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Oxidation of methanol on perovskite-type $La_{2-x}Sr_xNiO_4$ ($0 \leq x \leq 1$) film electrodes modified by dispersed nickel in 1 M KOH

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ABSTRACT

Finely-dispersed nickel particles are electrodeposited on high surface-area perovskite-type $La_{2-x}Sr_xNiO_4$ ($0 \leq x \leq 1$) electrodes for possible use in a direct methanol fuel cell (DMFC). The study is conducted by cyclic voltammetry, chronoamperometry, impedance spectroscopy and anodic Tafel polarization techniques. The results show that the apparent electrocatalytic activities of the modified oxide electrodes are much higher than those of unmodified electrodes under similar experimental conditions; the observed activity is the greatest with the modified $La_{1.5}Sr_{0.5}NiO_4$ electrode. At 0.550 V (vs. Hg|HgO) in 1 M KOH + 1 M CH_3OH at 25 °C, the latter electrode delivers a current density of over 200 mA cm^{-2}, whereas other electrodes of the series produce relatively low values (65–117 mA cm^{-2}). To our knowledge, such high methanol oxidation current densities have not been reported on any other non-platinum electrode in alkaline solution. Further, the modified electrodes are not poisoned by methanol oxidation intermediates/products.

1. Introduction

Direct methanol fuel cells (DMFCs) are promising electrochemical energy converters for a variety of applications due to their simplicity, low pollution and high efficiency [1–3]. Nevertheless, commercialization of DMFCs suffers from two major problems, namely, a high overpotential (η) for the methanol oxidation reaction (MOR) [4,5] and methanol crossover from the anode to the cathode [6,7]. The latter problem can be minimized by using a low methanol concentration and employing a modified proton exchange membrane (PEM) [8]. In order to improve the reaction kinetics and lower the overpotential, considerable efforts have recently been made towards developing new electrodes with greatly enhanced electrocatalytic activities [9–30]. Most of these investigations have focused on Pt-based or Pt-Ru bimetallic systems mainly in acid electrolytes. Although Pt is a very efficient electrocatalyst for the MOR, it suffers loss in activity with time due to accumulation of surface poisoning intermediates such as CO formed during the oxidation reaction [5]. Moreover, noble metals are expensive and not readily available. There is naturally a serious demand to develop inexpensive and active electrode materials from non-noble metals for use as anodes in alkaline DMFCs. An alkaline electrolyte is considered superior to an acid one in respect of both, kinetics and material stability. A much wider range of materials, particularly pure as well as mixed oxides, are stable in alkaline solutions and can be used either as anodes or support materials for the dispersion of noble and other metals.

Oxides of V, Fe, Ni, In, Sn, La, and Pb [31] as anode materials have not shown any practical activity for methanol oxidation. By contrasts graphite supported perovskite-modified Pt electrodes exhibit much higher electrocatalytic activities, compared with smooth Pt or graphite supported-Pt electrodes, towards MOR in 1 M NaOH at 25 °C [32]. Recently, Raghuveer and Vishwanathan [33] investigated the electro-oxidation of methanol on bulk and nanocrystalline $La_{1.8}Sr_{0.2}CuO_4$ in 1 M KOH + 1 M CH_3OH and observed currents of 1.9 and 5.2 mA cm^{-2} at 0.6 V (vs. Ag|AgCl (scan rate = 25 mV s^{-1}), respectively. Raghuveer et al. [34] obtained 0.38, 1.47 and 1.84 mA cm^{-2} at E = 0.60 V (vs. Hg|HgO) on $La_{1.8}Sr_{0.2}CuO_4$, $La_{1.6}Sr_{0.4}CuO_4$ and $La_{1.9}Sr_{0.1}Cu_{0.9}Sb_{0.1}O_4$ in 3 M KOH + 2 M CH_3OH. Similar studies carried out by Yu et al. [35] gave 18.8 and 7.7 mA cm^{-2} on $La_{0.75}Sr_{0.25}CuO_{3-\delta}$ and $La_{0.75}Sr_{0.25}CoO_{3-\delta}$ at E = 0.60 V (vs. Ag|AgCl) in 1 M NaOH + 1 M CH_3OH (scan rate = 20 mV s^{-1}).

