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Facile synthesis of Zr- and Ta-based catalysts for the oxygen reduction reaction

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ABSTRACT

Cathode catalysts for direct alcohol fuel cells (DAFCs) must have high catalytic activity for the oxygen reduction reaction (ORR), low cost, and high tolerance to the presence of methanol or ethanol. Pt is the benchmark catalyst for this application owing to its excellent electrocatalytic activity, but its high cost and low tolerance to the organic fuel permeating through the membrane have hindered the commercialization of DAFCs. Herein we present a facile synthesis route to obtain organic fuel-tolerant Zr- and Ta-based catalysts supported on carbon. This method consists of a simple precipitation of metal precursors followed by a heat treatment. X-ray diffraction analyses confirmed that the obtained samples were crystalline ZrO_{2-x} and $\text{Na}_2\text{Ta}_2\text{O}_{11-x}$ having crystallite sizes of 26 and 32 nm, respectively. The thermal treatment effectively increased the activity of the catalysts towards the ORR, although further optimization is necessary. Both catalysts exhibited a high tolerance to the presence of methanol with only a moderate reduction in ORR activity even at high methanol concentration (0.5 mol/L).

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1. Introduction

Direct alcohol fuel cells (DAFCs) are candidate power sources for portable applications and auxiliary power supply units owing to their high theoretical energy conversion efficiency, high energy density, and low operating temperature [1]. However, DAFCs suffer from a series of drawbacks that must be solved before their wide commercialization is possible. These include a low power density, fuel cross-over, and high component cost, especially their Pt-based catalysts and Nafion-based membrane. The dependence on expensive and scarce Pt resources is still a major obstacle, particularly for the large-scale production of fuel cells.

Many investigations have been recently carried out to develop Pt-free electrocatalysts for low-temperature fuel cells. Although Fe- and Co-based catalysts for the oxygen reduction

reaction (ORR) have been studied for over 50 years, significant breakthroughs have been achieved only very recently [2–5]. However, although the activity of these catalysts has been increased sufficiently for them to be considered potential competitors to Pt-based catalysts in terms of activity [6], significant efforts are required to further enhance their stability.

Another interesting approach is the use of group 4 and 5 metal oxides (Ti, V, Zr, Nb, Hf, Ta) [7,8], which are characterized by an excellent stability in acid media [9]. Group 4 and 5 metal oxides become active towards ORR when their surface is suitably modified. These surface modifications are intended to change the oxidation state of the metal species to form active and stable catalytic sites that are able to adsorb oxygen molecules. These sites are generally characterized by oxygen vacancies, which render the electronic density of states more Pt-like. Four modification methods for such metal oxides have been

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described by Ota et al. [7]: (1) Formation of complex oxide layers containing active sites; (2) substitutional doping with nitrogen; (3) creation of oxygen defects; and (4) partial oxidation of metals with carbon and/or nitrogen.

The active sites of catalysts based on group 4 and 5 metals have not yet been elucidated. More fundamental research is necessary to understand the origin of their catalytic activity for the ORR and to develop new strategies to obtain both a high quality and high density of active sites. Until now, the best results have been obtained with partially oxidized Ta and Zr carbonitrides obtained by electron sputtering [10–12] or by heat treatment above 1000 °C [13–15]. In the present work, we used a facile synthetic technique comprising fast precipitation of metal oxides onto carbon black and subsequent thermal treatment in Ar at 900 °C to create active catalytic sites. In this way, we successfully prepared Ta and Zr substoichiometric oxides having suitable activity towards the ORR and tolerance to the presence of methanol.

2. Experimental

2.1. Preparation

Ta- and Zr-based catalysts were supported on carbon black. Carbon black (Ketjenblack DJ-600 EC) was dispersed in water (0.3 mg/mL) under sonication for 1 h. An appropriate amount of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Fluka) or TaCl_5 (Alfa Aesar) was then dissolved in the carbon black slurry under vigorous stirring and sonicated for 1 h. The amounts of metal precursors added were controlled to obtain catalysts containing 50 wt% carbon black and 50 wt% metal oxide. The pH of the slurry was then adjusted to 10.9 with 1 mol/L NaOH solution and the reaction was left under vigorous stirring for another 3 h. The catalyst was filtered, thoroughly washed with deionized water, and dried under vacuum at 120 °C for 1 h and then overnight at 60 °C. Finally, the resulting material was subjected to heat treatment in Ar atmosphere at 900 °C for 90 min.

