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Morphological and electrochemical study of Mn_xO_y nanoparticle layers prepared by electrospraying

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HIGHLIGHTS

- Mn_xO_y nanoparticles were deposited directly on stainless steel foil by electrospray.
- The effect of the deposition period on the final layer morphology was described.
- Electrochemical oxidation effects on layer morphology were systematically studied.

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ABSTRACT

We are using the electro-hydrodynamic atomization technique (also called electrospraying) for the deposition of fine nanoparticle thin layers of different morphologies. This deposition method has a potential to enable massive fabrication of nanostructured products, but it is necessary to optimize the spraying process to reach the required product qualities. We focus on the preparation of basic (without carbon additives) nanostructured manganese oxide layers deposited on stainless steel substrates. The system of nanostructured MnO_2 (with additives) is commonly used as the electrode in energy storage applications (batteries, supercapacitors). The electrochemistry of deposited layers is influenced mainly by MnO_2 morphology, which strongly depends on the spraying conditions. Here we carry out the basic study of the nanostructured manganese oxide layer morphology evolution and its electrochemical changes during: (i) the electrospraying deposition period, (ii) the thermal treatment of deposits, and (iii) the electrochemical oxidation. During the electrochemical oxidation the deposited layers change their morphology and structure resulting in fine nanostructured MnO_2 in the form of nanorods. This is a desired product for energy storage applications as confirmed by cyclic voltammetry. Morphology and composition analyses were carried out using Raman microscopy, XPS, SEM and AFM. A comprehensive fundamental analysis of the manganese oxide deposition and transformation processes is presented with the emphasis on the evolution of the deposited layer morphology.

1. Introduction

Manganese oxides (Mn_xO_y) are nowadays in the focus of many research groups, because of their unique electrochemical, catalytic, environmental and also economic characteristics. These properties of Mn_xO_y enable their use in many applications, e.g., as catalysts (Einaga et al., 2013), pigments (Pike et al., 2007), electrode materials for batteries (Gao et al., 2011) and supercapacitors (Nam and Kim, 2006; Dai et al., 2006, 2007; Ma et al., 2007; Shen et al., 2012). In all these applications, nanostructured materials with large active surfaces are utilized.

Many methods suitable for the preparation of thin nanostructured layers, such as chemical vapour deposition, sputtering and electrodeposition, have relatively low depositions rates and require high-vacuum environment or higher deposition temperatures. This is resulting in increased production costs.

As an alternative for the nanostructured layer preparation we decided to use the electro-hydrodynamic atomization technique, also known as electrospray. This method produces high quality nanoparticles by the dispersion of aerosol droplets in a high voltage electric field. It is a simple and easy-to-build technique with high reproducibility and the produced nanoparticles have a narrow size distribution. Electrospraying does not require any special pre-treatment for

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the deposition (heating, inert atmosphere, vacuum, etc.) and works well at ambient conditions. However, an elevated temperature of the substrate results in a finer nanoparticle deposition together with increased layer porosity and also enables potential reactions and surface modifications. Additional advantages of electrospraying are the suppression of nanoparticle agglomeration and simple scale-up (Jaworek, 2010).

This paper describes the preparation of manganese oxide layers by the electrospraying technique and their fundamental analysis with respect to electrochemical properties and morphology. Our target is to elucidate the dependence of the deposited layer morphology on the electrospraying parameters. As this work is a basic morphological study, we have deposited layers without various carbon additives, other metal dopants or platinum and gold current collectors, which are commonly used in the energy storage applications. Stainless steel was used as the substrate due to its elasticity and good electric conductivity. The deposition process was optimized to improve the electrochemical properties of the prepared layers and their subsequent treatment (calcination, electrochemical oxidation) was carried out to reach the desired structure and electrochemically most important oxidation state of the manganese oxide (IV). The effects of heat treatment and electrochemical oxidation on the final layer morphology and internal structure were studied by atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Electrochemical properties were investigated by cyclic voltammetry. We focus on the evolution of the manganese oxide layer morphology and its electrochemical properties during: (i) electrospraying deposition, (ii) thermal treatment, and (iii) electrochemical oxidation. We also discuss the mechanism of nanoparticle deposition during the electrospraying and suggest several improvements for the further development of electrospray prepared electrodes that can find applications in low costs energy storage systems.

