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Dynamical changes of a Ni-Fe oxide water splitting catalyst investigated at different pH

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ABSTRACT

Mixed Ni-Fe oxide electrocatalysts have shown high catalytic activity for the oxygen evolution reaction (OER) in alkaline electrolyte. Fundamental research on mixed Ni-Fe OER catalysts has largely focused on high pH, while the OER activity near neutral pH has remained poorly studied.

Here we review the activity of an amorphous mixed Ni-Fe oxyhydroxide catalyst supported on carbon ($NiFeO_x$/C) in 0.1 M KOH pH 13, in 0.1 M borate buffer (B_i) pH 9.2, and in 0.1 M phosphate buffer (P_i) pH 7.0. The OER catalytic performance was found to decrease in the order of pH 13 > pH 9.2 > pH 7. In contrast to pH 13 and 9.2, the catalyst cycled in pH 7 showed an instantaneous decrease in OER activity and a simultaneous loss of the $Ni(OH)_2$/NiOOH redox peak. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) showed the formation of crystalline areas upon CV cycling, which appeared more Ni enriched after cycling in pH 7. Deactivated electrodes cycled in pH 13 recovered the OER activity along with a partial reappearance of the Ni redox peak when subsequently cycled in pH 13. SEM-EDX spectroscopy confirmed compositional changes in the bulk during cycling at different pH, with an extensive leaching of Ni in pH 7. Our study provides new insight into the OER activity upon exposure to different electrolyte conditions, which unveils a highly dynamic Ni-Fe oxide framework.

1. Introduction

Conversion of energy to generate sustainable fuels such as O_2 and H_2 through electrochemical water splitting require efficient catalysts of inexpensive and abundant materials [1–13]. Binary transition metal electrocatalysts of mixed Ni-Fe have proved amongst the most efficient catalysts for the oxygen evolution reaction (OER) in alkaline electrolyte [12,13,19,21–24,32–34,37,41] with intrinsic activities at comparable levels to those reported for highly active noble metal based catalysts [14–16] and has proven suitable for practical applications such as solar driven water splitting [17–20]. Despite plentiful of investigations in alkaline conditions [21–24] not much information has yet been retrieved about the OER activity of mixed Ni-Fe catalysts near neutral pH [13]. The fact that Ni-Fe based catalysts possess lower OER activity around neutral pH might limit their potential application. In a study by Smith et al [13] a turnover frequency (TOF) of 1.4 s^{-1} was reported for co-deposited Fe-Ni films in 0.5 M borate buffer pH 9.2 at 400 mV OER overpotential. Incidential Fe incorporation from remaining impurities in alkaline electrolyte first highlighted by Corrigan et al [2], was further investigated by Trotochaud et al [22], which showed that the OER activity in conditioned NiOOH films were correlated to the incorporated Fe content. It was also shown by the same group that the OER active phase in $(Fe)NiO_x$ catalysts is the layered oxyhydroxide, as evidenced from *in situ* transformation of a rock salt structure into the active hydrated state upon conditioning in alkaline electrolyte [32]. Gong et al [33] studied a Ni-Fe-LDH/CNT electrocatalyst and found that highest OER activity was achieved with carbon support, with a reported TOF of 0.56 s^{-1} in 1 M KOH at 300 mV overpotential based on total metal loading. Investigations of Ni-Fe based catalysts thus show promising activities at moderate pH, however questions regarding the activity and stability in a wider range of ambiances yet remain open. An understanding of the differences observed in intrinsic activity and the influence on structure in Ni-Fe based catalysts due to changes

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Abbreviations: OER, oxygen evolution reaction; η_{OER}, overpotential for the oxygen evolution reaction; TOF, turnover frequency; $i_{geom.}$, geometric current density; i_{mass}, mass based activity; P_i, phosphate buffer; B_i, borate buffer; KOH, potassium hydroxide; DEMS, differential electrochemical mass spectrometry; i_{MS}, ion current; TEM, transmission electron microscopy; EDX, energy dispersive X-ray spectroscopy; SAED, selected area electron diffraction; TXRF, total reflection X-ray fluorescence.

