Electrocatalysis of anodic oxygen-transfer reactions: alpha-lead dioxide electrodedeposited on stainless steel substrates

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Dense and uniform films of alpha-PbO₂ were electrodeposited on the surfaces of various types of stainless steel. In strongly alkaline media, these films were found to be very stable and exhibited significant electrocatalytic activity for the oxidation of Cr(III) and CN⁻. In acidic media, alpha-PbO₂ films deposited on type-416 stainless steel, which had been passivated by anodization in a phosphate solution, were relatively stable and exhibited catalytic activity for oxidation of Mn²⁺. Rate constants for the anodic oxygen-transfer reactions of Cr(III), CN⁻ and Mn(II) were estimated from data obtained at rotated disk electrodes.

I. Introduction

Electrolytically deposited PbO₂ can exist in two polymorphic forms. The beta-form, deposited from acidic solutions of Pb(II), has a slightly distorted rutile structure. The alpha-form, deposited from neutral and slightly alkaline solutions, has the columbite form [1, 2]. Deposition of alpha-PbO₂ from 2M NaOH saturated with PbO(s) has also been described [3].

Electrodes consisting of films of both alpha-PbO₂ and beta-PbO₂ formed by electrodeposition on inert substrates have been applied successfully for numerous anodic electrosynthetic reactions [2, 4]. Noble metal substrates, while receiving much attention in the laboratory, are too expensive to be practical as substrates for PbO₂-film electrodes of large area intended for industrial applications. Alternately, more economical materials receiving attention have included Pb, Pb alloys, graphite, Ti, and plastics [5-10]. Matantsiev [11] tested Ni, Al, Cr, Fe, Armoiron®, ferrosilicon, and stainless steel, and concluded that these materials are not appropriate as substrates.

Research to improve the performance of lead-acid batteries has considered the effects of metal impurities (for example, Ag, As, Co, Mn, Ni, Se, Sn, Te, V and Ti) on structure, oxygen stoichiometry, crystal morphology and self-discharge rates [12]. Recently, films of Bi-doped beta-PbO₂ electrodeposited on Au and Pt rotating disk electrodes (RDEs) were demonstrated to have increased electrocatalytic activity for several anodic oxygen-transfer reactions, as compared to pure beta-PbO₂ films on the same substrates [13]. We also have preliminary data indicating that PbO₂ films doped with Fe(III) exhibit a moderately increased activity for oxidation of several compounds [14].

Research summarised here was based on the premise that iron and/or stainless steels (SS) can be useful as inexpensive substrates for pure and modified PbO₂-film electrodes. The manufacture of passive 'iron-black' films (Fe₃O₄), and phosphate-containing films on Fe and Fe-alloys, has become a mature technology [15] and these coatings can protect the substrates during exposure to highly corrosive conditions. It is well known, for example, that iron tanks are used successfully for storage and shipment of concentrated nitric and sulphuric acids. The corrosion resistance of stainless steels (SS) is provided by very thin surface films of passive oxides which are self-healing in a wide variety of corrosive environments. It has been reported [15] that SS can be highly resistant to 50% boiling caustic soda and some austenitic steels can withstand strong acid. Furthermore, PbO₂ films might offer additional protection to SS substrates because of their stability in strongly acidic and alkaline media. These facts inspired us to test various passivated SS substrates for use in the preparation of PbO₂-film anodes.

Passive oxide films can be formed at the surfaces of Fe and Fe-alloys. Furthermore, passive phosphate-containing films can be formed anodically in phosphate media. Beneficial modification of the electrodeposited films was expected to result from incorporation of one or more of the components of the stainless steels into the deposited PbO₂ films (i.e., Fe). Two basic questions pervaded this research: (i) Can PbO₂ films on stainless steel substrates function satisfactorily at large positive values of applied potential in various aqueous...
media? (ii) Do these electrodes exhibit improved catalytic activity for O-transfer reactions in comparison with pure PbO₂ films on noble metal substrates?

2. Experimental details

2.1. Reagents

All chemicals were AR Grade from Fisher Scientific, Alfa Products, or Aldrich Chemicals. Water was purified in a NANOpure II system (SYBRON/Barnstead). Supporting electrolytes were 1.0 M HClO₄, 0.50 M H₂SO₄, 0.014 M NaHCO₃/0.011 M Na₂CO₃ (pH 10.0), 0.30 M H₂OAc/0.50 M NaOAc (pH 5.0) and 2.0 M NaOH. Anodic passivation of SS surfaces was performed in 1 M Na₃PO₄/4 M H₃PO₄ (pH 0.7). Other reagents included Cr(NO₃)₃ · 9H₂O, NaCN, and Mn(NO₃)₂.

