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Non-metallic working electrodes for high temperature systems

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The fabrication of Pyrex-sealed non-metallic electrodes (SnO_2, RuO_2 and glassy carbon) and their electrochemical characterization in LiCl–KCl (450° C), $NaHSO_4$–$KHSO_4$ (250° C) and $LiNO_3$–KNO_3 (175° C) eutectics are presented. Semiconducting SnO_2 films prepared on Pyrex substrates were sealed into Pyrex by using a simple glass-blowing technique. SnO_2 electrodes with leak-tight seals are versatile in high temperature systems and have been used to prepare RuO_2 electrodes usable in fused salts. A convenient method for obtaining a good glassy carbon-to-Pyrex seal is presented for the construction of glassy carbon electrodes. A comparison of these electrodes in blank melts has been made with special interest in the electron tunnelling nature of SnO_2 and the electrocatalytic activity of RuO_2.

1. Introduction

The construction of working electrodes with a good performance is essential for voltammetric studies in high temperature molten salt systems. When preparing electrodes for use in such high temperature media, two problems are usually encountered. The first is the fabrication of electrodes with a defined working area, desired geometry and low surface roughness. In view of the material problems associated with high temperatures, sealing or embedding them into an inert material is also difficult practically. Generally, Pyrex is the most reliable sealing material usable in all melts except fluoride and highly basic melts. The second problem is the stability of electrode materials in the working potential range. Noble metals, even Pt and Au, are not always inert at anodic potentials where their use is complicated by anodic dissolution or surface oxidation depending on the melt properties. Owing to poor seals between glass and metals, workers have been using seal-free electrodes constructed under an anodic limitation imposed by the electrode itself. The seal-free electrode is simply a very thin foil with a fine contact wire, referred to as the flag type construction.

Tungsten and glassy carbon (GC) can be sealed into Pyrex. Pyrex-sealed W electrodes have been used in some melts [1, 2], but are not generally recommended [3]. On the other hand, Pyrex-sealed GC electrodes are very common in high temperature systems [1, 4–7], being usable up to the anodic limit of melt decomposition, e.g. chlorine evolution in chloride melts. However, carbon is electrochemically consumed in oxygen-containing melts such as bisulphate and nitrate melts [8, 9]. In this connection some conductive metal oxides prepared on inert substrates are of interest for electrode construction for high temperature work, if the oxide has sufficient chemical durability and thermal stability in fused salts.

It is said that Pyrex will not wet carbon, and a silicon coating technique to improve the GC-to-Pyrex seal has been reported by Levy and Farina [4] and a silica coating technique by Laitinen *et al.* [5]. These methods, however, include the use of special gaseous reactants and troublesome operations. A simple method of obtaining a good GC-to-Pyrex seal would be desirable. Semiconductive tin oxide films prepared on Pyrex substrates were used as stable indicator electrodes in chloride melts [10–15], and also in oxygen-containing melts as shown later. In the previous construction of SnO_2 electrodes [10–12], we employed a boron nitride sealant between a Pyrex sheath and a SnO_2-coated Pyrex rod, but it was not sufficiently effective in preventing the melt from penetrating into the seal. Recently we established a technique for obtaining a leak-tight

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seal between Pyrex and SnO_2-coated Pyrex. This technique may be useful in the preparation of SnO_2-based novel electrode systems because a SnO_2 surface with a definite area can serve as both catalyst support and current collector. Ruthenium oxide, one of the most interesting electrode materials, can be used successfully as a working electrode in this manner.

In this paper we describe the fabrication and use of Pyrex-sealed SnO_2 and SnO_2-based RuO_2 electrodes. A simplified method for obtaining a good GC-to-Pyrex seal is also presented. An electrochemical characterization of the oxide electrodes in several melts is given in comparison with that of GC.