2.2. Characterization

The obtained catalysts were characterized by X-ray diffraction (XRD) using a Philips X-pert 3710 X-ray diffractometer operating at 40 kV and 20 mA with $\text{Cu K}\alpha$ radiation. The total metal content in the catalyst was determined by burning the carbon support in air through thermogravimetric analysis up to 950 °C in a Netzsch STA analyzer. Scanning electron microscopy-energy-dispersive X-ray (SEM-EDX) analysis was carried out at 25 kV using a FEI XL30 SFEG microscope. Standard commercial oxides were analyzed under the same instrumental conditions to calibrate for the oxygen content. Transmission electron microscopy (TEM) analyses of the catalysts were carried out by first dispersing the catalyst powders in isopropyl alcohol. A few drops of the solution were deposited on carbon film-coated Cu grids and analyzed with a FEI CM12 microscope.

2.3. Electrochemical studies

Electrochemical studies were carried out using a three-electrode cell in 0.5 mol/L H_2SO_4 electrolyte at room temperature. A saturated calomel electrode ($\text{Hg}|\text{Hg}_2\text{Cl}_2$, sat. KCl) was used as the reference electrode, and a high surface Pt coiled wire was used as the counter electrode. A rotating disk electrode (RDE) was used as the working electrode, which consisted of a thin film of the catalyst (100 $\mu\text{g}/\text{cm}^2$) deposited on a glassy carbon disk (5 mm). Sample ink for the RDE was prepared by sonicating the catalyst (2 mg/mL) in iso-propanol and Nafion (ionomer to catalyst weight ratio = 0.30). The best catalyst in terms of electrocatalytic activity was further investigated for the ORR in the absence and presence of methanol using a gas diffusion electrode (GDE). The methanol concentration in the 0.5 mol/L H_2SO_4 aqueous electrolyte was varied between 5 and 500 mmol/L. Oxygen was directly fed to the electrode backing layer in this configuration. The GDE was prepared according to a procedure described elsewhere [16]. The gas diffusion layer and the catalytic layer were laminated on carbon cloth backings. A hydrophobic backing layer (LT 1200 W ELAT, E-TEK) was used to reduce flooding effects in the sulfuric acid half-cell. The catalytic layer was composed of 30 wt% Nafion® ionomer and 70 wt% catalyst, with a catalyst loading of ca. 1.4 mg/ cm^2 . Cyclic voltammetry and linear sweep voltammetry analyses were carried out using an Autolab Metrohm potentiostat/galvanostat. For the RDE configuration, polarization curves were obtained in the idle mode, i.e., no rotation was applied.

3. Results and discussion

Fig. 1 shows the XRD patterns of the untreated and thermally treated ZrO_x/C and TaO_x/C catalysts. No diffraction peaks were observed in the untreated catalysts, owing to the amorphous structure of both the carbon support and the metal species. The thermally treated Zr-based catalyst (Fig. 1(a)) exhibited the base-centered monoclinic structure ($\text{P}2_1/\text{c}$) of ZrO_2 (JCPDS 83-0940). The peaks were shifted towards slightly higher Bragg angles, which means that there was a slight contraction of the lattice parameters. This may be attributed to the presence of oxygen vacancies, causing cell contraction. The crystallite size was determined to be 25.7 nm, calculated from the (-111) peak broadening at $2\theta = 28.3^\circ$ using the Scherrer equation.

The thermally treated Ta-based catalyst (Fig. 1(b)), on the other hand, exhibited an unusual crystalline structure, the orthorhombic structure of $\text{Na}_2\text{Ta}_8\text{O}_{21}$ (JCPDS 28-1137). In fact, no peaks matching the typical orthorhombic structure of Ta_2O_5 were found (JCPDS 25-0922). The presence of Na within the Ta oxide structure meant that both cations, Ta^{5+} and Na^+ , co-precipitated in a single structure during the pH correction. This co-precipitation did not occur in the case of Zr. The peaks were slightly shifted towards higher Bragg angles with respect to those reported for the $\text{Na}_2\text{Ta}_8\text{O}_{21}$ orthorhombic structure, as observed for the Zr-based catalyst, which may have been caused by cell contraction resulting from the presence of oxygen vacancies. The crystallite size was calculated to be 32.5 nm from the (360) peak broadening at $2\theta = 26.1^\circ$ using the Scher-

Fig. 1. XRD patterns of untreated and heat-treated catalysts. (a) Zr-based; (b) Ta-based.

rer equation.

