Short communication

Potential application of Ni and Co stabilized zirconia as oxygen reduction reaction catalyst

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ABSTRACT

A new facile template method for the preparation of Ni, Co doped ZrO_2 self-assembled electrocatalysts for oxygen reduction reaction was employed. The effect of the Ni and Co incorporation into ZrO_2 lattice on the structural, textural, surface chemistry and its activity on ORR was emphasized. As X-ray diffraction reveals, the pseudo-cubic lattice of the tetragonal ZrO_2 polymorph (t-ZrO_2) is stabilized when Ni and Co are co-doping ZrO_2. The results indicate that the synergetic effects arisen from the intimate electronic interaction of the mixed oxides present in the lattice of the zirconia phase, i.e. $Ni_{1-x}Co_xO$ (or NiO and CoO) in NCZ enhance the electrocatalytic activity of the catalyst.

1. Introduction

The expansion of energy consumption and infrastructure worldwide, which currently is strongly focused on fossil fuels and nuclear energy sources, makes a tremendous necessity to develop new low environmental impact processes of conversion of chemical energy. Together with the increasing world population tendency, it is expected that the global demand for energy will be more than double by the mid-century and perhaps more than triple by the end of the century; satisfying this demand is necessary in order to achieve vibrant technological progress, economic growth and most importantly, political stability over the coming decades [1–5]. Although the energy consumption rate becomes very hardly sustainable for humanity, the biggest problem for the immediate future is not the imminent depletion of fossil fuel deposits, but the consequences derived from its combustion. In this regard, it appears that the development of fuel cell technology, which provides clean and sustainable energy through direct electrochemical conversion, is one of the most promising solutions to solve these problems [4–6]. Because of their ability to rapidly function at ambient temperature, the polymer electrolyte membrane fuel cells (PEMFCs) are the first choice solution for mobile applications. In

PEMFC the chemical energy of hydrogen and oxygen (air) is converted into usable electrical energy. The main electrochemical reactions are:

$$\text{Anode}: H_2 \rightarrow 2H^+ + 2e^- \quad (HOR) \tag{1}$$

$$\text{Cathode}: \frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \quad (ORR) \tag{2}$$

$$\text{Overall}: H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{3}$$

If the problems of the hydrogen oxidation reaction (HOR) have been mainly solved by using CO-tolerant nanocatalyst systems [7,8] in contrast, the oxygen reduction reaction (ORR) is still nowadays the object of intense research studies. Besides the world limited resources of Pt and especially its prohibitive price, Pt based cathodes limitations such as CO deactivation, time dependent drift or fuel crossover effect [9–11] have hindered the widespread commercialization of fuel cells and have accelerated the search for new non-Pt alternative catalysts. The most challenging problem of PEMFCs cathode is the replacement of platinum-based catalyst.

Therefore, a lot of research has been devoted for the development of electrocatalysts with low noble metal content or even for non-noble metal systems, as for example electrocatalysts derived from polyaniline, iron, and cobalt or noble metal-free hydrazine based materials [4,12–18]. Different synthesis routes were approached for obtaining materials based on transitional metal oxides in order to improve the

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electrochemical performance of the PEMFCs cathodes [4,17,18]. Thus, Goubert-Renaudin et al. [19] found that the activity towards ORR in alkaline medium of the antraquinone graphed on NiO/Carbon was lower than cobalt polypyrrole carbon (Co–Ppy–C) composites. Bing et al. [20] developed Pt–Pd alloys deposited on $(Nb_{0.07}Ti_{0.93}O_2)Ywt\% - C(1 - Y)wt\%$, $Y = 25–75$ (weight) electrocatalysts for ORR. They investigated the effect of the synthesis conditions such as solvent and inorganic precursor concentrations, carbon amount used for preparation of the composite on the structural and electrochemical performance. The importance of metal oxide component in improvement of durability of electrocatalysts was revealed [20]. Different metal oxides such as $ZrO_{2 - x}$, $Co_3O_{4 - x}$, $TiO_{2 - x}$, $SnO_{2 - x}$ and $Nb_2O_{5 - x}$ obtained by sputtering showed ORR activity [21,22,23]. Okamoto et al. [24] suggests that defects such as O vacancies on the surface may participate in ORR and contribute to a sustainable catalytic cycle. However noble metal free ORR electrocatalysts suffers of a relatively low conductivity. Alternative to improve the conductivity (electronic and ionic) is to create ionic defects (anionic or cationic) by new methods of synthesis, partial substitution of cations or finding new oxides mixtures.

In this line, the goal of this study is to find non-precious metal catalyst as an alternative solution for ORR electrocatalysts, which is a requirement for practical application of PEMFCs. The guiding concept was to use more ordered chemical structures, as self-assembled materials based on zirconia. The self-assembled materials represent building blocks that are formed from interatomic and intermolecular interactions, other than traditional covalent, ionic and metallic bonding forces which possess special properties.

The present work focuses on the direct synthesis of Ni, Co doped ZrO_2 by a self-assembling method using Triton ×100, non-ionic surfactant, as template. We used this non-ionic surfactant as template for the obtaining the porous structure and to decrease the particles size, for improving the electrocatalytic performance. After the thermal treatment the hydrophilic polyethylene oxide chains and hydrophobic groups from Triton ×100 are removed and thus porosity is created, providing a proper transport of the oxygen through the catalysts layers. Since few studies were orientated over bimetallic catalysts supported on zirconia and their state needed further investigations and elucidations, ZrO_2 was chosen because it is a cheap, abundant and relative stable ceramic oxide and therefore represents an important candidate for such applications, while Ni and Co as active sites to modify zirconia surface by creating defects required to adsorb the oxygen molecules. The effect of the Ni and Co incorporation into ZrO_2 lattice on the structural, textural, surface chemistry and its activity on ORR is further emphasized.

