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Towards core-shell bifunctional catalyst particles for aqueous metal-air batteries: NiFe-layered double hydroxide nanoparticle coatings on γ-MnO_2 microparticles

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ABSTRACT

Herein, we investigated the synthesis of a bifunctional catalyst particle system for aqueous metal-air batteries. To target a system which possesses both, oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) capabilities, γ-MnO_2 microparticles were combined with NiFe layered double hydroxides (LDH) to a core-shell system. NiFe-LDH can be optimized in its constituency to yield a very low onset potential (at 10 mA cm^{-2}) for the oxygen evolution reaction of only 569 mV vs. Hg/HgO. We investigated different coating processes (in-situ precipitation coating and sonochemical assisted coating) in order to create a bifunctional system of LDH shell@γ-MnO_2 core. It was found that the overall catalytic functionality of the bifunctional system strongly depends on the coating process, as this ultimately determines the surface nature and thus the behavior in ORR and OER reactions, respectively, of this core-shell system.

1. Introduction

The demand for energy storage systems for mobile and stationary applications is rapidly increasing. Currently, the most widespread energy storage system for mobile applications like notebooks or mobile phones is the lithium-ion battery (LIB) technology. However, this technology is already exploited close to its limits regarding the extractable theoretical energy density (387 Wh kg^{-1}) [1]. Therefore, due to their much higher theoretical energy densities, metal-air batteries come into focus as the battery systems of the future. For instance, the theoretical energy density of Li-O_2 (aq) is 3582 Wh kg^{-1} and for the Zn-air system, the values are still remarkably high at 1086 Wh kg^{-1} [1]. The working principle of metal-air batteries is that during discharge, oxygen is reduced to hydroxide ions. This reaction is called the oxygen reduction reaction, ORR. During charging, oxygen is formed. This reaction is called the oxygen evolution reaction, OER [1,2]. Unfortunately, one of the greatest challenges for this kind of batteries is the high overpotential by the air-cathode, i.e., at the so called gas diffusion electrode "GDE" and which occurs with both, the ORR and the OER. To reduce the overpotentials for the OER and the ORR, respectively, suitable catalysts are needed. That is why there is an ongoing search among many different classes of materials to find the best catalyst system. Examples of the most promising candidates that were reported so far include noble metals, transition metal oxides and carbon materials [2–4]. The highest catalytic activity for the OER, which is also very important for electrochemical oxidation of water, is observed for catalysts including Pt, Ru, Ir and Ni [4–6]. Detrimental to the use of these catalysts are the high costs for the noble metals and the heat treatment, necessary during synthesis [6].

Herein, we report on a system which is free of any noble metals, fast, simple and cheap to synthesize and which shows a promising potential. The key material class we focused on in our work is the class of the so called layered double hydroxides (LDH). LDHs are anionic clays with positively charged metal hydroxide layers which can be intercalated with anions such as carbonate [7]. LDH-based materials are interesting for a broad range of applications as they for instance may act as adsorbers for anions, as adsorbers for gases but also as flame-retardant agents to name but a few [8–15]. By using Ni and Fe as metal cations in the LDH structure, a very active OER catalyst can be obtained, which was reported recently [16–22].

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Ideally, a particle with bifunctional properties is favoured, i.e., a particle system that possesses both, OER and ORR capabilities. We targeted this by a core-shell approach where we used the NiFe-LDH as shell, coated on an ORR active microparticle core. The approach to use bifunctional particles instead of mixing both catalysts has a crucial advantage when it comes to processing the materials. In a later application of the catalysts in a gas diffusion electrode it is difficult to distribute two different types of particles (with different particle size, morphology, surface chemistry etc.) homogenously in the reactive layer of the electrode. Any special inhomogeneity bears the danger to yield non-controllable fluctuations in the final catalytic performance of the system. Thus, the device design and production process is much easier if only one catalyst particle is used, which bears a bifunctional activity.

Initially, we investigated the electrochemical OER activity of NiFe-LDH particles as function of their structure/composition, which was varied by either deliberately intercalating carbonate or recrystallizing the structure upon a post-synthesis thermal treatment. From the results of these initial investigations, the best NiFe-LDH structure was selected to create a bifunctional catalyst particle by combining the OER-active NiFe-LDH with micron-sized γ-MnO_2 catalyst particles which are known to be ORR active. By evaluating different coating approaches, we found a relation between the coating mechanism and the ORR and OER potential of this bifunctional system.

2. Experimental

2.1. Chemicals

$NiCl_2 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ were purchased from Sigma Aldrich, Germany at 99.999 % purity grade, NaOH pellets were obtained from VWR, Germany and Na_2CO_3 from abcr GmbH, Germany (purity: 99.5 %). The γ-MnO_2 microparticles were synthesized as described in an earlier work from us [23]. Potassium hydroxide pellets, *n*-propanol and Nafion solution (5 wt-% solution) were purchased from Sigma Aldrich, Germany. All chemicals were used as received without further purification.