2. Experimental procedure

2.1. *Pyrex-sealed SnO_2 electrode*

Polycrystalline, Sb-doped SnO_2 films were prepared on clean Pyrex substrates using a spray technique [10, 11]. Acidic tin chloride solutions (3M $SnCl_4$ + 1.3M HCl) containing 2 mol% $SbCl_3$ were sprayed on to Pyrex surfaces heated at 500° C. The film thickness was about 0.5 μm and the doping levels determined by the Mott–Schottky relationship obtained in 1M H_2SO_4 ranged from 3×10^{20} to 5×10^{20} cm^{-3}.

A Pyrex sheet (5×5 cm^2, 3.2 mm thickness) coated with the oxide was cut into rectangular pieces and a Pyrex rod provided with a notch at one end was welded to the piece as shown in Fig. 1a. A gold layer which worked as an electrical contact was painted onto the SnO_2 surface through the rod by using a gold paint (C-5040, Sumitomo Mining Co.). After 10 min firing of the paint at 500° C, the pieces were cleaned in a methanol solution of NaOH and then in an acid mixture of concentrated HNO_3 and H_2SO_4.

Sealing into Pyrex was done by welding Pyrex directly to the SnO_2 surface. The piece of Pyrex, one side of which had been coated with the heavily-doped SnO_2 and partly with the thin gold layer, was placed in a Pyrex tube closed at one end, and provided with a narrow section slightly larger than the piece of Pyrex. By lowering the pressure at the open end and heating the narrow section to the softening point with a very fine flame, the piece was coated with Pyrex glass as shown in Fig. 1b. Skill and care were needed to obtain a good seal, free of a thin void between the glass and the oxide film. The presence of the void, which resulted in an optical stripped pattern, was easily detectable by visible inspection, and such a failure was rejected. This glass-to-glass seal proved leak-tight, and the thin film of SnO_2 interposed between them was still conductive after the sealing procedure. However, it is necessary to avoid excess firing leading to the decomposition of SnO_2.

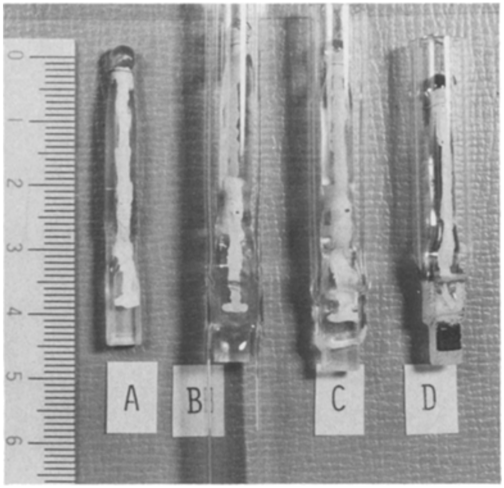

Fig. 1. Fabrication of electrode. (a) Pyrex substrate coated with SnO_2 and Au, (b) SnO_2-coated Pyrex sealed into Pyrex tubing, (c) finished SnO_2 electrode and (d) RuO_2 electrode. The SnO_2 surface has been coated with RuO_2 produced by thermal decomposition.

The closed part of the Pyrex tube was cut off to expose the free surface of SnO_2 by using a small diamond saw attached to a Dremel tool. Several turns of a lead wire were wound onto the notch at the other end. Fig. 1c shows a finished electrode. The working area and tightness of the sealing were checked using the Cottrell equation in potential step experiments in aqueous 1M KCl containing $Fe(CN)_6^{4-}$.

2.2. *SnO_2-based RuO_2 electrode*

The surface of the Pyrex-sealed SnO_2 electrode was coated with RuO_2 produced by thermal decomposition of $RuCl_3$ as shown in Fig. 1d. By dipping the electrode into a propanol solution of $RuCl_3 \cdot 3H_2O$ (0.02 or 0.2M) and heating the oven-dried material at 500° C for 20 min, a blue-black, compact layer was prepared. This procedure was repeated to attain uniform coating, and finally the electrode thus prepared was annealed for 10 h at 500° C in air.

