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Electrochemical characterization of temperature dependence of plasma-treated cobalt-oxide catalyst for oxygen reduction reaction in alkaline media

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ABSTRACT

This work presents the oxygen reduction reaction (ORR) activity of three different plasma-synthesized cobalt oxides supported on carbon (CoO_x/C) in 0.1 M KOH and 0.1 M K₂CO₃ at 323 and 348 K. To evaluate the stability of the catalyst material, cyclic voltammograms (CVs) were recorded. To investigate the catalytic activity, a high-temperature rotating ring-disk electrode (RRDE) was used. Cobalt based catalyst materials seem to be a good alternative to costly platinum-based catalysts. This work shows the temperature dependent catalytic activity of plasma-treated cobalt acetate precursor material. This work showed that the increase of temperature to 323 K resulted in an increase in activity for ORR for the three catalyst materials, but a further temperature increase up to 348 K leads to a decrease in activity.

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Introduction

The proposition that oxides of abundant non-noble metals like cobalt and manganese could be used in alkaline media to enhance the oxygen reduction reaction (ORR) for alkaline fuel cells (AFC) is receiving more attention [5,8–11]. The ORR in alkaline media is faster than in acidic media [12,13] and achieves the highest efficiency of low temperature fuel cells [14].

The four-electron pathway for ORR is the direct reduction of oxygen (O₂) to water (H₂O) [15], but it is also possible for oxygen to be reduced via two subsequent two-electron pathways which leads to the formation of intermediate hydroperoxide anion (HO₂⁻) as by-product [16,17]. If HO₂⁻ is formed, it might decrease the efficiency and damage the membrane [18]. Additionally, membranes are more stable in carbonate solutions due to the fact that carbonate ions are less nucleophilic than hydroxide [1]. Furthermore, CO₂ constitutes another

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impurity in AFC using air as oxidizer. Hydroxide anions can react with CO_2 to carbonate ions. There is an equilibrium between hydroxide, carbonate and bicarbonate ions in aqueous media [2,3]. The carbonate ions react with potassium cations forming salts which can block the electrodes and reduce performance of the AFC [2–4]. In this work we investigated the influence of hydroxide and carbonate media on the ORR. In order to enhance the ORR on the cathode side, non-precious metal catalyst, as cobalt oxides, can be used in alkaline media [5–7,19]. As known from literature, plasma-synthesized catalysts showed enhanced selectivity, higher activity and stability than pyrolyzed non-noble metal oxide catalysts for fuel cells in acidic media [20]. Under low temperature plasma-treatment, the precursor material morphology did not change, and this treatment leads to a better particle size distribution [20]. In literature it is shown that the higher the plasma-power for the synthesis of cobalt polypyrrole catalysts and iron based catalysts from iron acetate in nitrogen gas phase, the higher the percentage of conversion to oxides. The nitrogen content in the catalyst material can lead to a higher activity of those catalyst material [21–23]. Based on previous work at 298 K, it was expected that the catalyst material synthesized with highest N_2 -plasma-power achieved the highest ORR activity [24]. Since the catalyst activity is characterized for use in alkaline fuel cells, it is recommended to investigate the catalyst activity at the operating temperature of around 333 K. So the set-up was constructed to heat the electrolyte up to 348 K and the catalytic activity was investigated at 298, 323 and 348 K.

Materials and methods

Three different plasma-synthesized cobalt oxide catalysts (CoO_x/C) were investigated. The samples were synthesized that 20 wt% cobalt was supported on Vulcan XC. A description of synthesis and characterization of these materials is published elsewhere [24]. For this work the three different samples are named according to the plasma-treatment at different plasma-power: $\text{CoO}_x/\text{C}_{300\text{W}}$, $\text{CoO}_x/\text{C}_{450\text{W}}$ and $\text{CoO}_x/\text{C}_{600\text{W}}$. To deposit the catalyst on the electrode surface, catalyst ink was prepared by a mixing one of the N_2 plasma-treated catalyst powders ($\text{CoO}_x/\text{C}_{300\text{W}}$, $\text{CoO}_x/\text{C}_{450\text{W}}$ or $\text{CoO}_x/\text{C}_{600\text{W}}$) in a solution of isopropanol and Millipore water (18 $\text{M}\Omega$ cm) and a commercial available alkaline ionomer [24]. The electrodes were deposited with catalyst ink to achieve a catalyst loading of $20 \mu\text{g}_{\text{Co}} \text{cm}^{-2}$. For comparison commercial available platinum supported on carbon (20 wt% Pt/C, Sigma Aldrich, Germany) was investigated using the same procedure as used for the cobalt oxide catalyst materials. Fresh electrolytes were prepared from K_2CO_3 powder (Sigma Aldrich, Germany) or KOH powder (Merck, Germany) and Millipore water (18 $\text{M}\Omega$ cm). During preparation and measurement, contact with glass was avoided. To record CVs, a bipotentiostat (Autolab, 132 N, Nova Version 1.10, Metrohm, Filderstadt, Germany) was used. A first working electrode consisting of a catalyst covered glassy carbon disk electrode (GC-WE) of a rotating high temperature ring-disk electrode (PINE, Durham, USA) and a second platinum ring working electrode were used [24]. The electrolytes were purged either

