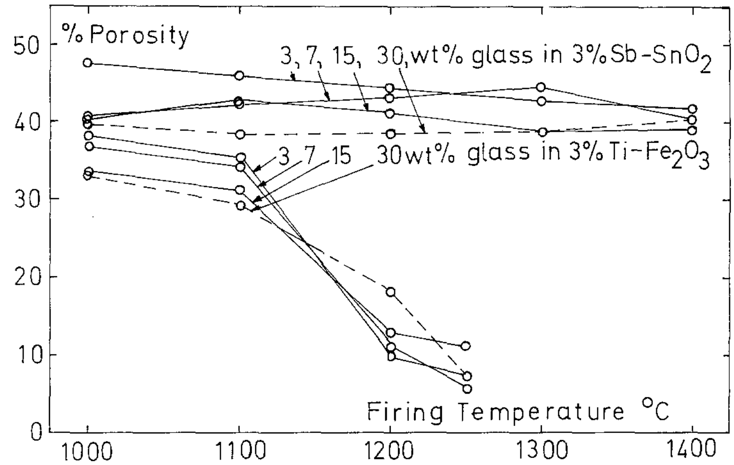

Fig. 5. Open porosity of glass-semiconducting oxide pellets after successive 3 h firings.

silver-epoxy coating, and the whole assembly was cured at 110°C for 3 h to ensure rapid setting of the epoxy. Using a plastic weighing bottle as a mould, the electrode was then encapsulated in epoxy resin (Araldite), taking care not to cover the glass coated surface. The other two electrodes were similarly encapsulated.

Fig. 7 shows the results of the corrosion scans on the three electrodes. The resistance between the electrode and the tip of the Luggin capillary of the reference electrode was measured by the interruptor technique. All the results are plotted as *iR* free values. As expected the corrosion current of the mild steel electrode is extremely high and the flatness of its *V–i* curve strongly suggests that the corrosion process is under different control. It is interesting to note that the corrosion of the Ti-doped glass coated mild steel electrode is about three orders of magnitude lower than that of the mild steel electrode (0·6–1·6 V versus RHE), indicating that the coating offers good protection of the mild steel against attack by HCl. The *V–i* curve at the above potential range is in parallel with the *V–i* curve for mild steel, again indicating diffusion control. The results for the Ti-doped Fe$_2$O$_3$ pellet in the same potential range clearly showed that the oxide is extremely corrosion-resistant, the current being two orders of magnitude lower than the corrosion current obtained on the glass coated electrode. Above 1·6 V versus RHE, both electrodes start to evolve Cl$_2$ and their performances are very similar. The slightly higher performance obtained for the glass-coated electrode may be due to greater surface roughness. In order to evaluate the corrosion resistance of the two electrodes over longer periods at this potential range, the electrodes were operated at 1000 A m^{-2} for 50 h and the quantity of iron in the solution determined by atomic absorption. By assuming that the iron in the solution is produced by the oxidation of Fe to Fe^{3+}, one can then calculate the corrosion current under these conditions. The results are plotted as single points: i'_c for the Ti-doped Fe$_2$O$_3$ glass coated electrode and i_c for the Ti-doped Fe$_2$O$_3$ pellet.

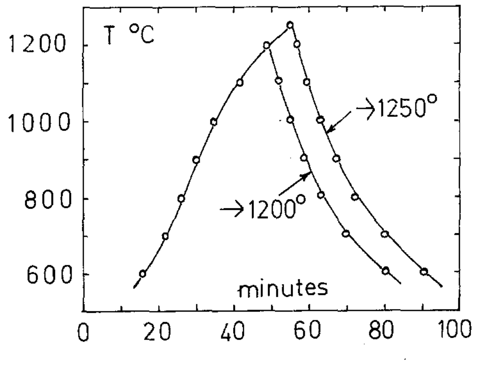

Fig. 6. Firing temperature cycles.

