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Preparation of manganese oxide - graphite electrodes by electrophoretic deposition

Juan A. Argüello[a], Arisbel Cerpa[a], Mohammad H. Alanbari[a], Juan Carlos Fariñas[b], Rodrigo Moreno[b,*]

[a] Universidad Europea de Madrid (UEM), Calle Tajo, s/n, 28670 Villaviciosa de Odón, Madrid, Spain
[b] Instituto de Cerámica y Vidrio (CSIC), Calle Kelsen 5, 28049 Madrid, Spain

A B S T R A C T

Manganese oxide is a promising active material for supercapacitors (SCs) with pseudocapacitance due to its high capacitance and its environmentally friendly character. This paper deals with the preparation of electrodes for supercapacitors consisting of manganese oxide supported onto graphite by electrophoretic deposition. Manganese oxide powders were characterized and dispersed in water by controlling the colloidal and rheological behavior in order to obtain stable suspensions. Optimized manganese oxide suspensions were deposited onto graphite electrodes by electrophoretic deposition. The deposited mass per unit area in the electrodes was optimized by controlling the applied current density and the deposition time. It has been demonstrated that the introduction of a binder helped to improve the adherence to graphite; otherwise the deposit thickness obtained by EPD is limited and no films can be obtained by simply dipping. These conditions allowed us to obtain more homogeneous deposits with higher specific energy than without binder.

1. Introduction

Due to high fossil fuel dependency and climate change, contamination and environmental conflicts are increasing reverting also in higher gasoline prices. Clean energy and electric vehicles with a sustainable storage system are in demand. Batteries and fuel cells are developed because they can store a high amount of specific energy but they have low specific power. This means the rate of specific energy is released slowly. For electrical vehicles, or other devices, high relation between specific energy and power is required which can be achieved by the use of supercapacitors (SCs). SCs have high specific power like conventional capacitors but owing to its low specific energy, there has been increased interest by scientists to develop the specific energy. Pseudocapacitors are becoming the solution. The main way of storing energy by pseudocapacitors is by redox reactions and less than 10% electrostatically [1]. There are many active materials that have pseudocapacitance such as RuO_2, MnO_2, IrO_2, Mn_3O_4, NiO, Co_3O_4, and $NiCo_2O_4$, among others. However, according to Brousse et al. [2] only RuO_2, MnO_2 and Mn_3O_4 are considered pseudocapacitance active material. Ruthenium oxide achieves high capacity values [3–5] but it is expensive, environmentally unfriendly and difficult to acquire. This is why the use of manganese oxide is desired as an active material due to its characteristics and due to the fact it does not have the same

drawbacks that RuO_2 does.

There are very few studies about electrophoretic deposition (EPD) technique developed for the deposition of manganese oxide on conductive electrodes [6–8] and there does not seem to be any study about EPD of manganese oxide in graphite electrodes.

Manganese oxide is well-known to have the ability to provide a high specific capacitance [9–13] but due to its low conductivity does not reach high levels of specific energy. Some researchers are using graphene for increasing the conductivity of manganese oxide [14–19]. The compatibility of graphite electrodes with graphene make these electrodes suitable for assembling SCs. Therefore this paper contains a valuable approach for using these kinds of composites since the optimization of the EPD of MnO_2 is a first approach for the design of the composites.

In this paper a facile, fast and reproducible way of assembling SCs has been developed through the design and the specific energy of graphite electrodes with manganese oxide as active material using the EPD technique in water by controlling the physicochemical properties of the used powder, its colloidal behavior and the deposition parameters in order to achieve the desired control on the thickness and uniformity of the MnO_2 deposit.

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2. Experimental procedure

As starting material a commercially available MnO_2 powder used in the ceramic industry was used. The starting powder was previously characterized by measuring the particle size distribution, the morphology of the particles and agglomerates, the specific surface area, the density, and the crystalline phases. Particle sizes were measured by laser diffraction using a Mastersizer S (Malvern, United Kingdom) instrument. Measurements were performed in 100 ml deionised water and 0.001 g of solids content; the suspension was dispersed by mechanical mixing and further sonication for 1 min using a 400 W sonication probe (dr. Hielscher, UP400S, Germany). The chemical analysis was performed through wavelength dispersive X-ray fluorescence (WD-XRF, PANalytical model Magic X spectrometer with a Rh anode tube and 2.4 kW power, The Netherlands). The powder microstructure was observed by scanning electron microscopy (SEM, JEOL JSM 6335 F, Japan) and transmission electron microscopy (TEM, JEOL 2100, Japan). The specific surface area was determined by single point BET adsorption (Micromeritics ASAP 2020, USA) and crystalline phases were determined by X-ray diffraction (XRD, Bruker D8 Advance, Germany) with a CuK_α source $\lambda=1.5405$ Å. Diffraction patterns were collected for 2θ angles between $10 < 2\theta < 80°$ at $2.5\ min^{-1}$ using a step size of 0.002°.

Suspensions were characterized by measuring the zeta potential as a function of pH using the microelectrophoresis technique assisted with laser Doppler velocimetry (Zetasizer NanoZS, Malvern, UK). Samples were prepared in deionised water at a solids concentration of $0.005\ g\ l^{-1}$ using $KCl\ 10^{-2}\ M$ as inert electrolyte. HCl and KOH were used for pH adjustments. In addition, zeta potential measurements were also performed for suspensions dispersed with a commercial polyelectrolyte (Duramax D3005, Rohm & Haas, USA), which has a content of active matter of 35% and a typical molecular weight of 2400 D. The stability of the suspensions was also characterized by sedimentation tests using the multiple light scattering – near infrared technique (MLS-NIS, Turbiscan Classic, Formulation, France) with a laser source with a wavelength of 850 nm.

