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Perovskite-based bifunctional electrocatalysts for oxygen evolution and oxygen reduction in alkaline electrolytes

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ABSTRACT

Due to the high cost of precious metal-based electrocatalysts for oxygen reduction and oxygen evolution, the development of alternative low cost and efficient catalysts is of high importance for energy storage and conversion technologies. Although non-precious catalysts that can efficiently catalyze oxygen reduction and oxygen evolution have been developed, electrocatalysts with high bifunctional activity for both oxygen evolution and reduction are needed. Perovskites based on modified lanthanum cobaltite possess significant activity for the oxygen evolution reaction. We describe the synthesis of a bifunctional oxygen electrode with simultaneous activity for the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) in alkaline media by direct growth of nitrogen-doped carbon nanotubes on the surface of a perovskite containing Co and Fe by means of chemical vapor deposition. The difference in the overvoltage between ORR (at 1 mA/cm^2) and OER (at 10 mA/cm^2) was below 880 mV in 0.1 M KOH. The formation of H_2O_2 during the ORR was reduced by at least three fold when using the bifunctional catalyst as compared to the non-modified perovskite. Long-term durability tests indicate stable performance for at least 37 h during the OER and 23 h during the ORR.

1. Introduction

Unitized regenerative fuel cells and metal-air batteries are among the most promising technologies for renewable energy conversion and storage. However, their large scale deployment is largely restricted by the unavailability of high performance and cost-effective bifunctional oxygen electrodes which can reversibly catalyze both the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR).

The routinely studied electrocatalysts for the ORR as well as the OER contain precious metals such as Pt, Pd, Ir and Ru [1–3] in acidic electrolytes. However, in addition to the scarcity of the materials which prevents their large scale application, the related catalysts suffer from low stability and sensitivity to poisoning. The development of non-noble metal or non-metal catalysts for the ORR [4–7] and the OER [3,8] was proposed. In particular, the ORR can be successfully catalyzed using a number of different materials including supported or non-supported oxides or metal nanoparticles [6,9,10], as well as nitrogen or heteroatom doped carbon that can be additionally modified by introducing transition metal cations [11,12]. The latter are the most active catalysts for substitution of precious-metal catalysts for ORR due to the presence of metal cations like Fe and Co coordinated to the nitrogen atoms incorporated in the carbon matrix. These N-coordinated metal ions are considered to serve as the main active sites, where oxygen can be adsorbed and reduced [6,11,13]. Furthermore, non-metal heteroatom-doped carbon materials (N, P, S, B) [7,14–16] also possess reasonable catalytic activity towards the ORR due to the charge delocalization in the carbon matrix yielding positively charged active species able to adsorb oxygen [15,17].

Among the electrocatalysts for OER, numerous transition metal compounds, e.g. oxides with perovskite structure (ABO_3), have received wide attention due to their high activity and durability for the OER especially when used in alkaline media [18–21]. Varying the type of rare or alkaline earth metal cations (A site) and *3d* transition metal cations (B sites) along with their ratio, their OER

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activity can be substantially improved to become comparable to that of precious metals based benchmark catalysts [19,20,22,23]. Partial metal substitution can significantly influence not only the state of charge and distribution of ion vacancies within the perovskite structure but also its conductivity, and ultimately the OER performance [18,19,24,25].

Oxides with spinel and perovskite structures have been reported to exhibit bifunctional activity for both reactions. The transition metal cations can serve as a bifunctional active site for both ORR and OER depending on the potentials applied [10,21,26]. However, their activity for ORR is generally limited due to their low intrinsic conductivity. Hence, the main challenge on the way towards bifunctional oxygen electrodes is to combine catalytically active sites for OER and ORR into one highly effective bifunctional system. It was previously shown that one effective way to create bifunctional electrocatalysts is the integration of ORR and OER active materials into a composite which retains the individual properties [9,27] or forms new bifunctional active sites [2,28,29]. Catalysts in which ORR active sites are introduced into OER active materials or vice versa, may have advantages due to a better control of active site distribution. However, most of these composite materials exhibit a much higher activity for one reaction over the other, or they possess limited stability. Moreover, in addition of the minimization of the overpotential difference between the onset of OER and ORR it is at least similarly important to improve the longterm stability of the catalyst film, to favorably tune gas and electrolyte permeability and to assure a low resistance of the material [26].

