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Manganese dioxide electrocatalysts for borohydride fuel cell cathodes?

B. Šljukić *, D.M.F. Santos, C.A.C. Sequeira

ICEMS, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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ABSTRACT

Electrocatalysts of manganese dioxide (MnO_2) supported on activated carbon (AC) were prepared by low-temperature (ltMnO_2/AC) and high-temperature (htMnO_2/AC) procedures. Structure, morphology and composition of the synthesised materials were investigated by X-ray diffraction analysis, transmission electron microscopy and thermogravimetric analysis. Activity of the two prepared electrocatalysts for the oxygen reduction reaction (ORR) was investigated in alkaline media and ORR kinetic parameters evaluated from rotating disc electrode measurements. It was found that the ORR proceeds as two-electron process at ltMnO_2/AC-based electrode, while it proceeds as four-electron process at htMnO_2/AC-based electrode. The two electrocatalysts were further investigated for application as cathode materials in direct borohydride fuel cells. For that purposes the ORR at MnO_2/AC was investigated in the presence of borohydride in alkaline solution and in the temperature range from 25 to 65 °C. It could be observed that the activity of ltMnO_2/AC for the ORR is significantly suppressed in the borohydride-containing solution whereas htMnO_2/AC still showed high activity for the ORR.

1. Introduction

Oxygen reduction reaction (ORR) keeps attracting attention due to its involvement in numerous electrochemical processes, including metal corrosion, water electrolysis and energy storage/conversion. One of the ORR applications is for fuel cells (FCs) that directly convert chemical energy of the oxidation of a fuel into electrical energy in a continuous process. FCs are seen as alternative power sources, efficient and clean, that could replace the existing fossil fuel-based technologies for application in portable devices as well as in vehicles [1]. Direct borohydride fuel cells (DBFCs) present a group of alkaline fuel cells that employs oxidation of sodium borohydride ($NaBH_4$) [2] as the anodic reaction and reduction of oxygen (O_2) [3] or hydrogen peroxide (H_2O_2) [4] as the cathodic reaction. DBFCs have many advantages in relation to other types of fuel cells including high cell voltage, high efficiency, good energy density, fuel's stability and non-flammability, product's low toxicity and recyclability [5–8]. Efficient energy conversion in DBFCs and FCs in general depends on the materials used for anode and cathode, as they determine the cell voltage. Modification of the electrode surface with a catalyst is a common approach to improve ORR kinetics, with platinum (Pt) being the most commonly used electrocatalyst to date due to its high activity, conductivity and stability [9]. However, its high cost limits the commercial production and application of DBFCs, as well as other types of FCs. Thereafter, there is a wide research for alternative electrocatalysts to be used for cathodes and anodes in FCs [10–12]. Literature reports point out manganese oxide (MnO_2) as a possible alternative cathodic material due to its abundance, low cost and high electrocatalytic activity [13–15]. MnO_2 exhibits comparable activity for the ORR but less susceptibility to contamination than Pt-based catalysts [16]. Investigation of Pt, gold (Au), silver (Ag) and MnO_2-based electrocatalysts for the ORR in alkaline medium showed that though activity of Pt, Au and Ag is higher in pure sodium hydroxide solution, their activity decreases in the presence of traces of borohydride [17]. On the contrary, the activity of MnO_2-based electrocatalyst changes only slightly upon the addition of borohydride in trace quantities [17].

Electrocatalytic activity of MnO_2 for the ORR in alkaline solutions arises from the presence of hydrogen (H) atoms and hydroxyl (OH) groups at the oxide surface [18]. ORR electrocatalysed by MnO_2 is believed to proceed either by four-electron direct reduction of O_2 to OH^- ions or by two successive two-electron processes with hydroperoxide ion (HO_2^-) as intermediate [19,20]. The latter involves reduction of O_2 to HO_2^- mediated by the Mn(IV)/Mn(III) couple, with MnO_2 further facilitating either the HO_2^- intermediate species electroreduction to OH^- or its chemical disproportionation into O_2 and OH^-. As HO_2^- ions are corrosive, materials such as MnO_2 that catalyse their decomposition are desirable for applications in DBFCs.

Herein one reports the preparation of activated carbon (AC)-supported MnO_2 electrocatalysts by two different methods, involving low- and high-temperature procedures. Both methods lead to direct synthesis of MnO_2 onto AC thus providing higher dispersion of the catalyst on the high-surface area carbon support. These

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* Corresponding author.
E-mail address: biljana.paunkovic@ist.utl.pt (B. Šljukić).

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procedures allow a better anchorage between the support and the catalyst than in the case of simple mixing. AC has been chosen as support material due to its exceptional porosity, with typical surface area ranging from 500 to 1500 $m^2\ g^{-1}$. Moreover, the use of AC closely simulates the conditions in DBFCs, where carbon is often used as catalyst's support in cathodes [15].

The catalytic activity of MnO_2 depends on its morphology and crystal structure [21–24]. In the case of MnO_2 supported on a carbon substrate, the activity of the electrocatalysts for the ORR is influenced by the nature of the support itself as well. Furthermore, dopants such as nickel are known to affect the ORR mechanism and possibly change it from two-electron process at undoped MnO_x/C to four-electron process at doped MnO_x/C [25,26]. The present study deals with the effect of the preparation procedure on the structure of MnO_2/AC and its influence on the performance of the composite as cathode electrocatalyst in DBFCs. Structure, morphology and surface chemistry of the carbon-supported MnO_2 that are generally linked to its physicochemical properties and catalytic activity for the ORR are characterised by X-ray diffraction (XRD) and transmission electron microscopy (TEM) herein. Electrocatalytic activity of the two electrocatalysts is investigated in respect to the ORR in alkaline media using cyclic voltammetry (CV), linear scan voltammetry (LSV) and chronoamperometry (CA). Rotating disc electrode (RDE) measurements are used to determine the reaction kinetic parameters. In order to explore the two electrocatalysts' potential application in DBFCs, the influence of the operational conditions, namely presence of borohydride and temperature, on the ORR kinetics is investigated as well.

