Sci. Bull.
DOI 10.1007/s11434-016-1025-y

www.scibull.com
www.springer.com/scp

Article

Engineering Sciences

Characterization of different plasma-treated cobalt oxide catalysts for oxygen reduction reaction in alkaline media

**Lisa M. Uhlig · Gustav Sievers · Volker Brüser ·
Alexander Dyck · Gunther Wittstock**

Received: 6 November 2015 / Revised: 11 January 2016 / Accepted: 12 January 2016

Abstract Plasma-synthesized cobalt oxide supported on carbon has been analyzed for its use for electrocatalytic oxygen reduction reaction (ORR) in alkaline anion exchange membrane fuel cells (AEMFC). This work presents the ORR activity in 0.1 mol L^{-1} KOH and 0.1 mol L^{-1} K_2CO_3 at 25 °C. Cyclic voltammetry (CV) was used to determine the potentials at which the ORR occurs and to evaluate the stability of catalyst. Moreover, a rotating ring-disk electrode (RRDE) was used to investigate the activity of the catalysts and the formation of the by-product hydroperoxide anion (HO_2^-) as well as to identify the preferred pathway of the ORR. Calculated kinetic parameters for the ORR for the cobalt catalysts are shown in this work together with a comparison to a commercial platinum catalyst. However, the cobalt oxide produced more by-products which could lead to damage of the membrane in a fuel cell through a radical attack of the polymer backbone.

Keywords Oxygen reduction reaction · Alkaline media · Electrocatalytic activity · RRDE · Cobalt catalyst · Alkaline fuel cell

SPECTIAL TOPIC: Materials for Energy Conversion

L. M. Uhlig (✉) · A. Dyck
NEXT ENERGY, EWE-Research Centre for Energy Technology, 26129 Oldenburg, Germany
e-mail: Lisa.Maria.Uhlig@next-energy.de

L. M. Uhlig · G. Wittstock
Faculty of Mathematics and Science, CIS - Center of Interface Science, Institute of Chemistry, Carl von Ossietzky University of Oldenburg, 26111 Oldenburg, Germany

G. Sievers · V. Brüser
Leibniz Institute for Plasma Science and Technology, 17489 Greifswald, Germany

1 Introduction

Platinum, one of the most frequently used electrocatalysts, is a rare element and thus expensive. This represents a road block for the wide use of fuel cell technology, in particular if grid-scale applications are considered. For such application area, alkaline fuel cells (AFC) are becoming more and more interesting because they allow the use of non-precious metal oxide catalysts like manganese or cobalt oxides [1–5]. Furthermore, the oxygen reduction reaction (ORR) in alkaline media is faster than in acidic media [6, 7] and AFCs reach the highest efficiency of all low temperature fuel cells [8]. Two pathways are described for the ORR: the two- and four-electron paths [9]. The two-electron pathway leads to the formation of hydroperoxide anion HO_2^- as by-product, which decreases the efficiency and may damage the expensive membrane by a radical attack of the polymer. The four-electron pathway is the direct reduction of oxygen to H_2O [10] which is the preferred pathway for the ORR where low content by-product is produced. This reaction dominates at platinum electrocatalysts [11], and just ~4 % of by-product is formed with 10 wt% Pt/C in 0.1 mol L^{-1} KOH [12].

Compared to pyrolized transition metal oxide catalysts, plasma-synthesized catalysts show a higher activity, enhanced selectivity and better stability according to examples in Ref. [13]. A low temperature plasma treatment of precursor material does not change the morphology of the material and leads to a better particle size distribution [14]. In addition, an enrichment of the surface with nitrogen can lead to an enhanced performance of catalyst material [15–17].

In this work, a cobalt catalyst was obtained by impregnating a carbon support with cobalt(II) acetate (CoAc/C) and treating these materials in a nitrogen plasma.

This process converts cobalt(II) acetate to cobalt oxide (CoO_x/C) which is supposed to be the catalytically active component. CoO_x/C was investigated in 0.1 mol L^{-1} KOH and 0.1 mol L^{-1} K_2CO_3 at 25 °C on rotating ring-disk electrodes (RRDE) for three CoO_x/C materials after different plasma treatments. KOH electrolyte was chosen because of the high activity observed in this electrolyte. However, anion exchange membranes in AFC can be damaged faster in the presence of hydroxide, as shown for a poly(arylene ether sulfone) polymer membranes functionalized with quaternary ammonium cations [18, 19] while membranes are much more stable in carbonate solutions because the carbonate ion is less nucleophilic than hydroxide [18]. Furthermore, fuel cells that operate with air as oxygen source and hydroxide electrolytes will absorb CO_2 from air to react to carbonates and bicarbonates with lower dissociation rate that lowers the ion conductivity and decreasing the performance of the entire fuel cell [9, 20].

