ARTICLE IN PRESS

Journal of Electroanalytical Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Ad hoc tailored electrocatalytic MnO_2 nanorods for the oxygen reduction in aqueous and organic media

S. Orsini[a], E. Pargoletti[a,b,*], A. Vertova[a,b,c], A. Minguzzi[a,b,c], C. Locatelli[a,b,c], S. Rondinini[a,b,c], G. Cappelletti[a,b]

[a] *Università degli Studi di Milano, Dipartimento di Chimica, Via Golgi 19, 20133 Milano, Italy*
[b] *Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via Giusti 9, 50121 Firenze, Italy*
[c] *ISTM-CNR, Istituto di Scienze e Tecnologie Molecolari, c/o Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy*

ARTICLE INFO

Keywords:
Manganese dioxide
Electrocatalyst
Aqueous medium
Tetra Ethylene Glycol Dimethyl Ether (TEGDME)
Oxygen Reduction Reaction (ORR)
Metal-air devices

ABSTRACT

Metal-air batteries are one of the most promising electrochemical systems for energy storage and conversion. Herein we report promising results by exploiting manganese dioxide nanoparticles as ORR electrocatalysts. MnO_2 nanorods were prepared through a hydrothermal synthesis, *i.e.* by varying both the salt precursors (*i.e.* manganese sulphate or chloride) and the oxidizing agents (*i.e.* ammonium persulfate or potassium permanganate). All the nanopowders were finely characterized on structural, morphological and surface points of view. Then, their electrocatalytic power was tested either in aqueous 0.1 M potassium hydroxide or in Tetra Ethylene Glycol Dimethyl Ether (TEGDME)/$LiNO_3$ 0.5 M electrolytes, by using Gas Diffusion Electrodes (GDEs) and Glassy Carbon (GC) as cathodes, respectively. All the nanoparticles promoted the ORR by causing a shift of the onset potential up to 100 mV in both solvents. Nevertheless, this shift was different according to the solvent/electrolyte used: in the case of the ether-based solvent, different values are obtained by adopting the synthesized MnO_2 powders. Thus, we hypothesized that the structural/surface properties of MnO_2 samples are leveled in the aqueous medium (*i.e.* in a −OH rich solvent, the hydroxyls can interact with the homologs on the MnO_2 surface), contrary to what occurs in the organic solvent. Furthermore, a different behavior was observed also on the kinetic point of view thus leading to diverse interpretations of the oxygen reduction mechanism, especially in TEGDME.

1. Introduction

Nowadays, the contemporary society widely depends on the exploitation of reliable devices for the electrochemical energy storage/conversion. In particular, the consciousness of both the low-carbon economy and the environmental sustainability has greatly promoted the development of renewable chemical power sources, such as batteries and fuel cells [1]. Moreover, the progress in the long-range electrical vehicles field is strictly connected with the development of electrical supplies that can guarantee high energy density, low cost, increased safety and environmental compatibility [2]. For this purpose, one of the main fields being widely explored refers to metal-air batteries. Technologies like lithium-air or zinc-air batteries could deliver a much higher energy density with respect to the one obtained by the common lithium-ion devices [3]. For example, over the past decades, increased efforts have been made towards the development of aprotic Li-O_2 cells with the achievement of promising results [4], hence showing the great potential of these systems.

However, there are still some challenging aspects to deal with and, among them, there are two major problems to phase out: *i*) the slow kinetics of the Oxygen Reduction Reaction (ORR, which is the main cathodic reaction in metal-air batteries) that hinder the electrochemical performances of the final devices [5,6], and *ii*) the chemical stability of either the carbon cathodes or the solvent/electrolyte adopted [3,7]. For the former, a successful strategy to accelerate the ORR consists in using both metal and oxide-based electrocatalysts [8–12]. In this context, our group has largely employed cavity-microelectrodes [13,14] to rapidly characterize the electrocatalytic behavior of newly synthetized composite nanomaterials (for both oxygen reduction and evolution reactions), that can be used in metal-air batteries. As already demonstrated in our previous work [15], the presence of α-MnO_2 nanoparticles can facilitate the cathodic reaction by shifting the onset potential of about 100 mV (value comparable to those obtained with the well-performing platinum-based electrocatalysts [16]). Nevertheless, these promising