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in conditions such as electrolyte composition or pH could prove indispensable when designing highly active electrode materials for electrochemical water splitting near neutral pH.

We report studies of a solvothermally prepared amorphous Ni-Fe oxyhydroxide OER catalyst described as $[Ni_{1-x}Fe_x(OH)_2]^{x+}$ $[A^{n-}{}_{x/n}]\cdot mH_2O$, supported on carbon (Vulcan XC-72r) post synthesis, herein denoted as $NiFeO_x/C$, with a Ni:Fe composition of 62:38 at. %. Determination of the OER activities were carried out in 0.1 M KOH pH 13, in 0.1 M borate buffer (B_i) pH 9.2, and in 0.1 M phosphate buffer (P_i) pH 7 using a standard rotating ring disc electrode (RDE) setup. To obtain qualitative measurements of the voltammetric $Ni(OH)_2/NiOOH$ redox peak at different pH, an electrolyte switching protocol was applied where the electrodes were consecutively cycled in a sequence of KOH-P_i-KOH or KOH-B_i-KOH. An initial pre-cycling of 150 cycles in 0.1 M KOH was carried out prior to the measurements to fully activate the electrodes in terms of stabilizing the initial increase of the charge under the Ni redox peak. Physical characterization of electrodes cycled at different pH was carried post-analysis using transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), and selected area electron diffraction (SAED). In situ differential electrochemical mass spectrometry (DEMS) was used to estimate Faradaic efficiencies of O_2 and to identify volatile products released upon exposure to the different electrolytes and pH.

2. Experimental

2.1. Catalyst preparation

The Ni-Fe catalyst with a composition of 62:38 at.% Ni:Fe was synthesized by mixing 2.93 mL of 0.1 M $Ni(NO_3)_2\cdot 6H_2O$ (99.999% trace metals basis, Aldrich) and 1.47 mL of 0.1 M $Fe(acac)_3$ (99.5% trace metal basis, ALDRICH) and dissolved in 20 mL of benzyl alcohol (puriss., 99–100.5%, Alddrich), with addition of 10 mM 1,2-benzenediol (>99%, Sigma–Aldrich); analogous to a reported solvothermal approach [25]. All chemicals were used as received without further purification. The reaction mixture was sealed in a special microwave vial (Anton Paar) and heated in a microwave-assisted autoclave (Anton Paar) to 190 °C with a heating ramp of 16.5 °C/min, and held for 15 min. The particles were supported on 80 wt.% of Vulcan® XC-72r (Cabot) which was added to the reaction mixture after cooling down to room temperature. The catalyst–carbon mixture was agitated for 30 min by sonication and left additional 24 h under stirring. The product was washed 5 times with high purity ethanol; sonicated for 5 min and collected by centrifugation at 7500 rpm for 10 min. The catalyst was finally freeze dried and the powder was stored under inert atmosphere until use.

2.2. Physical characterization

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to determine the metal content of the as-prepared catalyst powder used for calculations of total metal loadings in the catalyst ink for rotating disc electrode measurements. Data was collected using a Varian 715-ES spectrometer coupled to a CCD detector. The sample was digested in an acid mixture of $HNO_3:H_2SO_4:HCl$ to a ratio of 1:1:3 and heated to 180 °C for 15 min using microwave irradiation. The sample probes were diluted with >20 mΩ cm milliQ water. Standard solutions with known concentrations of Ni and Fe (Sigma–Aldrich) were co-analyzed with the samples.