The adhesion of RuO_2 to the underlying SnO_2 film proved quite satisfactory, the latter working well both as a catalyst support and as a current collector. When the electrode was subjected to gentle scraping or thermal shocks, no damage was observed. SEM observation of the surface revealed a pore-free structure and X-ray analysis showed the presence of all the principal RuO_2 peaks in comparison with those of the ASTM card index (File No. 21-1171).

2.3. *Pyrex-sealed GC electrode*

To improve the seal between GC and Pyrex, we tried a SiO coating technique instead of a Si or SiO_2 coating technique [4, 5]. GC rods of 3 mm diameter (GC-20, Tokai Carbon) were polished slightly with carborundum and treated with an acid mixture of chromic and sulphuric acids. The cleaned GC rods were first coated with SiO by vacuum evaporation. The thickness of SiO was not determined, but it was not very thin because the evaporation time was relatively long (~ 5 min). The rods were then transferred into a quartz tube and heated to red heat with a torch under reduced pressure. This procedure was necessary to ensure a good seal and avoid bubble formation at the GC–glass interface. Finally the rod was sealed into a Pyrex tube using the same technique as described above. After cutting off the end to expose the circular cross-section of the rod, the GC surface was polished to a mirror finish with AB Alpha Polishing Alumina (Buehler Ltd).

This technique is more convenient than the other two, and we realized that the rejection rate was less than with the SiO_2 coating technique which we had used in previous studies [5–7]. The GC-to-glass seal was found to be durable throughout several thermal cycles between working temperatures in melts (450° C in LiCl–KCl) and room temperature.

2.4. *Melt preparation*

The eutectic mixture of Analar grade LiCl–KCl was first treated with dry Cl_2 and then with dry HCl. Details of the purification procedure have been described previously [10–13].

The bisulphate melt was the eutectic mixture (50 : 50 wt%) of Analar grade $NaHSO_4$ and $KHSO_4$ supplied from Wako Pure Chemical Ltd. These reagents were oven-dried and used without further purification.

The nitrate melt was also the eutectic mixture of 43 mol% $LiNO_3$ and 57 mol% KNO_3. The anhydrous forms supplied from Merck (Suprapur grade) were oven-dried under vacuum and the fused mixture was subjected to prolonged scrubbing with dry N_2 to eliminate a trace of water.

3. Results and discussion

3.1. *LiCl–KCl at 450° C*

Background traces of SnO_2, RuO_2 and GC electrodes in LiCl–KCl at 450° C are shown in Fig. 2. In comparison with the previously constructed electrodes [10, 11], the newly developed SnO_2 electrode showed significantly reduced background levels. The anodic limit in each case is chlorine evolution, and the *I–E* do not show anodic degradation. In the course of potential cycling the RuO_2 electrode showed a distinct anodic wave at about − 0.1 V for the first few scans, but it disappeared rapidly converging to the steady current level shown in Fig. 2b. This can probably be attributed to the oxidation of a lower

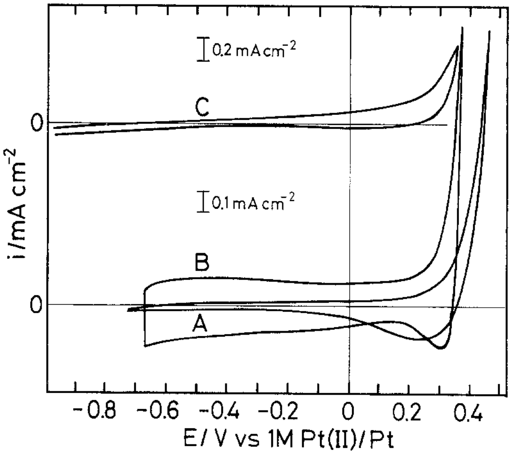

Fig. 2. Background traces in LiCl–KCl eutectic at 450° C. (a) SnO_2 electrode, (b) RuO_2 electrode and (c) glassy carbon electrode. $v = 0.05\ V\ s^{-1}$.

valency state of ruthenium present in the oxide. The cathodic limits of the oxide electrodes are not clearly defined. When negative potentials are applied beyond the limit shown in Fig. 2, the cathodic currents gradually increase in an erratic way and finally result in a reduction of the oxides.