The composition of the Ta-based catalyst and its approximate degree of substoichiometry was determined by EDX analysis. A careful calibration of the oxygen content was made by determining the oxygen sensitivity factor under the same instrumental conditions using a standard commercial Ta₂O₅ sample. The EDX analysis results (Table 1) indicated an atomic composition of Na₂Ta₈O₂₁, which is in agreement with the previous hypothesis of a crystalline structure with oxygen vacancies (Na₂Ta₈O_{21-x}, with $x = 6$).

The creation of oxygen vacancies was the result of the annealing process in the presence of the carbon support, which acted as a reducing agent. The related processes for the Zr-based and Ta-based catalysts, respectively, are expressed in Eqs. (1) and (2):

Thermogravimetric analysis (TGA, Fig. 2) showed that both samples had the same amount of catalyst phase on the carbon

Fig. 2. Thermogravimetric curves of the catalyst samples measured in air at a heating rate of 5 °C/min.

support, about 50 wt%. Interestingly, zirconia appeared to catalyze the decomposition of the carbon to a larger extent than the Ta-phase. This may also indicate a larger interaction between the catalyst and support in the case of the Zr sample. Such an effect may cause a lower availability of the catalytic sites for the oxygen reduction.

TEM analysis was carried out to study both the particle size distribution and the shape of the primary catalyst particles. The first evidence found was the occurrence of a modification of the typical Ketjenblack morphology. In fact, the usual morphology, randomly oriented graphitic basal planes with a “fingerprint”-like appearance [17], was altered to that typical of amorphous carbon, with some evidence of exfoliation (Fig. 3). This effect was more apparent for the Zr-based catalyst, in agreement with the TGA results. Individual primary particles were more evident in the Zr-based catalyst and were round in shape (Fig. 3(a)). The primary particles of the Ta-catalyst were less visible because they mostly formed large agglomerates (Fig. 3(b)). In both catalysts, some regions contained isolated large crystalline particles that were round in the case of the Zr-catalyst and faceted in the case of the Ta-catalyst. This bimodal distribution meant that an accurate estimation of the mean particle size was not easy to obtain from the TEM images. The typical particle size of both catalysts was generally smaller than that observed by XRD. However, as discussed above, there were some regions characterized by particles much larger in size than the mean value determined from the peak broadening in the XRD patterns. Because the volume of sample analyzed by XRD was several orders of magnitude larger than that analyzed by TEM, the value derived from the XRD results was considered to be more reliable.

The ORR was studied in 0.5 mol/L H₂SO₄ aqueous solution

Fig. 3. TEM images of ZrO_x/C900 (a) and TaO_x/C900 (b).

Table 1

EDX analysis results for the heat-treated TaO_x/C900 catalyst.

Element	Atomic composition (%)
Ta	5.10
O	9.96
Na	1.32
C	83.61

Fig. 4. Linear sweep voltammetry curves of heat-treated $\text{ZrO}_x/\text{C900}$ (a) and $\text{TaO}_x/\text{C900}$ (b) catalysts in O_2 and N_2 atmosphere, 0.5 mol/L H_2SO_4 , idle mode RDE, $100 \mu\text{g}$ catalyst/ cm^2 . The scan rate was 5 mV/s.

using a half-cell configuration. The catalysts were deposited as a thin film on a glassy carbon RDE. Fig. 4 shows the polarization curves obtained in nitrogen and oxygen atmosphere at 5 mV/s and in idle mode for the thermally treated Zr and Ta catalysts. The difference between the current obtained in O_2 and that obtained in N_2 is attributed to the ORR. The onset potential, defined as the potential between the O_2 curve and the N_2 curve at a current difference of $-0.2 \mu\text{A}/\text{cm}^2$ [8], was 0.38 V vs RHE (TaO_x/C) and 0.44 V vs RHE (ZrO_x/C) for the untreated catalysts. The catalysts subjected to heat treatment exhibited higher onset potentials of 0.46 V vs RHE ($\text{TaO}_x/\text{C900}$) and 0.47 V vs RHE ($\text{ZrO}_x/\text{C900}$). Ota et al. [8] observed that oxide-based catalysts exhibit an onset potential that is 0.3–0.4 V more negative than that of catalysts based on partially oxidized carbonitrides of Ta and Zr. Nevertheless, the heat treatment of the carbon-supported Ta and Zr oxides significantly improved their catalytic activity for the ORR.