---

[*] Corresponding author at: Università degli Studi di Milano, Dipartimento di Chimica, Via Golgi 19, 20133 Milano, Italy.
E-mail addresses: silvia.orsini2@studenti.unimi.it (S. Orsini), eleonora.pargoletti@unimi.it (E. Pargoletti), alberto.vertova@unimi.it (A. Vertova), alessandro.minguzzi@unimi.it (A. Minguzzi), cristina.locatelli@unimi.it (C. Locatelli), sandra.rondinini@unimi.it (S. Rondinini), giuseppe.cappelletti@unimi.it (G. Cappelletti).

http://dx.doi.org/10.1016/j.jelechem.2017.05.035
Received 20 February 2017; Received in revised form 12 May 2017; Accepted 18 May 2017
1572-6657/

Please cite this article as: Orsini, S., Journal of Electroanalytical Chemistry (2017), http://dx.doi.org/10.1016/j.jelechem.2017.05.035

results were obtained in alkaline medium, which is not recommended in Li-air batteries, due to the different electrochemical reactions involving lithium and oxygen. Indeed, for this reason, the gravimetric and volumetric capacities of an aqueous Li-O_2 cell are much lower compared to those of an aprotic battery [17,18]. Hence, organic solvents should be utilized with a special consideration for their chemical stability during the charge/discharge cycles of the battery. Despite lots of attempts to find solvents that are stable towards the activated oxygen species (*i.e.* superoxides and peroxides that form during the oxygen reduction), none of them were found to be fully resistant [3]. Recent studies have reported that ethers are relatively stable solvents with low reactivity towards the superoxide ions [19], due to their high oxygen solubility and low dielectric constants. Moreover, as reported by Sharon et al. [3], the addition of $LiNO_3$ in polyether solutions can improve both the oxygen reduction and evolution reactions, since NO_3^- anions stabilize Li^+ cations that form during the discharge process.

Therefore, in this work we studied the electrocatalytic activity of novel manganese dioxide nanoparticles (synthesized starting from diverse salt precursors/oxidizing agents) both in alkaline and organic solvents. In particular, we adopted Tetra Ethylene Glycol Dimethyl Ether (TEGDME) as the organic medium [20], in the presence of lithium nitrate as the electrolyte, and we have either compared the shift of the onset oxygen reduction potential or studied the ORR on the kinetic/mechanistic points of view. As concerns the latter investigation, since literature about Tafel elaborations in the ether-based solvent is rather scarce [21], novel and promising results have been obtained.

2. Material and methods

All the chemicals were of reagent-grade purity and were used without further purification; doubly distilled water passed through a Milli-Q apparatus was utilized. All the reagents used were purchased from Sigma-Aldrich.

2.1. Synthesis of MnO_2 nanorods

In this work, a hydrothermal method previously optimized in our laboratory [15] was used, consisting in the reaction of stoichiometric manganese sulphate monohydrate ($MnSO_4{\cdot}H_2O$) as the salt precursor, with ammonium persulfate ($(NH_4)_2S_2O_8$, MS_N compounds) or potassium permanganate ($KMnO_4$, MS_K samples) as the oxidizing agents. Moreover, by exploiting $KMnO_4$ oxidant, we also prepared MnO_2 nanoparticles starting from manganese chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$) precursor giving rise to MCl_K compounds. No further calcination steps were required, since all the washed [15] nanopowders have shown a high degree of crystallinity (see in the following).

2.2. Sample characterizations

X-ray Powder Diffraction (XRPD) analyses were performed on a Philips PW 3710 Bragg-Brentano goniometer equipped with a scintillation counter, 1° divergence slit, 0.2 mm receiving slit and 0.04° soller slit systems. We employed graphite-monochromated Cu K_α radiation (Cu $K_{\alpha1}$ $\lambda = 1.54056$ Å, $K_{\alpha2}$ $\lambda = 1.54433$ Å) at 40 kV × 40 mA nominal X-rays power. Diffraction patterns were collected between 20° and 90° with a step size of 0.1° and a total counting time of about 1 h. A microcrystalline Si-powdered sample was used as a reference to correct for instrumental line broadening effects.

Transmission Electron Microscope (TEM) analyses were performed on LIBRA 200 EFTEM (Zeiss) instrument operated at 200 kV accelerating voltage. The TEM grids were prepared dropping the dispersed suspension of nanoparticles in isopropanol onto a holey-carbon supported copper grid and drying it in air at room temperature overnight.