2. Materials and methods

2.1. Electrospraying

Electrospraying is a method of creating a liquid dispersion by electrical forces. It is based on the application of a high voltage electric field on a conductive liquid. It is known for over 100 years that conductive liquids, which are carried through a needle into a high voltage field, create the so called “Taylor cone” on the needle tip (Rayleigh, 1882). The liquid changes its typical hemispherical shape to a cone like one due to the presence of repulsive electrical forces. Increasing the strength of the electrical field causes the emission of small and highly charged aerosol droplets from the cone tip to the counter electrode. The droplets are composed of a volatile solvent with dissolved particle precursors. During their flight to the counter electrode, solvent evaporation takes place and causes the shrinking of the droplets, which increases the surface charge density. When the surface charge density reaches Rayleigh's limit, the repulsive forces of the charges overcome the surface tension and the droplet is dispersed into several smaller ones by the Coulombic repulsion. This process of solvent evaporation and spontaneous droplet splitting is repeated several times before the droplets or solid particles reach the counter-electrode. Nano-sized droplets/particles are thus deposited at the counter electrode surface (residual solvent is evaporated). The emission of aerosol droplets can be observed in several spraying modes, which are described in detail elsewhere (Jaworek, 2010). The cone-jet spraying mode was used in all our experiments, because it produces fine nanoparticles with a good reproducibility.

2.2. Manganese oxide layer preparation

A 0.02 M manganese acetate solution was used as the precursor for the electrospraying deposition of manganese oxides on stainless steel substrates. The solution was prepared by dissolving manganese acetate in a mixture of water (20 vol%), ethanol (20 vol%) and isopropanol (60 vol%). The as prepared solution was pumped through a stainless steel needle (internal diameter 0.8 mm) with a narrow tip by a syringe pump PHD Ultra with the flow-rate set to 1000 $\mu l\ h^{-1}$. The distance between the electrodes (needle and counter electrode with the substrate) was 4 cm. The voltage of 7.8 kV was supplied by a high voltage power amplifier of our own construction. The counter electrode with the substrate was heated to 200 °C during the deposition. These parameters were chosen based on our previous experience to ensure narrow particle size distribution and good reproducibility. According to these parameters, the deposition rate was estimated by atomic absorption spectrometry to be approximately 0.5 mg/h of Mn_xO_y. The deposition time was set according to the required layer thickness. The produced electrodes (i.e., substrates with deposited layers of Mn_xO_y nanoparticles) were then heated (calcinated) for 3 h in a furnace with programmable temperature profile.

2.3. Electrochemical oxidation of manganese oxides

The optimization of design and manufacturing methods of manganese oxide electrodes are the main challenges for improving their electrochemical properties. It is widely accepted that MnO_2 exhibits better electrochemical behaviour (e.g., capacitance) when compared to other manganese oxides (or hydroxides) such as $Mn(OH)_2$, Mn_2O_3 or Mn_3O_4. According to Taguchi et al. (2006), this is due to the significant differences in the conductivities of various manganese oxides. The conductivity of manganese oxides containing trivalent Mn(III) is low in comparison to that of MnO_2 or amorphous manganese (hydro)oxides containing Mn(IV). This is assigned to the Jahn–Teller distortion of the $Mn^{III}O_6$ octahedral crystal structure. Structural changes of the manganese oxide electrode can therefore influence the electrochemical activity.

Electrospraying of a manganese acetate solution produces a nanostructured layer of manganese oxides of lower oxidation states (II, III). For electrochemical applications, the manganese oxides must be oxidized to the (IV) state. Djurfors et al. (2006) found that the following series of oxides is generated during electrochemical oxidation: $MnO \rightarrow Mn_3O_4 \rightarrow Mn_2O_3 \rightarrow MnO_2$. Equations proposed for this oxidation mechanism by Pilla et al. (2004) involve the creation of the intermediate hydrated oxide MnOOH, which is subsequently oxidized to MnO_2 (Nijjer et al., 2000). During electrochemical transformation from MnO to MnO_2, the deposited layer develops a finer porous structure (Xia et al., 2011). The electrochemical oxidation was in our case performed using the cyclic voltammetry in 1 M aqueous Na_2SO_4 electrolyte. To completely oxidize the layer to Mn (IV), several hundred potential cycles from 0 to 0.8 V have to be carried out. The increase of the layer capacitance indicates the progress of the oxidation. The transition of the deposited mixed oxides Mn_xO_y to MnO_2 was confirmed by Raman spectroscopy and X-ray photoelectron spectroscopy.

2.4. Raman spectroscopy

Raman measurements were carried out on a DXR Raman microscope (Thermo Scientific). Three excitation lasers were used, namely 532, 633 and 780 nm. The laser spot size (connected with spatial resolution) varied from 1 to 4 μm^2, depending on the used laser and magnification lens. Laser power was always in the range from 1 to 14 mW to ensure that no laser-induced reactions take place (Bernard, 1993; Widjaja and Sampanthar, 2007; Shim et al., 2011).