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were acquired on a FEI Tecnai G^2 Microscope 20 S-Twin with a LaB_6-cathode at 200 kV accelerating voltage and GATAN MS794 P a CCD detector (ZELMI Centrum, Technical University of Berlin). Catalysts were conditioned by cycling in KOH, P_i, and KOH between the potential limits of ca. 1–1.7 V vs. RHE (herein abbreviated V_{RHE}) after iR compensation, see more details in Section 2.3. Catalysts were prepared by dispersion of the powder in isopropanol by sonication and drop-casted onto Cu-lacey coated TEM grids. TEM images were analyzed using software packages from ImageJ. The catalyst compositions of local spots were determined using the energy dispersive X-ray spectroscopy (EDX) unit with an (EDAX) r-TEM SUTW detector. The intensities were estimated from the *K*-lines.

Scanning electron microscopy (SEM) using a JEOL JSM-7401F high resolution field emission SEM operated at 10 kV, were acquired on an intact electrode after each step of consecutive KOH-P_i-KOH cycling; 150 cycles in KOH, 20 cycles in 0.1 M P_i pH 7, and re-activated electrodes after 20 cycles in 0.1 M KOH. The electrode had a metal loading of ca. 30 μg Ni + Fe cm^{-2}. The catalyst composition was analyzed using EDX over a larger area of the electrode. The potential limits were kept between ca 1–1.75 V_{RHE} after iR-compensation, see more details in Section 2.3. Energy dispersive X-ray analysis (EDX) was carried out over a larger area after each step to estimate the bulk Ni:Fe composition. EDX analysis was acquired at 16 kV using a Quantax 400 detector (BrukerAXS Microanalysis GmbH, Germany). Quantifications of the Ni and Fe content were obtained from the K lines, and the total metal content estimated from the integrated *K*-line area normalized to acquisition time.

Total reflection X-ray fluorescence analysis (TXRF) was carried out of acid digested electrodes collected after each step in the consecutive cycling; KOH-P_i-KOH and KOH-B_i-KOH, to obtain the total metal content and catalyst composition. The electrodes were cycled between ca 1–1.75 V_{RHE} after iR compensation. In each step, a cycled electrode initially containing ~30 μg cm^{-2} catalyst, was digested in 300 μl of HCl (37%, Merck) by sonication for 10 min, and mixed with 300 μl of 1 mg/mL of Ga-standard solution (Merck). The TXRF analysis was acquired using a PicoTAX spectrometer equipped with a 40 kV using a Si-drift detector (Röntec).

2.3. Electrochemical characterization

The OER activity was determined using a rotating disc electrode (RDE) setup in a standard 3-electrode configuration, with a Pt-mesh as counter electrode separated by a porous glass frit, and a reversible hydrogen reference electrode (Gaskatel) connected via a Luggin capillary. All measurements were recorded using a GAMRY 600 reference potentiostat in 0.1 M KOH (semiconductor grade, 99.99% trace metals basis, Aldrich), in 0.1 M phosphate buffer ($KHPO_4$, P_i, 99.99% trace metal basis), and in 0.1 M borate buffer (H_3BO_3, B_i > 99.8%, puriss., Aldrich). Electrolytes were degassed with N_2 for 20 min prior to each measurement and a protective atmosphere was kept by purging throughout the measurement. Catalyst inks were prepared by dispersing catalyst powders in a mixture of 150:100:1 of milliQ:2-propanol:5 wt.% Nafion® and homogenously dispersed by ultrasonication for 15 min before drop coated onto glassy carbon electrodes (Φ = 5 mm, Pine Instruments). The total metal loading was varied between 1–20 μg Ni + Fe cm^{-2}. The glassy carbon electrodes were prior to drop coating polished with 0.1 μm alumina MicroPolish (Buehler) using a Nylon cloth followed by 0.05 μm alumina polishing suspension (Buehler) using a Microcloth, and rinsed with milliQ-aceton-milliQ using sonication for 5 min in each step, and finally carefully rinsed with milliQ. Different catalyst loadings were achieved by dropping a different volume of in the ink onto the electrode. The rotation speed was set to 1600 rpm. In the pH switching experiments, the electrolyte was consecutively changed from KOH-P_i-KOH or from KOH-B_i-KOH, and each electrolyte was held in a separate electrochemical cell and the electrodes were rinsed in milliQ water (>20 mΩ cm) in between