2. Experimental

2.1. Catalysts preparation

The synthesis method approaches a self-assembling process using non-ionic surfactants (Triton ×100 and polyvinylpyrrolidone (PVP)) as template and tripropylamine (TPA) as chelating agent. Polyvinylpyrrolidone (average mol wt 360,000) can act as a dispersant/stabilizer agent and it can control the particle size. Nickel (II) acetylacetonate (95%,) cobalt (II) acetate (99.995% trace metals basis) - and zirconium (IV) propoxide solution were used as inorganic precursors and 1-propanol as solvent. The ratio Triton ×100:TPA:PVP was 1:6:9. In a typical synthesis, Triton ×100 and PVP were dissolved in 1-propanol with magnetic stirring to form the template micellar solution. Tripropylamine (TPA) was added to the inorganic precursors dissolved in 1-propanol. After all the reactants had completely dissolved, the reaction mixture was added to the template micellar solution, under vigorous stirring. The obtained solutions were treated at 40 °C, under continuous stirring, for 6 h. The gels obtained have been dried at room temperature followed by thermal treatment at 600 °C for 8 h. The obtained samples – NiO (15 mol%) doped ZrO_2, Co (15 mol%) doped

ZrO_2 and Ni (7.5 mol%) –Co (7.5 mol%) doped ZrO_2 are labeled as NZ, CZ and NCZ, respectively.

2.2. Catalysts characterization

X-ray diffraction analyses were carried out on a Shimadzu XRD-7000 diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å, 40 kV, 40 mA) at a scanning speed of 0.10° min^{-1} in the 2θ range of 6–70° with a step size of 0.02° and scan time of 2° min^{-1}. The crystallite sizes were calculated using Scherrer's formula $D = k\lambda / \beta \cos \theta$, where D is the average crystallite size, k a constant equal to 0.89, λ the wavelength of X-rays and β is the corrected half width. Raman spectroscopy was performed using a Horiba spectrometer, equipped with a He-Ne ($\lambda = 633$ nm) laser. The spectra were recorded in the 100–800 cm^{-1} range.

Scanning electron microscopy (SEM, Quanta 3D, FEI, The Netherlands). The images were recorded with a Field Emission Gun FEI Quanta 3D microscope operating at 2 kV.

Porosity Analysis (BET) - Brunauer–Emmett–Teller adsorption–desorption isotherms of N_2 were investigated using a Micrometrics instrument (ASAP2010) by N_2 adsorption at the nominal temperature of liquid nitrogen (-196 °C) and at a wide relative pressure range from 0.01 to 0.995. Prior the analysis, the samples were degassed at 150 °C for 5 h using helium.

The differential thermal analysis and thermogravimetric analysis of the dried precursors were carried out using a TG-DTA analyzer Shimadzu DTA-60 instrument on 4–6 mg samples in N_2 atmosphere with a heating rate of 5 °C min^{-1} from room temperature to 900 °C, using alumina as reference.

UV-vis spectra were recorded using a UV3600 UV-vis Shimadzu spectrophotometer equipped with Shimadzu ISR-3100 Integrating Sphere Attachment and two light sources - D_2 (deuterium) lamp for the ultraviolet range WI (halogen) lamp for the visible and near-infrared range. The spectra were recorded in the range of 220–2600 nm with a wavelength step of 2 nm, working with a slit width of 8 nm (for 220–800 nm) and 32 nm (for 800–2600 nm). The UV-vis spectra were measured using samples diluted with extra pure barium sulfate (purchased from Nacalai Tesque).

Surface analysis performed by X-ray photoelectron spectroscopy (XPS) was carried out on PHI Quantera equipment with a base pressure in the analysis chamber of 10^{-9} Torr. The X-ray source was monochromatized Al Kα radiation (1486.6 eV) and the overall energy resolution is estimated at 0.65 eV by the full width at half-maximum (FWHM) of the Au4f$_{7/2}$ photoelectron line (84 eV). Although the charging effect was minimized by using a dual beam (electrons and Ar ions) as neutralizer, the spectra were calibrated using the C1s line (BE = 284.8 eV) of the adsorbed hydrocarbon on the sample surface (C—C or $(CH)_n$ bondings).

2.3. Electrochemical measurements

The Ni, Co doped ZrO_2 catalysts as well as the zirconia (Z) were deposited onto graphite electrode and used as working electrode. Firstly, the NCZ catalyst (6 mg) was dispersed in distilled water (2 mL) and isopropanol (2 mL) by ultrasonication for 5 h. The deposition of NCZ catalyst on graphite electrode (NCZ/G) was made by dropping 500 μL of mixture on the surface graphite (s = 1 cm^2). A 5% Nafion solution (2 μL) was finally added on in order to immobilize the catalyst on the graphite electrode. Prior to the deposition, the graphite electrode was mechanically polished, rinsed with distilled water and dried at room temperature. The deposition of Z, NZ and CZ catalysts on graphite electrode, labeled as Z/G, NZ/G and CZ/G, was obtained by the same procedure presented above.

The electrochemical performance of the NZ, CZ and NCZ catalysts deposited on graphite electrode towards oxygen reduction reaction (ORR) was studied by Linear Sweep Voltammetry in a potential range of 0.2 V to -1 V at 20 mV s^{-1} in alkaline solution (KOH 0.1 M). Prior to each