The difference between the current measured in oxygen (j_{O_2}) and the current measured in nitrogen (j_{N_2}), i.e., $j_{\text{ORR}} = j_{\text{O}_2} - j_{\text{N}_2}$, is reported in Fig. 5 for both the untreated and thermally treated catalysts. The thermal treatment led to a significant increase in current density. This increase should be attributed to either an improvement in the crystallinity of the sample, as

Fig. 5. Polarization curves, $j_{\text{ORR}} = j_{\text{O}_2} - j_{\text{N}_2}$, for the untreated and thermally treated catalysts, obtained in 0.5 mol/L H_2SO_4 , idle mode RDE, $100 \mu\text{g}$ catalyst/ cm^2 . The scan rate was 5 mV/s.

observed by XRD, and/or to the creation of surface defects that became active for oxygen adsorption. The thermally treated catalyst based on Ta exhibited a slightly higher activity than the one based on Zr. Regarding a particle size effect, as is well known, surface area is inversely proportional to particle size and mass density. According to the crystallite size and density of the samples, the $\text{ZrO}_x/\text{C900}$ catalyst had, in principle, a higher surface area than the $\text{TaO}_x/\text{C900}$ catalyst owing to its lower crystal size (24 nm) and its lower density ($5.8 \text{ g}/\text{cm}^3$) than those of $\text{TaO}_x/\text{C900}$ (32 nm and $7.6 \text{ g}/\text{cm}^3$, respectively). Unlike for noble metal catalysts, in-situ determination of the electrochemically active surface area was not possible in the present case; we should thus assume that the catalytic active area of the catalysts was directly related to their theoretical surface area.

Despite the higher surface area of the Zr-based catalyst, the Ta-based catalyst exhibited slightly better catalytic activity (same metal loading in the electrode). This difference indicates a higher intrinsic activity of the Ta-based catalyst compared with that of the Zr-based catalyst. Besides their different chemistry and surface area, the catalysts also had different particle shapes, being essentially round for ZrO_2 and mostly faceted for the Ta-phase (Fig. 3). The oxygen reduction process is a structure-sensitive reaction and the presence of faceted particles may affect this process.

These results indicate that our facile synthesis method is a promising way to obtain group 4 and 5 metal-based non-noble catalysts active for the ORR owing to abundant surface defects. Nevertheless, further optimization is essential to increase their catalytic activity, especially at low overpotentials. This could be accomplished by reducing the crystal size by thermal treatment at a lower temperature that is still high enough to obtain an oxygen-defective structure, or by using a higher surface area carbon support and/or lower metal oxide loading on the carbonaceous support.

Besides their suitable oxygen reduction activity, the thermally treated catalysts also showed excellent tolerance to the presence of a high concentration of methanol. The tolerance to methanol poisoning was investigated for the best performing catalyst, i.e., $\text{TaO}_x/\text{C900}$. Fig. 6 shows the effect of the concentration of methanol in the electrolyte solution on the oxygen reduction activity. In the presence of a high methanol concen-

Fig. 6. Polarization curves of heat-treated TaO_x/C catalyst obtained in GDE configuration, with oxygen flowing through the back side, in the absence and presence of methanol of different concentrations in 0.5 mol/L H₂SO₄, 1.4 mg catalyst/cm². The scan rate was 5 mV/s.

tration (0.5 mol/L methanol) the change in ORR activity was quite moderate and essentially unchanged, whereas a reverse current (oxidation) is generally obtained for Pt catalysts at methanol concentrations larger than 100 mmol/L [18].

4. Conclusions

Zr- and Ta-based catalysts on a carbon support were easily prepared by a precipitation procedure and subsequent heat treatment in inert atmosphere. XRD analyses evidenced the structures of ZrO₂ and Na₂Ta₈O₂₁ with crystal sizes of 26 and 32 nm, respectively. A shift of the diffraction peaks towards higher Bragg angles suggested the occurrence of oxygen vacancies in

the crystalline structure. The heat treatment was effective in improving the catalytic activity towards the ORR. However, a modification of the carbon black support morphology occurred upon thermal annealing and the shape of primary particles appeared different for the two catalysts as well as the interaction between the catalyst phase and carbon. Suitable tolerance to methanol was also found. However, further optimization of crystal size, e.g., using high surface area supports, decreasing the amount of metal oxide loaded on the support, and/or reducing the heat treatment temperature, may be beneficial to enhance the catalytic performance.

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Graphical Abstract

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Facile synthesis of Zr- and Ta-based catalysts for the oxygen reduction reaction

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A facile synthesis method including an annealing treatment for Zr- and Ta-based catalysts is reported. Highly crystalline and substoichiometric ZrO₂ and Na₂Ta₈O₂₁ phases were supported on carbon, and showed both good activity towards ORR and methanol tolerance.

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