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Short communication

Nanostructured nickel nanoparticles supported on vulcan carbon as a highly active catalyst for the hydrogen oxidation reaction in alkaline media

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HIGHLIGHTS

- Ni_{ED}/XC-72 displays the HOR mass activity similar to commercial Pd/C catalyst.
- Highly active Ni nanoparticles are nanostructured and partially oxidized.
- Ni_{ED}/XC-72 is a promising alternative to PGM catalysts at the anodes of AMFCs.

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ABSTRACT

An alkaline membrane fuel cell (AMFC) is considered as a promising technology allowing to convert chemical energy of a fuel, for example hydrogen, into electricity. The use of alkaline electrolytes opens up possibility of utilizing low-cost transition metal catalysts, which are unstable in acidic electrolytes. Herein, we developed a facile and efficient method to prepare carbon-supported nickel nanoparticles of small size (10 nm) at high metal loading (42 ± 3 wt%) by electrodeposition. The resultant Ni_{ED}/XC-72 catalyst exhibits remarkably high mass activity in the hydrogen oxidation reaction, which can be further enhanced by partial oxidation of the metal surface. The activity achieved amounts to ca. 22 $A \cdot g_{Ni}^{-1}$, thus being comparable to the values reported for commercial 20% Pd/C catalyst (38 $A \cdot g_{Pd}^{-1}$). The excellent electrocatalytic performance indicates that the Ni_{ED}/XC-72 catalyst can be considered as a replacement of the precious metals at the anodes of AMFCs.

1. Introduction

Increasing energy demand and diminishing of fossil fuel resources have largely stimulated development of renewable energy sources during the past decades. Owing to its environmental friendliness and high energy density, hydrogen is perceived as one of the most promising energy carriers of the future [1]. The energy stored in hydrogen can be converted into electricity in a fuel cell (FC), where hydrogen oxidation reaction (HOR) occurs at the anode, while oxygen reduction reaction (ORR) proceeds at the cathode. Among hydrogen-fed FCs, the proton exchange membrane FC (PEMFC) technology has had the most progress until now. However wide commercialization of PEMFCs is hindered by the high price of noble metal catalysts (mainly Pt). Even if significant progress has been achieved in decreasing the total content of platinum-group metals (PGMs) in PEMFC stacks, despite all efforts it remains high and has stayed at almost the same level during the past five years [2]. One of the promising approaches to reduce the price of FCs is to replace proton- by anion-exchange membranes and thus PEMFCs by AMFCs, which can be PGM-free [3–5]. The ORR, being the main source of the efficiency losses in PEMFCs, is faster in alkaline media and can be catalyzed by some PGM-free catalysts with comparable to Pt rate [6–8]. However the HOR activities of PGMs are hundred times lower in alkaline compared to acid media [9], requiring much higher loading of the catalysts to achieve similar to PEMFC performance. This stimulates the development of Pt-based and especially PGM-free anode catalysts with desirable activity in the HOR. Recent achievements in this field have been summarized by Cong et al. [10].

Among non-noble metals, Ni has been perceived as one of the most promising catalysts for the anodes of AMFCs [11]. It is inexpensive, shows good corrosion stability in alkaline environments and has been

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widely explored as a catalyst for the hydrogen evolution reaction (HER) (see Refs. [12,13] and refs. therein). In early studies Raney Ni doped with other transition metals was used [14–17], but showed relatively low activity in the HOR, especially due to insufficient ratio between the utilized active surface area and the mass of the catalyst. Recently Ni alloys, such as NiCoMo [18], NiCu [19,20] and NiMo [21] have been shown to demonstrate higher activity in the HOR compared to pure Ni. The activity enhancement was proposed to be due to a decrease of the hydrogen binding energy after addition of the second metal [18]. Similar effect could be achieved if the reactive metallic Ni sites coexist on the electrode surface with Ni oxide species (NiO_x) [22,23]. This remarkably boosts the activity of Ni catalysts in both the HER [24–27] and the HOR [22,23,28]. In addition, Zhuang and co-workers have demonstrated that the activity of Ni nanoparticles increases if they are supported on *N*-doped carbon nanotubes (Ni/N-CNT), presumably due to the electronic effect of the edge N atoms on d-orbitals of adjacent Ni sites [29]. However, despite all the efforts mass-weighted electrocatalytic activity of Ni-based catalysts in the HOR is still far from the values obtained using PGM catalysts.

In the present work, we synthesized nanostructured Ni nanoparticles supported on Vulcan XC-72 carbon (Ni_{ED}/XC-72) and investigated their electrocatalytic activity towards the HOR. The synthesis was performed by using electrodeposition technique. It allowed us to obtain metal nanoparticles of ca. 10 nm size, which were homogeneously distributed over the support surface and possessed high mass activity in the HOR. Further increase of the mass activity was achieved by partial oxidation of their surfaces. On account of the high activity in the HOR and low cost, the synthesized Ni_{ED}/XC-72 catalyst has great potential to be used at the anode of AMFCs.

2. Material and methods

2.1. Synthesis of Ni nanoparticles on XC-72 carbon

Nanostructured Ni_{ED}/XC-72 catalysts were prepared by potentiostatic electrodeposition of Ni from the bath containing 0.01 M $NiSO_4$ + 0.10 M $(NH_4)_2SO_4$ solution (obtained from $NiSO_4{\cdot}6H_2O$ (99.99%, Aldrich) and $(NH_4)_2SO_4$ (99.0%, Aldrich) granules) at $T = 298$ K using porous Vulcan XC-72 carbon (Cabot) as a catalyst support (see Supporting Information for the details). The amount of electrodeposited Ni was analyzed by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). The typical metal loading was estimated to be 42 ± 3 wt% (with respect to the total mass of the Ni_{ED}/XC-72 catalyst).