with nitrogen (N_2) or oxygen (O_2). The currents are converted to current densities using the geometric area of the disk and ring electrodes. All potentials are given versus RHE.

Results

After deposition of the catalyst material on the GC-WE CVs have been recorded in N_2 -purged electrolyte to investigate the stability of the catalyst material at 323 and 348 K in 0.1 M KOH and 0.1 M K_2CO_3 (Fig. 1). The recorded peaks between 0.9 and 1.45 V correspond to the oxidation and reduction of cobalt(II) and cobalt(III) [25,26]. The anodic peak at around 1.2 V is due to the oxidation of cobalt(II,III) oxide (Co_3O_4), cobalt(II) hydroxide ($\text{Co}(\text{OH})_2$), or cobalt(II) oxide (CoO), and the formation of cobalt oxide hydroxide ($\text{CoO}(\text{OH})$) [25].

The current densities for $\text{CoO}_x/\text{C}_{300\text{W}}$ in 0.1 M KOH were almost the same for both temperatures 323 and 348 K. As expected from previous measurements at 298 K, the current densities for $\text{CoO}_x/\text{C}_{450\text{W}}$ were higher than $\text{CoO}_x/\text{C}_{300\text{W}}$. Additionally, higher values are achieved at 323 K than at 348 K. The current densities for $\text{CoO}_x/\text{C}_{600\text{W}}$ were also higher than those for $\text{CoO}_x/\text{C}_{450\text{W}}$ and higher current values are achieved at 323 K for $\text{CoO}_x/\text{C}_{600\text{W}}$ (Fig. 1a). Also in 0.1 M K_2CO_3 the same trend was observed: The higher the plasma-power the higher the current densities and for all three samples the 323 K values were higher than at 348 K (Fig. 1b). The CVs for $\text{CoO}_x/\text{C}_{600\text{W}}$ at 348 K do not show the expected cobalt(II) and cobalt(III) redox peaks as observed in the other CVs. This phenomenon has to be clarified in further investigation.

Using the RRDE several CVs were recorded to investigate the ORR in both electrolytes at both temperatures. To oxidize the by-product HO_2^- the constant potential of the ring (E_R) was set to 1.2 V. The potential of the disk electrode (E_D) was varied from 1.1 to 0.05 V with scan rate of 5 mV s^{-1} and the current densities of the disk (j_D) and ring (j_R) were recorded (Fig. 2). For comparison also the ORR of 20 wt% Pt/C was investigated (Fig. 3).

In 0.1 M KOH the potential at which oxygen reduction starts is around 0.75 V and in 0.1 M K_2CO_3 around 0.7 V. The lowest slope was observed with $\text{CoO}_x/\text{C}_{300\text{W}}$ and the highest slope with $\text{CoO}_x/\text{C}_{600\text{W}}$ in both electrolytes at 323 K. With the platinum catalyst the potential at which the oxygen reduction starts is around 0.9 V in both electrolytes with a small shift in carbonate electrolyte, and it showed higher current densities in 0.1 M KOH due to higher conductivity compared to 0.1 M K_2CO_3 . With increasing temperature the current densities decreased for both electrolytes. In comparison, the cobalt oxide catalyst does not achieve similar limiting current densities as the commercial platinum catalyst. Although there are literature reports about a cobalt oxide catalysts synthesized by thermal decomposition achieving comparable high limiting currents as a commercial 20 wt% Pt/C [27].

For comparison of the activity, the values of the limiting current density j_{lim} at 0.40 V and also the mass based activity j_{mass} at 0.80 V using equation (1) has been determined (Fig. 4).

$$j_{\text{mass}} = \frac{j_{\text{kin}}}{m_{\text{Co}}} \quad (1)$$

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