Recently, Deshpande et al. [36] prepared a variety of ABO_3 and A_2BO_4 perovskite oxides (A = Sr, Ce, La and B = Co, Fe, Ni, Pt, Ru) by means of aqueous solution combustion synthesis and then measured their catalytic performance for methanol electro-oxidation by a rapid screening approach (NuVant System). They found that

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the performance of Sr-based perovskites was comparable with that of the standard Pt-Ru catalyst. Using a similar method, Lan and Mukasyan [37] synthesized a series of perovskites (ABO_3; A = Ba, Ca, Sr, La; B = Fe, Ru) and carried out their electrochemical characterization for methanol oxidation under conditions similar to those for DMFCs. The study demonstrated that the perovskites containing ruthenium at the B-site were promising candidates for the development of effective catalysts.

Very recently [38], we have prepared perovskite-type $La_{2-x}Sr_xNiO_4$ ($0 \le x \le 1$) oxides by a modified citric acid sol–gel route and used them as anodes for the electrocatalysis of methanol oxidation in 1 M KOH. These new electrodes have produced much higher current densities than those already reported for other perovskite oxides [33–35] under alkaline conditions, namely, 23.6, 47.3, 43.2 and 50.9 mA cm^{-2} for electrodes with $x = 0$, $x = 0.25$, $x = 0.5$ and $x = 1.0$, respectively, at 10 mV s^{-1} and $E = 0.60$ V (vs. Hg|HgO) in 1 M KOH + 1 M CH_3OH (25 °C). More importantly, these complex oxide anodes have not shown any surface poisoning during methanol oxidation by the intermediate products. To improve their electrocatalytic activities, the electrodes have been modified by dispersed nickel and have been investigated for their electrocatalytic properties towards the MOR in 1 M KOH. The results of this investigation are described here.

2. Experimental

2.1. Electrode synthesis

2.1.1. Materials

Methanol (Merck, GR), potassium hydroxide (Merck, GR), $Ni(NO_3)_2{\cdot}6H_2O$ (Merck, 97%), $La(NO_3)_3{\cdot}6H_2O$ (Merck, 99%, GR), $Sr(NO_3)_2$ (CDH, 99.5%, AR), $(CH_3COO)_2Ni{\cdot}4H_2O$ (Reidel, 99.5%, AR), L-ascorbic acid (s.d.fine., AR), boric acid (Merck, 99.5%) and nickel foil (0.25 mm thick, Aldrich 99.98%) were used as-received. Redistilled water was used for preparation and dilution of all the solutions.

2.1.2. Preparation of $La_{2-x}Sr_xNiO_4$ electrodes

Perovskite oxides, namely La_2NiO_4, $La_{1.75}Sr_{0.25}NiO_4$, $La_{1.5}Sr_{0.5}NiO_4$ and $LaSrNiO_4$ were synthesized by a modified citric acid sol–gel precursor method [39,40]. In this method, nitrates of the constituent metals (La, Sr, Ni) of the oxides were dissolved, as per stoichiometry, in 100 ml of distilled water (total metal ion concentration = 0.23–0.26 M) and to this solution a slightly excess quantity of citric acid (CA = 0.231–0.2605 M), 2.0 ml of ethylene glycol (E. Merck, Germany) and finally two drops of concentrated HNO_3 were added. Vigorous stirring was carried out while adding these ingredients. A gel was soon formed which was heated slowly to effect decomposition. The resulting substance was fired at 100 °C to ash which was ground with an Agate pestle and mortar and calcined at 600 °C for 6 h to obtain the desired products. The oxides, thus obtained, have a tetragonal primitive crystal structure with a crystallite size of 9–12 nm [40].

The electrodes of the oxides (i.e. Ni/$La_{2-x}Sr_xNiO_4$) were obtained by painting a slurry containing the oxide powder and glycerol on to a pretreated nickel plate followed by sintering at 380 °C for 1.5 h. Pretreatment of the support and electrical contact with the oxide films were made as described previously [41]. The oxide loadings were 4–5 mg cm^{-2}.