2.2. Synthesis of NiFe-LDH

For the synthesis of the selected LDH system that contains nickel and iron with a molar ratio of 2:1, 0.43 g (1.8 mmol) nickel(II) chloride hexahydrate ($NiCl_2.6H_2O$) and 0.24 g (0.9 mmol) iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were dissolved in 10 ml deionized water (*Solution I*). A *Solution IIa* was prepared by dissolving 0.24 g (6 mmol) sodium hydroxide (NaOH) in 40 ml deionized water under stirring. Optionally, 0.19 g (1.8 mmol) sodium carbonate (Na_2CO_3) was added to *Solution II* (denoted as *Solution IIb*). Subsequently, *Solution I* was added to *Solution IIa* (respectively *Solution IIb*) drop by drop with continuous stirring for 2 min. After stirring the product for another 3 min, the precipitate was washed. This was done by centrifuging the dispersion at a rotation speed of 5000 rpm for 15 min with a Z513 K, HERMLE centrifuge. Subsequently, the clear supernatant was decanted and the sedimented LDH was redispersed for 5 min in 25 ml deionized water. This procedure was repeated four times. Eventually, the product was redispersed in deionized water. The weight fraction of the solid content in the final dispersion was determined gravimetrically by drying a part of the suspension at 120 °C for at least 18 h.

To carry out recrystallization experiments, the whole procedure as described above to prepare NiFe-LDH with and without carbonate was repeated and the final product was taken and recrystallized for 114 h at 80 °C in deionized water.

2.3. Synthesis of a γ-MnO_2-core NiFe-LDH-shell composite particle system

γ-MnO_2 microparticles were coated by two different mechanisms with NiFe-LDH as follows:

2.3.1. Sonochemical assisted coating

100 mg of γ-MnO_2 microparticles were coated with 10 mg NiFe-LDH (10 wt% coating) by means of sonochemistry as follows: The γ-MnO_2 were dispersed in a NiFe-LDH suspension which contained 10 mg solid LDH. After the pH was adjusted to 8-9 with 1 M potassium hydroxide, the suspension was exposed to ultrasound for 5 minutes in total. This was done with a sonic horn (ultrasound device: Sonics & Materials VCX130) which exposed the dispersion to ultrasound pulses with a length of 2 s in burst mode every 5 s.

2.3.2. In-situ precipitation-coating

500 mg γ-MnO_2-particles were dispersed in *Solution IIa*. Subsequently, *Solution I*, containing Ni^{2+} and Fe^{3+} salts, was added drop by drop with stirring.

The samples that were received from the coating-procedures *A)* and *B)*, respectively, were treated identically afterwards as described in the following: To remove any non-deposited LDH, the reaction product was pressure-filtrated through a filter with a pore size of 0.8 μm and a pressure of $\rho = 1$ bar. The remaining micron sized composite core-shell particles (γ-MnO_2-core-LDH-shell) were washed and filtered again three times with 20 ml deionised water. Eventually, the product was dried until weight constancy for at least 18 h at 120 °C.

2.4. Electrochemical characterization

The catalytic activity (ORR and OER) of the particles was analysed by rotating disc electrode (RDE, pine instruments) measurements. 20 mg of catalyst particles were dispersed in 7.96 g H_2O, 2 g *n*-propanol and 40 μl Nafion solution (5 wt-% solution) by ultrasonic (Sonics & Materials VCX130) treatment for 5 min. To prepare the working electrode, 20 μl of the catalyst ink was dropped on a mirror polished glassy carbon RDE tip (diameter: 5 mm) and dried for 15 min at 35° C. All measurements were carried out in 1 M $KOH_{(aq)}$ with a glassy carbon rod as counter electrode and Hg/HgO (1 M $KOH_{(aq)}$) as reference electrode.

The ORR polarization curves were recorded in O_2 saturated 1 M $KOH_{(aq)}$ at a potential range between 0.1 V and −0.6 V vs. Hg/HgO and a scan rate of 5 mV s^{-1} at rotation rates of 100, 140, 250, 400, 900, 1600 and 2500 rpm. The ORR onset potential was calculated at a constant current density of -1 mA cm^{-2} and a rotation rate of 900 rpm. The corresponding OER curves were carried out in Ar saturated 1 M $KOH_{(aq)}$ in a potential range between 0.2 and 0.75 V vs. Hg/HgO and a scan rate of 5mV s^{-1} at a rotation rate of 900 rpm. The OER onset potential was calculated at a constant current density of 10 mA cm^{-2}.

2.5. Analytical instrumentation

The structure and morphology of the LDH particles were studied by scanning electron microscopy (SEM, Zeiss Supra 25 SEM) at 3 keV (field emission). The zeta potential of the particles as function of pH was measured with a Malvern Instruments Zeta Sizer Nano. For the zeta potential measurements, the pH was adjusted by 0.1 M NaOH and 0.1 M HCl. The crystal structure of LDH investigated using X-ray diffraction (XRD, PANanalytical 943006003002 Empyrean Series). The XRD patterns were recorded, using Cu Kα radiation ($\lambda = 0.15406$ nm) in a range