2 Experimental

2.1 Preparation of catalyst material

The catalyst material was synthesized at Leibniz Institute for Plasma Science and Technology (INP Greifswald) by inductively coupled radio-frequency plasma (27.12 MHz) which was generated in a vibrating bed reactor for the plasma treatment. A scheme and detailed description were published elsewhere [14]. An ethanolic suspension containing the catalyst support carbon (Vulcan XC-72) and cobalt(II) acetate tetrahydrate (Sigma-Aldrich) was evaporated by a rotary evaporator. The resulting mixture contained 20 wt% Co. Pure N_2 was used at a pressure of 10 Pa, and the three different samples were synthesized by varying the plasma power (300, 450 or 600 W) for 120 min. For this paper, the three different samples were named according the plasma treatment: CoO_x/C_300W, CoO_x/C_450W and CoO_x/C_600W. The precursor material cobalt(II) acetate tetrahydrate on Vulcan XC-72 (without plasma treatment) was named CoAc/C and was also investigated.

2.2 Materials

For the catalyst ink, a defined amount of each plasma-treated catalyst powders (CoO_x/C_300W, CoO_x/C_450W or CoO_x/C_600W), CoAc/C or 20 wt% Pt/C (Sigma-Aldrich, Germany) was suspended in a mixture of isopropanol and Millipore water (18 MΩ cm^{-2}) and a commercial available alkaline ionomer. The mixture was sonicated for 15 min using an ultra-horn sonifier (450D or 250D sonifier, Branson, MI, USA). To keep the inks homogenous after sonication, a magnetic stirrer was used. Finally, 10 μL of the ink was pipetted on the glassy carbon disk electrode to achieve loadings of 20 μg_{Cobalt} cm^{-2} of each CoO_x/C catalyst material. The solvent was evaporated under air with a rotator to achieve a homogenous coating of the catalyst material surface: The electrode was accelerated to ~700 r min^{-1} for 10 min, and then, the rotation speed was increased to 900 r min^{-1} and kept constant for 20 min until the ink had dried.

The electrolytes were prepared directly before the measurement from K_2CO_3 powder (Sigma-Aldrich, Germany) or KOH powder (Merck, Germany) and Millipore water (18 MΩ cm). For preparation, a polyethylene (PE) spatula and PE flask were used to avoid the contact of alkaline solutions with glass. Prior to every CV and ORR measurements, the electrolyte was purged with N_2 ($\geq$99.9 %) and O_2 ($\geq$99.9 %), respectively, at least 15 min.

2.3 Apparatus and measurements

A bipotentiostat (Autolab, 132 N, under software Nova version 1.10, Metrohm, Filderstadt, Germany) was used in a three- or four-electrode configuration for the investigation of the catalytic activity. The first working electrode was a glassy carbon disk electrode of a rotating ring-disk electrode (PINE, Durham, NC, USA) covered with catalyst. The Pt ring was used as second working electrode. The electrochemical cell was completed by a platinum mesh as auxiliary electrode (AUX) and a reversible hydrogen electrode (RHE, HydroFlex, Gaskatel, Kassel, Germany) as reference electrode (RE) immersed with salt bridges into the electrolyte. All potentials are reported versus RHE. A temperature-controlled electrochemical polytetrafluorethylene (PTFE) cell with PTFE cap was used in order to avoid glass corrosion in alkaline media [21]. Furthermore, PTFE tubes were used for gas supply. The setup was mounted in a Faraday cage. ORR was recorded at 5 mV s^{-1} in order to minimize the influence of the capacitive current. Currents are converted to current densities using the geometric area of the disk electrode and ring electrode.

Thermogravimetric analysis (TGA) with coupled Fourier transform infrared spectroscopy (FTIR) was performed using TGA 4000-Spectrum 100 TG-FT-IR (PerkinElmer, USA). The three different samples were heated under nitrogen stream from 30 to 900 °C with a heating rate of 20 °C min^{-1}. Transmission electron microscope (TEM, JEOL JEM2100F, JEOL Ltd., Tokyo, Japan) images were recorded for morphology analyses of catalyst materials. Likewise X-ray photoelectron spectroscopy (XPS) measurements were taken with an Axis Ultra DLD (Kratos, Manchester, UK) using monochromatized Al Kα radiation.