An interesting feature of the electrodes is that each has a unique functionality. The SnO_2 electrodes are n-type semiconductors, showing relatively small capacitive currents. The high-doped sample functions as a metal electrode because of the highly transparent nature of the space charge layer to electrons. This type of electrode, usually referred as an electron tunnelling electrode, has been used as an indicator electrode for examining highly noble redox species in LiCl–KCl [11, 12]. Poorly conducting films with carrier densities less than 10^{19} cm^{-3} prepared on the high-doped film indicate decreased tunnelling currents. We have studied the tunnelling current as a function of the carrier density in order to evaluate the reorganization energy in the LiCl–KCl solvent. The results obtained for Cu(II)/Cu(I) and Fe(III)/Fe(II) couples will be published elsewhere.

The RuO_2 electrodes are metallic conductors and are expected to have some electrocatalytic activity for gas electrode reactions. A comparative study carried out with GC and RuO_2 electrodes in $AlCl_3$–NaCl melts at 175° C showed a marked electrocatalytic effect of RuO_2 on the chlorine electrode reaction [17]. In LiCl–KCl at 450° C, however, RuO_2 had little catalytic effect when compared with the chlorine evolution on GC, although the reversibility was found to be greatly improved with a coating of RuO_2, as seen by comparison of curve B with curve A for SnO_2 in Fig. 2.

It is noteworthy that the initial potential may be set at 0.2 V on the reference scale when using those oxide electrodes in voltammetric experiments. This allows us to study the reduction of highly noble species such as UO_2^{2+} [13] and oxygen by cyclic voltammetry. The redox chemistry of many noble species in the melt still remains vague because carbon has been the only electrode material available in the potential region positive to the dissolution potential of Pt, i.e. about − 0.35 V on the reference scale. The use of the oxide electrodes together with GC electrodes would be quite valuable in future works.

3.2. *Bisulphate at 250° C*

Fig. 3 shows the background traces for SnO_2, GC and flag type Pt electrodes in a 'blank' bisulphate melt. The cathodic and anodic limits in the Pt case are hydrogen and oxygen evolution, respectively [18]. A surface redox process associated with anodic formation of Pt oxide and its reduction is quite striking as shown in curve B. As reported by many workers, there is a strong resemblance between the behaviour in aqueous solutions and bisulphate melts [18–20]. Hydrogen evolution on GC takes place with a high overpotential, while the anodic limit on GC is not due to oxygen evolution. According to Arvia *et al.* [8], carbon is electrochemically oxidized in the melt, yielding a gas mixture of $2CO_2$ and CO independent of the current density.

It is seen that the workable potential ranges of GC and Pt electrodes are narrow in comparison with that of SnO_2. In addition, Hg is reported to be spontaneously corroded in the melt [20], and it is not possible to apply the polarographic techniques using Hg. This severe restriction in the use of metals and carbon is ascribed to the strong oxidizing power and acidity of the melt. On the other hand, the SnO_2 electrode is stable in this highly acidic and oxidative melt, showing a wide potential span with a low background level and lack of surface oxidation phenomena. This

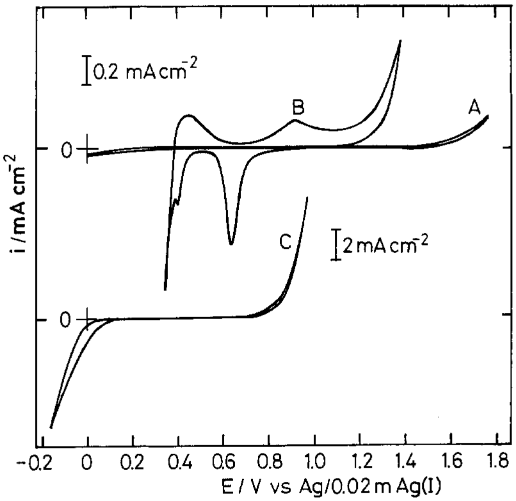

Fig. 3. Background traces in $NaHSO_4$–$KHSO_4$ eutectic at 250° C. (a) SnO_2 electrode, (b) Pt electrode and (c) glassy carbon electrode. $v = 0.05$ V s^{-1}.