2.2. Instrumentation

Noble metal disk electrodes included Au (0.196 cm²) and Pt (0.159 cm²) (Pine Instrument Co.). Stainless steel (SS) disks were constructed from the SS alloys 416 (0.196 cm²), and 302, 304, 317, and 321 (0.349 cm²) (Fry Steel Co.). Disk electrodes were mounted in a Model MSR Rotator (Pine Instrument Co.). Exhaustive electrolysis was performed at films deposited on cylindrical electrodes made from Pt-screen and 304-SS screen (Johnson-Matthey).

Electronic instrumentation included a Model RDE4 potentiostat (Pine Instrument Co.), a Model 551 potentiostat (ECO, Inc.), a Model 7035B X-Y recorder (Hewlett Packard), a Series 5500 stripchart recorder (Houston Instruments Co.), a model IV current source (E. H. Sargent and Co.), a Research Coulometer (U.K. Thompson Electrochem Ltd), a Zeromatic SS-3 pH meter (Beckman Co.), and a Model 197 digital multimeter (Keithley Instruments).

2.3. Procedures

The surfaces of SS disk electrodes were polished with 320-grit Carbimet paper strips followed by 1 µm diamond paste. Some SS substrates were passivated by anodic polarization (5 min at -192 mA) in the phosphate solution described previously. Dissolution of components of the SS surfaces was initially very rapid, as indicated by a slow initial rate for O₂ bubble formation. Passivation increased, as noted by the increased rate of O₂ formation, until reaching an apparent steady-state value after 3-4 min. The resulting electrode surfaces had a uniformly dark gray appearance.

In some cases, thin Au films were anodically deposited at constant current on SS substrates (1.0 mA cm⁻² for 20 min) from solutions containing 4.0 mg ml⁻¹ HAuCl₄ · 3H₂O, 6.4 mg ml⁻¹ KCN and 4.0 mg ml⁻¹ NaHPO₄ · 7H₂O. Alpha-PbO₂ films were deposited anodically for 3.0 min at 0.35-0.40 V from 2.0 M NaOH saturated with PbO₂(s). Bismuth-doped beta-PbO₂ films were deposited anodically at + 1.60 V for 20 min from solutions containing 1.0 mM Pb(II) plus 0.70 mM Bi(III) in 1.0 M HClO₄.

Positive and negative scan limits in voltammetric studies were chosen on the basis of onset of anodic evolution of O₂ and cathodic dissolution of the oxide films, respectively. All potentials were recorded and are reported as volts measured with respect to a saturated calomel electrode (V versus SCE).

2.4. Electrocatalytic comparisons

To facilitate intercomparison of the electrocatalytic activities of various electrodes, apparent heterogeneous rate constants (k_{app}, cm s⁻¹) were estimated from plots of the reciprocal of the anodic current (i), normalized for area (A) and bulk concentration of reactant (C_b), according to Equation 1. In Equation 1, J is the normalized current density (mA mM⁻¹ cm⁻²), n_{eff} is the effective number of electrons in the reaction (eq mol⁻¹), v is the solution kinematic viscosity (cm² s⁻¹), W is the rotation speed (rev min⁻¹), 3.091 is the constant for interconversion of the square roots of W and rotational velocity (rad s⁻¹), and F and D have their conventional electrochemical significance. The value of n_{eff} for kinetically coupled reactions can be smaller than the total number (n_{tot}) of electrons determined by exhaustive electrolysis. Values of electrode current (i) were measured at a constant applied electrode potential and were corrected for the background.

3. Results and discussion

3.1. Deposition of alpha-PbO₂ films

Several types of stainless steels were considered as substrates for anodic deposition of alpha-PbO₂. Members of the 300-series contain high levels of Cr and Ni, and are called "austenitic" stainless steels. These are considered to have high corrosion resistance. Members of the 400-series have a high iron content and have good mechanical properties, but with some sacrifice in corrosion resistance.

The voltammetric responses (i-E) for several bright (i.e., untreated) and passivated stainless steel (SS) rotated disk electrodes (RDEs) were obtained in 2.0 M NaOH after saturation with Pb(II) by addition of excess PbO(s) powder. The data are typified by i-E curves shown in Fig. 1. The background response obtained for the absence of PbO(s) (dashed lines) contains peaks and waves which are attributed to anodic dissolution of components in the SS substrates, as well as anodic formation and cathodic dissolution of surface oxide. It is obvious that the overpotential for O₂ evolution is larger at SS surfaces which had been anodically passivated (e.g., Curves A and C).