2.2. Physical characterization

The morphology and the microstructure of Ni_{ED}/XC-72 was studied by Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) using a JEOL 2100F and a LaB6-JEOL 2100 microscopes, respectively, operating at accelerating voltage of 200 kV.

X-ray photoelectron spectroscopy (XPS) measurements were performed in an ultra-high vacuum chamber (residual gas pressure $< 5 \times 10^{-6}$ Pa) equipped with a VSW Class WA hemispherical electron analyzer and a dual anode (Al and Mg Kα) X-ray source. Survey and high resolution Ni2p, O1s, C1s spectra were recorded in a constant pass energy mode (44 and 22 eV, respectively) at 0 take-off angle. The charging effect arising in the process of photoemission of electrons was taken into account by correcting the spectra with respect to C1s of the carbon line (284.8 eV). XP spectra were curve fitted after Shirley background subtraction, following the procedure described in Ref. [22].

2.3. Electrochemical measurements

Electrochemical measurements were performed in a three-electrode Pyrex glass cell, containing 0.10 M NaOH and thermostated at 298 K, using a Biologic SP-300 potentiostat. The counter electrode (Pt wire) and the reference electrode (Hg|HgO|0.10 M NaOH) compartments were connected with the working electrode chamber *via* a glass frit and a Luggin capillary, respectively. If not otherwise stated, all electrode potentials reported in the manuscript are referred to the reversible hydrogen electrode (RHE, $E_{Hg/HgO} = 0.928$ V *vs* RHE). Prior to each experiment, the glassware was cleaned by soaking in a H_2SO_4:H_2O_2 (1:1 v/v) mixture and then thoroughly washed with pure water (ELGA, 18.2 MΩ cm, TOC $<$ 2 ppb).

The cyclic voltammetry (CV) curves acquired in the potential interval from −0.06 V to 0.40 V were employed to estimate the electrochemical surface area (ECSA) of Ni (Fig. S1) considering the entire value of the anodic charge and the 0.514 mC cm^{-2} conversion coefficient [22]. The HOR catalytic activity was derived from the rotating disk electrode (RDE) voltammetric data obtained in H_2-saturated 0.10 M NaOH at $\nu = 5$ mV s^{-1} using an Autolab RDE-2 setup at the rotation rate (ω) of 1600 rpm. For this the micropolarization region ($-10 < E < 10$ mV) of the polarization curves was analyzed by linear fitting (Fig. S2). To study the influence of surface oxide species on electrocatalytic properties of Ni_{ED}/XC-72 catalyst, two states of its surface were considered: (i) preferentially metallic (hereinafter, “non-activated”), and (ii) partially oxidized (hereinafter, “Ch-activated” or “EC-activated” depending on the way of surface oxidation). The non-activated samples were studied immediately after the preparation, while to obtain the activated samples, the electrode was first subjected to oxidation either under contact with air (Ch-activated) or by applying positive potential (EC-activated) before measuring their activity. For more details, the reader is referred to the Supporting Information. To perform the XPS measurements the GC cylinders with Ni_{ED}/XC-72 catalysts were fixed on the sample holder immediately after electrochemical treatments and protected with a drop of purified water (aiming to minimize the contact with the ambient atmosphere). After that the holder was quickly (within 5 min) placed into the entry chamber of the XP spectrometer, degassed down to $P \approx 10^{-5}$ Pa and only then the sample was transferred to the main chamber of the XP spectrometer.

3. Results and discussion

TEM image taken from the Ni_{ED}/XC-72 sample (Fig. 1a) demonstrates a fairly homogeneous distribution of Ni nanoparticles with a mean diameter of 10 ± 2 nm over the surface of the carbon support. High resolution STEM images obtained in bright and dark fields (Fig. 1b and c) clearly show the nanostructured nature of Ni nanoparticles, which consist of crystallites of smaller size (ca. 3 nm) connected through intergrain boundaries. The value of the interplanar spacing was estimated from the STEM density profile (Fig. S3) as ca. 0.202 nm, corresponding to the (111) plane of Ni (0.2034 nm, calculated for theoretical lattice constant $a = 0.35238$ nm of crystalline Ni [ICDD PDF-2#00-004-0850]).

Fig. 2 shows the polarization curves registered in H_2-saturated electrolyte for freshly prepared Ni_{ED}/XC-72 sample (i.e. non-activated) and after partial oxidation of its surface (i.e. Ch- and EC-activated). The specific activity of non-activated Ni_{ED}/XC-72 in the HOR was found to be ca. 6 μA·cm_{Ni}^{-2}, which is nearly 3 times higher than the value reported for non-activated polycrystalline Ni (Table 1). This activity enhancement originates likely from the difference in the microstructure of these two samples. The grain size for polycrystalline Ni usually varies from 10 to 100 μm, which accounts for less than 0.03% of the grain boundary component [30–32]. On the contrary, nanostructured Ni_{ED}/XC-72 nanoparticles provide a high concentration of intergrain boundaries, whose positive influence on several electrocatalytic