Preparation and Characterization of Titanium Supported Spinel Electrodes

P.N. Gupta

Department of Chemistry, Guru Nanak Dev University, AMRITSAR 143 005

Attempts to deposit Pt onto less expensive metal substrates in order to prepare economical and dimensionally stable electrodes have been unsuccessful in general [1]. Some commercial Ru supported electrodes for "specific" oxidation have been reported in U.S. Patents [2], but the method of preparation and composition of the adhesion have been concealed therein, although, a few patents described method of preparation vividly [2a].

In this communication, the preparation of Ti-based cobalt metal spinel has been reported. They are found to resist chemical and electrochemical attack over long periods of their constant use and suffer the least loss of conductivity; they have reasonably satisfactory thermodynamic stability, low specific surface area, relatively high electric resistance and their utility in alkaline solution is extremely good.

A concentrated solution of a cobalt salt $Co(NO_3)_2.6H_2O$ was coated repeatedly and baked on a thin sheet of Ti till a layer of Co_3O_4 was suitably deposited. In a recent paper [3], a similar method has been tested for ternary compounds and a suitable stoichiometric composition was established on the electroconductive substrate.

After deposition / growth, any of the known methods [4-8] can be employed to characterize them. These electrodes find successful use as anode in the oxidation of hydrazobenzene to trans-azobenzene in alcoholic KOH solution.

EXPERIMENTAL

A Ti-sheet, (2 x 2 x 0.1 cm) abraded with emery paper, dipped in CCl_4 and air dried, dipped in 50% HNO_3 for 1 min. at 80°, rinsed with distilled water and air dried to a grey surface. Al_2O_3 (Brockmann) grit was blasted to a uniform rough surface and blown clean with air. About 6g. of $Co(NO_3)_2.6H_2O$ was dissolved to make 10 ml (~ 2M) solution. A saturated solution containing $Co(OH)_2$ in water or $CoCl_2.6H_2O$ in water or $Co(NO_3)_2.6H_2O$ in acetone or alcohol served equally well. A melt containing 5g. $Co(NO_3)_2.6H_2O$ and 1g. $Sr(HCOO)_2$ maintained at 75° was also used. The Ti metal sheet was brushed with the solution and placed 4-5 cm. above the infrared convector and heated for 4-5 min. The temperature of the sheet was noted to be 200°. After cooling in air, a subsequent coat was applied and baked again. Eight additional coats were applied in a similar manner. Final baking was done in an oven at 200° for 1 hr. Cooled in air, kept in water, the spinel oxide electrode was ready for use.

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Characterization of the Electrode

The electrodes were initially tested in a cell for electrolysis of water as anodes by electrolysing a magnetically stirred KOH solution for evolution of O_2 and H_2 at the two electrodes. The copper wire leading to circuit was covered with porous teflon and mounted on glass. The electrodes were partially immersed in the solution such that the two sides of only 2 cm x 1 cm x 1 mm remained unshielded.

The potential of the cell was measured in an indigenously fabricated glass cell in which anode and cathode compartments were separated through perforation. Anode compartment contained 5g. hydrazobenzene dissolved in 100 ml alcohol or 2M KOH along with a stirrer, a heating element and a thermometer. The reference elecrode was bridged through a luggin capillary. The potential was measured while current was flowing. It was found to be 1.775 V at 27° with a flow of 0.3 A cm^{-2}. The temperature coefficient was 0.0007V deg^{-1}. On continuous use for 2 months, it showed a variation of +0.005 V and on reuse after 2 months non-operational period, the voltage was recorded as 1.768V.

RESULTS AND DISCUSSION

The X-ray diffraction patterns for the "Scraped" sample of pure Co_3O_4 and those containing Sr ions (by Debye-Scherrer method)were found to confirm to the needs of spinel structures [1b]. Some lines shifted in the presence of Sr ions in which case a generalisation [9] was calculated to be true.

The metal Zr in place of Ti converted itself to ZrO_2 at 200°. Similarly, Hf revealed unstable multi layered structure but with weak adhesion. A fairly thin layer dropped out after 2-3 electrolyses-mainly due to internal stresses during growth on metal. Attempts to deposit Co_3O_4 on cylinderical graphite under limited O_2 supply lacked in consistency and reproducibility. Graphite was seen burning due to the reaction with excess O_2 during thermal treatment with cobaltites at elevated temperature. A sharp fall in resistance was noticed when the surface (Ti) was coated a second time in line with the observation made by Brushtein *et. al.* [10]. The coated surface of graphite did not show much change in resistance for unknown reasons.

The unnecessary heating at elevated temperatures for a long period reduced the effectiveness of electrode as anodes. The adhesion was weakened unduely by O_2 migration into the interior layer of the coating and affected the stability. The porosity was lost; only a concrete layer was noticed. More the Sr^{++} present, more was defect observed at higher temperatures. Since decomposition temperature of $Co(NO_3)_2$ is nearly 110°, heating at 200° was optimised for 1 hr.

A single coat was generally thin and visibly defective; at times patches were noted. Second and third coats removed patches but these were replaced with

numerous pinholes. At least 10 coats would ensure a safe and stable deposit. It may be noted that each layer was not of the same thickness. Sr^{++} provided the compactness and generally improved adherence. Earlier workers [11] reported that thickness between 0.02 mm to 0.1 mm was sufficient to serve as electrodes and between 16-10 coatings ensure this result for many of the substances.

Electrolysis of Azobenzene

The yellow solution was electrolyzed in the cell at 40-45° till it became brown. On cooling in a fridge for 4-5 hrs, a high crop of blood red crystals separated from the mother liquor. It was characterised by CHN analysis [C=79.101% H = 5.533%, N=15.376%]. PMR spectra [peaks for protons at δ = 7.9531, 7.9263, 7.5393 and 7.5139 ppm]. Some strong ir frequencies at 689.92, 776.53, 926.25 and weak absorption at 1452.14 indicate NH linkage: Mass spectra showed main peak (m/e) at AMU = 105 due to $C_6H_5N_2^+$ abund = 100 and at AMU = 28 due to N_2^+ were comparable with the literature values of azobenzene.

Hydrazobenzene to Azobenzene

A time consuming chemical oxidation [12] with interhalogen compounds produced 70% trans-azobenzene. The preparation is tedious and noxious gases dominate. Wawzonek and McIntyre [13] reported electrochemical oxidation of hydrazobenzene on Pt and/or Hg to get 55% azobenzene. On spinel electrodes, the compound was easily oxidised to trans-azobenzene by simple mechanistic transformation of 2e, $2H^+$ with yield of 75%. This compares well with the chemical oxidation yield but enormously less complicated in terms of time and chemicals.

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