The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (p/p_0) range of 0.05–0.20 (Coulter SA3100 apparatus). Desorption isotherms were used to determine the total pore volume using the Barrett-Joyner-Halenda (BJH) method.

X-ray photoelectron spectra were obtained using a Mprobe apparatus (Surface Science Instruments). The source was the monochromatic Al K_α radiation (1486.6 eV); a spot size of 200,750 mm and a pass energy of 25 eV were used. The 1s level of hydrocarbon-contaminant carbon was taken as the internal reference at 284.6 eV. The accuracy of the reported binding energies (B. E.) can be estimated to be around 0.2 eV and the resolution is equal to 0.74 eV.

2.3. Fabrication of the Working Electrodes (WEs)

Different Working Electrodes (WEs) were used depending on the solvent/electrolyte used. In the case of water/0.1 M KOH electrolyte, Gas Diffusion Electrodes (GDEs) fabricated following a general criterion already reported in our previous work [15] were utilized. Thus, a set of carbon slurries was prepared by mixing Carbon Vulcan XC-72R (Cabot®), Shawinigan Acetylene Black AB50 Carbon (SAB, Chevron Philips) and each of the as-synthesized MnO_2 nanopowders, using Milli-Q water as solvent (solid materials/H_2O ratio equal to 0.025). The relative weight ratio among the components was: C Vulcan:MnO_2:SAB:PTFE = 45:20:20:15, except for the reference GDEs which were prepared as follows: C Vulcan:SAB:PTFE = 65:20:15. After the complete wetting of the powders, a suspension of PTFE (10 wt% in water, used as binder) was added. The slurry obtained was stirred for further 10 min and it was subsequently spread on a 4.5 × 4.5 cm^2 carbon cloth. The complete evaporation of water was achieved by leaving the GDEs in a stove for 20 min at 60 °C. Finally, the electrodes were punched into 2.8 cm^2 disks with 2.2–3.4 mg cm^2 of active material. Instead, modified Glassy Carbon electrodes (GC by Amel, Italy; previously polished with diamond powder on a microcloth and rinsed with Milli-Q water) were adopted with Tetra Ethylene Glycol Dimethyl Ether (TEGDME)/0.5 M $LiNO_3$ electrolyte, since the present solvent permeates through the GDE pores. As concerns the latter, a set of carbon-based slurries has been prepared by mixing Carbon Vulcan XC-72R (Cabot®), each of the as-synthesized MnO_2 nanopowders and Nafion solution (5 wt%), using Milli-Q water as solvent (8 mL). The relative weight ratio among the components was: C Vulcan:MnO_2:Nafion = 4.0:1.0:1.5, except for the reference GC electrode which was prepared as follows: C Vulcan:Nafion = 3.3:1.0. Then, the obtained slurries have been sonicated for 20 min and modified GC cathodes were prepared by drop casting (10 μL) of these suspensions. Finally, the electrodes have been dried under a fume hood overnight in order to evaporate the solvent. The differences in cathodes composition were due to the adopted medium. Indeed, the choice of an aqueous solvent along with the possibility to exploit GDE-type cathodes needs to use two types of carbons (*i.e.* Carbon Vulcan XC-72R and SAB) and PTFE as binder, in order to achieve better electrochemical performances. Actually, Maja et al. [22] stated that GDEs containing SAB and PTFE show higher hydrophobicity (a basic feature for metal-air batteries) and a more homogeneous structure with long-term durability.

The labeling of both the gas diffusion and glassy carbon electrodes followed that of the powders: for example, GDE(MS_N) or GC(MS_N) identify the electrodes prepared using the MS_N catalyst.

2.4. Electrochemical characterization

For the same reasons reported in the previous paragraph, we adopted different experimental apparatus according to the solvent/electrolyte used. In the presence of water/0.1 M KOH electrolyte, we utilized a home-made *H-cell* (Fig. S1a) based on a Saturated Calomel Reference Electrode (SCE, R), inserted in a double-bridge filled with KNO_3 (Sigma-Aldrich ≥ 99%), and a Pt foil as the counter electrode (C). Instead, in the case of TEGDME/0.5 M $LiNO_3$ electrolyte, we exploited a three-electrodes conventional cell (Fig. S1b) based on a silver wire quasi-Reference Electrode (Ag/Ag_2O, R) and a Pt foil as the counter