6. Discussion

Since the corrosion scans indicated that the Ti-doped glass coating was not giving 100% protection to the mild steel, it is useful to obtain an estimate of the actual mild steel area that was exposed to the HCl. In region B, we have shown that the dis-

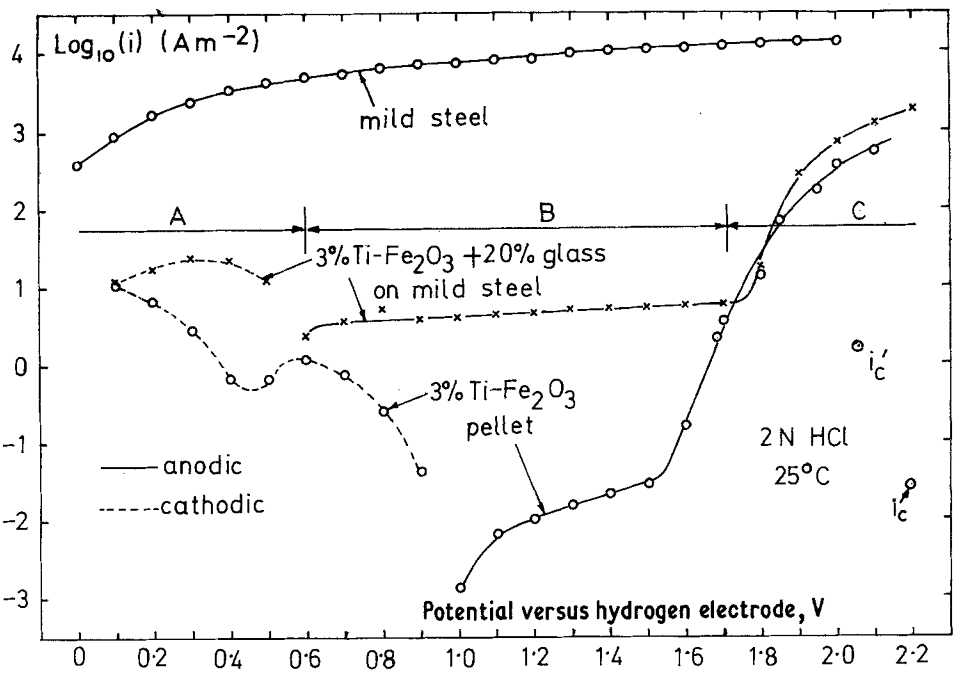

Fig. 7. Corrosion of Ti–Fe_2O_3 pellets, coated mild steel and mild steel.

solution of the coated mild steel corresponds to a diffusion limiting current.

The porosity may be estimated from the ratio of the currents on the coated electrode and on the mild steel electrode at 1000 mV. The ratio = 3·8/7550 = 0·005 = 0·5%. These results do not give any information regarding the pore structure but only indicate that the dissolution of the mild steel electrode was also diffusion controlled in agreement with the results plotted in Fig. 7. The value for the % open porosity is very much lower than the results given in Fig. 5. As mentioned earlier, the earlier results may be rather pessimistic due to the inclusion of pores left by the TiO_2 powder. Furthermore, the % of open porosity estimated by the present calculation only takes into account the open pores which are continuous from the surface to the bottom of the coating and hence gives a more realistic estimate of the area of mild steel which is unprotected.

The value of i_c' for the corrosion current of the glass coated mild steel electrode operated for 50 h is actually lower than the measured corrosion current at the lower potential range $B(< 1{\cdot}6\text{ V})$, where no chlorine evolution is taking place. This is not surprising if one considers that as chlorine is evolved inside a pore in the glass coating, it may drive part or the whole of the electrolyte from the pore, restricting the extent of corrosion of the mild steel.

The results of the preliminary investigation suggest that improvement in the coating technique or the use of more acid resistant metal could provide inexpensive, stable electrochemical anodes for a whole range of aqueous electrosynthesis processes. Such coated electrodes could have other electrocatalytic material deposited on the surface to improve their electrochemical performance, e.g. RuO_2 to reduce the Cl_2 evolution overvoltage.

7. Acknowledgement

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