Platinum–Oxygen Electrode in Molten Alkali-metal Nitrates

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Summary Platinum metal immersed in a $Cr_2O_7^{2-}$–CrO_4^{2-} solution of molten alkali metal nitrates behaves as an electrode reversible to oxide ion concentration.

WHILE it has been fairly well established that the platinum–oxygen electrode in molten alkali-metal nitrates responds to oxide ion concentration according to theory, several authors question the reversible reduction of oxygen gas to oxide ion at a platinum surface. Kust[1] and Shams El Din[2] and his co-workers have used the platinum–oxygen system as an indicator electrode to measure the concentration of oxide ion in molten nitrates. Their indicator electrode consisted of a platinum foil bathed in oxygen gas.

We have found that platinum in alkali-metal nitrate melts responds reversibly to oxide ion in the absence of oxygen gas provided the melt is buffered with respect to oxide ions. Therefore, a reference electrode was prepared by dipping a platinum wire into a solution of dichromate and chromate ions contained in a Pyrex glass tube separated from the bulk solution by a fine porosity fritted disc. The indicator electrode consisted of platinum foil dipping into the bulk melt. Titrations were carried out similar to those reported by Shams El Din and his co-workers using dichromate and dimolybdate as acids and carbonate, oxide, and peroxide as bases. We found that the expected equivalence point was obtained in all cases whether oxygen was bubbled over the electrode or not. We also purged the melt with nitrogen and bubbled nitrogen over the electrode and obtained the same results. The slope of the straight line obtained from Nernst plots for the $Cr_2O_7^{2-}$–CO_3^{2-} titrations gave a value which corresponds to a two-electron transfer at the electrode. Replacement of the above reference electrode by Ag/Ag^+ gave the same results except that all the potential readings were displaced by a constant value.

Our results indicate that when platinum metal is immersed in alkali-metal nitrate melts which contain a Lewis acid–base buffer this metal is transformed into an electrode which responds reversibly to oxide ion concentration but appears to be unresponsive to changes in the partial pressure of oxygen bubbled over the platinum surface. We propose that when platinum is placed in nitrate melts a film 'of platinum oxide is formed on the surface of the metal to yield an electrode of the type $Pt/PtO/O^{2-}$. Inman and Braunstein[3] claim that the shapes of chronopotentiograms they obtained while trying to oxidize nitrite ion in molten nitrates indicated that part of the applied current was being used to form an oxide film on the platinum electrode. In aqueous systems the form of the adsorbed oxygen on a platinum surface is still not determined unequivocally. Some workers suggest that a film of PtO is formed on the surface of Pt which has been exposed to oxygen, while other workers feel that oxygen dissolves in the Pt to form a Pt–O alloy.[4] The Pt–O alloy model does not describe our electrode because its stability and reproducibility would require the presence of oxygen at a fairly constant activity.

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[4] James P. Hoare, 'The Electrochemistry of Oxygen', Interscience, New York, 1968.