We propose a comparatively simple approach for the modification of nanoparticles of a perovskite ($La_{0.58}Sr_{0.4}Fe_{0.2}Co_{0.8}O_3$) by growth of nitrogen-doped carbon nanotubes (NCNTs) on their surface using chemical vapor deposition (CVD) at comparatively low temperatures (below 700 °C). Due to the presence of metal ions (Fe, Co) the perovskite nanoparticles themselves can serve as catalyst for the NCNTs growth on their surface taking into account that mixed oxides of Fe/Co are the most used catalysts for the CVD growth of carbon nanotubes [30,31]. The growth of NCNTs on the perovskite surface significantly improved the activity of the composite catalysts with respect to the ORR. In contrast to previous reports, in which carbon deposits were grown on the modified surface of lanthanum nickelate [32] or lanthanum cobaltite [33,34] in the proposed procedure no pretreatment steps such as impregnation of the oxide with Fe or Co salts are necessary. The OER activity was found to be unchanged or slightly improved with respect to the unmodified perovskite, however, the ORR activity was substantially improved. The difference between overpotentials for OER and ORR measured at fixed current densities was considerably decreased and the materials exhibited high stability over the tested time period. It has to be emphasized that unlike the case for acidic media, carbon corrosion is much less investigated in alkaline electrolytes especially at conditions of the OER. Taking into consideration that the high applied potentials for the OER are beyond the stability of most known substances including noble metal oxides, it becomes evident that introducing enhanced conductivity into intrinsically non-conducting electrocatalysts is only possible using carbon based materials. Evidently, this might lead to a compromise of the stability of the new catalyst.

2. Experimental

2.1. Preparation of electrocatalysts

The perovskite $La_{0.58}Sr_{0.4}Fe_{0.2}Co_{0.8}O_3$ which was used as substrate and catalyst for NCNT growth was prepared via a citrate complexation technique. The nitrates of the respective metals (La, Sr, Co, Fe) in the required stoichiometric concentration were dissolved first in distilled water, then citric acid (CA) in the molar concentration of 2:1 (CA: metal salts) was added to the nitrate salts solution under intensive stirring for around 3 h at 80 °C. After this, ethylene glycol (EG) was added dropwise to the mixture (1 ml of EG to each 1 g of CA). The viscous mixture obtained was first dried at 230 °C for several hours, then calcined in air first at 600 °C for 3 h and then at 900 °C for 24 h. Samples were further milled in ethanol with zirconia balls.

Nitrogen-doped carbon deposits, mostly nanotubes, were grown on the perovskite nanoparticle surface using CVD. 100 mg of the perovskite powder was placed in a quartz boat that was inserted into the center of a tubular quartz reactor placed inside a 3-zone tube furnace with automatic temperature and gas flow control. First, pure N_2 was flushed into the reactor for 15 min, then the temperature was ramped at 10 °C min^{-1} until the synthesis temperature (640–680 °C) was reached under continuous N_2 flow (100 ml min^{-1}). After this, a $C_2H_4/NH_3/He$ mixture (30:7:63 volume ratio, 100 ml min^{-1}) was passed through the reactor for 30 min. After the synthesis, the furnace was cooled down to room temperature under nitrogen atmosphere. The composite materials were used for physical and electrochemical characterization without any further treatment.

2.2. Physical characterization

Scanning electron microscopy (SEM) images were recorded using a Quanta 3D FEG scanning electron microscope (FEI^{TM}) operated at 20.0 kV. X-ray diffraction (XRD) studies were performed on a D4 Endeavour instrument (Bruker) using Cu-Kα radiation. Elemental analysis was performed using VarioEL III analyzer (Elementar Analysensysteme) to determine the concentration of C, N and H. Transmission electron microscopy (TEM) as well as energy-dispersive X-ray spectroscopy studies were carried out using a TECNAI G220 S-TWIN transmission electron microscope with LaB6-Cathode, 200 kV accelerating voltage and 0.24 nm point-resolution.

2.3. Electrochemical measurements

Electrochemical measurements were performed in a coaxial three-electrode cell. Glassy carbon rotating disk (RDE) and rotating ring-disk (RRDE) electrodes (4 mm and 5.6 mm diameter, respectively) modified with the catalyst film were used as working electrodes, a Ag/AgCl/3 M KCl was used as reference electrode and a platinum mesh as counter electrode. Catalyst inks were prepared using 5 mg of the catalyst powder dispersed in a mixture of ultrapure water, ethanol and Nafion solution (5 wt.%, Sigma Aldrich) with a volume ratio of 49:49:2. Inks were sonicated for at least 20 min to assure a homogeneous dispersion. RDEs were polished before each measurement with 1 μm and 0.3 μm alumina pastes. 5.3 μL and 10.6 μL of catalyst ink were cast onto the RDE and RRDE, respectively, and air dried to obtain a catalyst layer with a nominal loading of 210 $\mu g\,cm^{-2}$.

Electrochemical measurements were performed with an AutolabIII/FRA2 potentiostat (Metrohm-Autolab) with a RDE 710 rotator (Gamry Instruments) in oxygen saturated 0.1 M KOH as electrolyte. The coaxial cell geometry in which the working electrode is surrounded by the Pt mesh counter electrode and the RE is placed outside the counter electrode creates a symmetrical distribution of current lines. This diminishes the influence of the electrode position on the determination of the uncompensated solution resistance leading to a more precise determination of the ohmic drop [35]. Electrochemical impedance spectroscopy (EIS) was performed before each experiment at open circuit potential (OCP) using perturbation frequencies between 10 kHz and 200 Hz with an AC amplitude of 10 mV_{pp}. The electrolyte resistance was