2.1.3. Preparation of Ni-modified $La_{2-x}Sr_xNiO_4$ electrodes

Nickel was electrodeposited on $La_{2-x}Sr_xNiO_4$ electrodes from an acetate bath at a constant pH of 5.2 as reported elsewhere [42]. The composition of the electrolytic bath was 0.28 M nickel acetate + 0.4043 M boric acid + 10 mg ascorbic acid + 3 drops acetic acid. Electrodeposition was carried out at 25 °C in a conventional three-electrode, single-compartment, Pyrex glass cell at a constant current density of 20 mA cm^{-2} for 300 s. The auxiliary and reference electrodes were Pt-foil and Hg|HgO, respectively. After deposition, the complex oxide electrode (i.e., Ni/$La_{2-x}Sr_xNiO_4$/Ni) was removed from the cell, washed with distilled water, dried in air, and then used for the study.

2.2. Electrocatalyst characterization

2.2.1. Physicochemical

Nickel deposited on $La_{2-x}Sr_xNiO_4$ was examined by a SEM–EBSD integrated system (Hitachi, S3400N). The mass of electrodeposited nickel on each oxide film was determined by analyzing the electrolytic bath solution before and after Ni deposition by means of an atomic absorption spectrophotometer (AAS – PerkinElmer – 2380). The particle size of the powders used for preparation of the oxide electrode was measured with a particle size and shape analyzer (ANKERSMID, Holland).

2.2.2. Electrochemical

A conventional three-electrode, single-compartment, Pyrex glass cell, fitted with a pure Pt-foil (~8 cm^2) counter electrode and a Hg|HgO|1 M KOH reference electrode, was employed for electrochemical investigations. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Tafel polarization studies were conducted with an electrochemical impedance system (PARC, USA) attached with a potentiostat/galvanostat (Model 273 A), a lock-in-amplifier (5210) and a computer (COMPAQ P4). The CV of each electrocatalyst was investigated between 0 and 0.65 V (vs. Hg|HgO) in 1 M KOH with and without methanol at 25 °C. Before recording the final voltammogram, each electrode was cycled for five runs at a scanning rate (ν) of 50 mV s^{-1} in 1 M KOH. The anodic polarization curves (E vs. $\log j$) were recorded using a run program with conditioning time = 200 s, conditioning potential = 0.35 V, initial delay = pass, $\nu = 0.2$ mV s^{-1}, initial potential = 0.35 V, and IR interruption = 10 s.

The EIS study of the electrodes was performed in 1 M KOH + 1 M CH_3OH with an ac voltage amplitude of 10 mV at a constant dc potential. The frequency range employed in the study was 0.1–25 × 10^3 Hz. The equivalent-circuit parameters were analyzed by the software, ZSimpWin.

All electrochemical experiments were performed in argon deoxygenated electrolytes at 25 °C. The potential values reported in the text are given against the Hg|HgO, 1 M KOH electrode.

3. Results and discussion

3.1. Morphology/particle size

Scanning electron micrograph (SEM) images of Ni as-deposited on La_2NiO_4, $La_{1.75}Sr_{0.25}NiO_4$, $La_{1.5}Sr_{0.5}NiO_4$ and $LaSrNiO_4$ show that the surface of each oxide consists of highly dispersed granules. The SEM images of two representative oxide catalysts, La_2NiO_4 and $La_{1.5}Sr_{0.5}NiO_4$ with and without Ni deposition, are presented in Fig. 1. The oxide surface unmodified with Ni seems to be somewhat less compact [38]. It is worth mentioning that all the oxide catalysts and procedures for obtaining their films were the same as reported elsewhere [38].

The quantity of Ni deposited on La_2NiO_4, $La_{1.75}Sr_{0.25}NiO_4$, $La_{1.5}Sr_{0.5}NiO_4$ $LaSrNiO_4$ films is 0.91, 2.79, 2.32, and 1.59 mg cm^{-2}, respectively.

Values of the mean particle size of powders of the oxide with $x = 0$, $x = 0.25$, $x = 0.5$ and $x = 1.0$ are 21.41, 19.38, 0.84 and 0.8 μm,