Once studied the colloidal stability suspensions were prepared to solids contents of 5–20 wt% by sonication at the same conditions described above for the preparation of the coatings. These suspensions were characterized in terms of their rheological behavior using a rotational rheometer (MARS, Thermo Haake, Germany) at 25 °C. A double-cone and plate system provided with a solvent trap was used as measuring system. Measurements were performed up to a shear rate of $1000\ s^{-1}$ with up and down ramps of 300 min and soaking time of 1 min.

Coatings were prepared by both dipping and electrophoretic deposition (EPD) onto graphite substrates. A commercial graphite sheet with a thickness of 0.4 mm was used. Dipping tests were performed with a homemade lift at a withdrawal rate of $2\ mm\ s^{-1}$. EPD experiments were performed in galvanostatic mode for current densities of $1.25–10\ A\ cm^{-2}$ and deposition times of 1–20 min, using a power source (KEITHLEY, mod. 2611 Ohio, USA). The separation distance between the electrodes was maintained at 2 cm. Suspensions were maintained under slow agitation to avoid possible sedimentation phenomena during the deposition tests.

Coated substrates were dried in an oven at 60 °C for 24 h. The deposited mass was evaluated by weighting before and after the EPD tests. The morphology and texture of the coatings was examined by atomic force microscopy (Nanotec, model Cervantes, Spain) under tapping mode in which a Si cantilever is driven to oscillate up and down at its resonance frequency of 330 kHz applying a force of $42\ N\ m^{-1}$.

Electrochemical characterization of the coatings was performed using a potenciostat (Metrohm, Autolab, Switzerland) controlled by Gpes software for the determination of voltametry and chronoamperometry tests and the Fra software for the measurements of electrochemical impedance spectroscopy (EIS) using a 3 electrodes system

Table 1
Chemical composition obtained by WD-XRF of the starting MnO_2 powder.

Oxide	Concentration (wt%)
Na_2O	0.51
MgO	0.15
SO_3	0.95
K_2O	0.11
MnO_2	98.2

where a platinum electrode was used as the counter electrode, an Ag/AgCl (saturated KCl) electrode was used as the reference electrode, and a 6 M KCl solution was used as the electrolyte. In order to calculate the equivalent series resistance (Resr) the EIS technique was used by fitting the results from 106 to 0.1 Hz with a 0.05 V voltage giving a total amount of 60 measurements. The specific capacitance was measured by chronoamperometry. It is well known that this technique is more accurated than voltammetry or EIS for calculating the specific capacitance [20–29]. From the discharge curve the Eq. (1) was used:

$$C_{sp} = \frac{I}{m \bullet s} \tag{1}$$

where Csp is the specific capacitance, m is the active mass load and s is the slope of the discharge curve.

3. Results and discussion

The chemical composition obtained by WD-XRF of the starting MnO_2 powder is shown in Table 1. The chemical analysis reveals that the total content of impurities is lower than 2%. The main impurity is SO_3 (< 1%). This powder has a specific surface area of $50\ m^2\ g^{-1}$ and a density of $4.35\ g\ cm^{-3}$. The particle size distribution of the as-received powder is presented in Fig. 1, in which the curves are plotted in terms of intensity (Fig. 1a) and volume (Fig. 1b). It can be seen that there is a first contribution with particles having an average size of 200 nm and a larger fraction of up to 5 μm. In the intensity plot it can be observed that the larger particles contribute with a low intensity peak but the total volume gives a very intense peak. This means that although the number of particles of the larger fraction is small their contribution to the total volume is very intense due to the large agglomeration state. In the figure the results of five different measurements are presented in order to show their reliability. The morphology of the powder can be observed in the TEM pictures shown in Fig. 1c and Fig. 1d. As it can be observed, the particles are faceted with the shape of nanorods with longer dimensions ranging from 10 to 200 nm, but there are also strong agglomerates of those particles with submicronic dimensions. The presence of such agglomerates is more clearly appreciated in the characteristic SEM picture shown in Fig. 1e.

In Fig. 2 the XRD pattern of the MnO_2 powder is plotted. The reflections are coincident with the JCPDS 14−0644 file corresponding to the γ-phase. The peaks are poorly defined and have low intensity indicating a low crystallinity. The more intense plane is (131) that corresponds with a 2θ angle of 34.5° and the interplanar distance is 0.42 nm, which is in good agreement with that determined from TEM observations (Fig. 1d). In addition, the Raman spectrum of the as-received powder is shown in Fig. 2b. A sharp, well defined signal is obtained at a Raman shift of $630\ cm^{-1}$ that corresponds to the vibration of the bonds between Mn and O. There is also a broad band at larger shifts that are indicative of the hydration state.

The colloidal stability of aqueous suspensions of the as-received powder was studied through zeta potential measurements. Fig. 3a shows the variation of zeta potential with pH, where it can be observed that the isoelectric point (iep) occurs at acidic values of pH, i.e. pH 4. This is an expected value for a tetravalent single oxide MO_2, such as TiO_2 or SiO_2 as it is well known that the iep decreases with increasing oxidation state of the metal [30]. In that plot it can be observed that