2. Experimental

2.1. Synthesis of MnO_2/AC

High-temperature synthesis of MnO_2/AC starts by adding 1 g of activated carbon (AC 1, Norit) into 25 ml of saturated manganese nitrate ($Mn(NO_3)_2$, Barral) solution. The mixture is blended using magnetic stirring for 1 h followed by filtration. Once the blend is dried at room temperature, it is heated to 320 °C at 10 °C min^{-1} rate and left at that temperature for 10 h, leading to conversion of nitrate precursor into oxide.

Low-temperature synthesis method starts by impregnation of AC in a saturated potassium permanganate ($KMnO_4$, Merck) aqueous solution by stirring AC (200 mg) in precursor solution (5 ml) for 1 h. The $KMnO_4$/AC composite is separated from the solution by decanting and left to dry at room temperature. Subsequently, the sample is calcinated at 120 °C overnight, resulting in the transformation of permanganate precursor into MnO_2 as verified by characterisation of the modified powder.

2.2. Electrocatalysts characterisation

Structural and morphological properties of the MnO_2/AC electrocatalysts have been examined by XRD and TEM and the oxide content in the composites determined using thermogravimetric analysis (TG) data. XRD analysis was done using Philips 1050 Bruker D8 Advance with Cu $K\alpha_{1,2}$ radiations in 10–70° 2θ range with 0.05° step and 2 s exposition time, while TEM images were obtained using a HITACHI H-8100 electron microscope. TG curves were recorded using the TA SDT Model 2960 with measurements carried out under air flow at 10 °C min^{-1} heating rate.

2.3. Electrochemical measurements

Electrocatalytic activity of the synthesised MnO_2/AC materials for the ORR was investigated by preparing catalytic ink with the synthesised materials and spreading the ink onto a glassy carbon electrode (GCE, 5 mm diameter, Pine Instruments, Co.). Catalytic ink was made by adding 5.0 mg of the electrocatalyst (ltMnO_2/AC or htMnO_2/AC) with 50 μl of Nafion (5 wt.%, Aldrich) into 750 μl of ethanol (p.a., Merck) and ultrasonically mixing for 30 min. The working electrode (MnO_2/AC/GCE) was prepared by pipetting 20 μl of the corresponding catalytic ink onto a polished GCE and leaving it to dry at room temperature. Current densities were calculated using the geometric surface area of the electrode.

All electrochemical measurements were performed using a PAR 273A potentiostat/galvanostat with the PowerSuite software package in a single-compartment cell using a conventional three-electrode set up. Pt foil served as counter electrode with saturated calomel electrode (SCE, Metrohm) reference completing the circuit. All potentials given are relative to the SCE. Supporting electrolyte used was 1 M or 4 M sodium hydroxide (NaOH, 99%, Merck). In some experiments, sodium borohydride ($NaBH_4$, 96%, Panreac) was added to the supporting electrolyte in the concentration range 0.3–0.5 M for investigation of ORR on MnO_2/AC in DBFC conditions. Nitrogen gas (N_2, 99.998%, Air Liquide) was bubbled into solution for 10 min to remove dissolved O_2 before commencing the measurements. Conversely, for the ORR investigations, O_2 (99.998%, Air Liquide) was bubbled into solution for 10 min prior to measurements. At the beginning of each measurement, the working electrode was kept at the initial potential for 30 s to ensure identical initial surface state for all the experiments in a given solution. For all RDE measurements, the rotation speed (ω) of the electrode was adjusted using a Tachyprocesseur speed control unit (Radiometer Analytical).

Temperature influence on the ORR at MnO_2/AC composites, in the absence and in the presence of borohydride, was investigated in the temperature range from 25 to 65 °C, controlling the temperature by water circulation using a Ultraterm 6000383 P-Selecta bath.

3. Results and discussion

3.1. Electrocatalysts characterisation

The XRD patterns of MnO_2/AC composite prepared *via* low-temperature procedure, ltMnO_2/AC, contained broad peaks corresponding to amorphous α-MnO_2. Also, XRD analysis evidenced traces of Mn in this composite. However, XRD pattern of composite made following the high-temperature procedure, htMnO_2/AC, showed that crystalline tetragonal dioxide was formed. Furthermore, the analysis revealed that, in this case, other manganese oxides, namely Mn_2O_3 and Mn_3O_4, were formed as well in smaller amounts.

The amount of manganese oxides in the composites was calculated from TG data and it was found that in the case of low-temperature composite somewhat less than 20% of manganese oxide was incorporated into the activated carbon, while this amount was higher in the case of high-temperature composite.

Exploration of the morphology of the prepared MnO_2/AC composite materials by TEM (Fig. 1) revealed that htMnO_2/AC particles of ca. 40 nm size agglomerated to form a composite with layered structure. ltMnO_2/AC composite particles were not well dispersed on the carbon support surface, but more clustered inside the pores of the carbon support.

3.2. Investigation of oxygen reduction

CV investigation of ltMnO_2/AC/GCE in O_2-saturated 1 M NaOH solution showed two reduction peaks, at −0.40 and −1.00 V (Fig. 2A). In the CV of the same electrode recorded in O_2-free