interesting feature associated with high oxygen overpotential is analogous to the electrode behaviour of SnO_2 in aqueous systems, where the oxygen evolution involving the electron tunnelling needs high overpotentials, but simple electrode processes usually show nearly reversible behaviour [21].

In view of the narrow potential ranges of the usual indicator electrodes, voltammetric studies on redox couples in the melt are very scarce. Besides hydrogen and oxygen electrode reactions [8, 19], only the VO^{3+}/VO^{2+} couple has been studied with a Pt microelectrode [20]. Taking advantage of the high oxygen overpotential of SnO_2, which makes it possible to study an anodic process without a background contribution, we have examined the oxidation processes of VO^{2+}, Mn^{2+} and Tl^+ by cyclic voltammetry, and further studies on other redox species are in progress. In connection with this, preliminary experiments indicated that the flat band position of the SnO_2 electrode was about 0.1 V on the reference scale. Thus the current behaviour can be explained in terms of electron tunnelling.

3.3. *Nitrate at 175° C*

The background traces for SnO_2, RuO_2 and Pt electrodes in nitrate at 175° C are compared in Fig. 4. The anodic limits are due to the melt decomposition leading to NO_2 evolution [22, 23]. The small humps observed for the RuO_2 and Pt electrodes can be ascribed to the presence of residual impurities, probably a trace of NO_2^- [23].

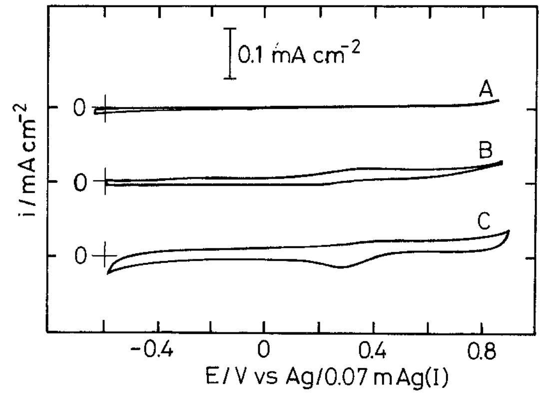

Fig. 4. Background traces in $LiNO_3$–KNO_3 eutectic at 175° C. (a) SnO_2 electrode, (b) RuO_2 electrode and (c) Pt electrode. $v = 0.05$ V s^{-1}.

The voltammetric behaviour of RuO_2, as would be expected, was found to be very similar to that of Pt in electro-oxidation of Cl^- and Br^- in the melt, while the SnO_2 electrode whose flat band potential was about − 0.6 V on the reference scale indicated high overpotentials for the gas evolution reactions [24]. Considering that Pt indicator electrodes have a wide potential span and great stability, we would say that the use of oxide electrodes in place of Pt electrodes has little advantage.

Recent studies on this melt have dealt with the redox chemistry of the O_2–O_2^-–O_2^{2-}–O^{2-} system in the presence of some oxygenated forms such as H_2O/OH^- and CO_2/CO_3^{2-} [25–27]. Zambonin *et al.* [25, 26] suggested that some electrode reactions proceed involving *in situ* metal oxides as surface catalysts. Noble metal surfaces are certainly covered with their oxides in this highly basic and oxidative medium when they are immersed into the melt [28]. In this respect, the artificial oxide electrodes produced in a reproducible manner may be valuable in a study of electrocatalytic effects.

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