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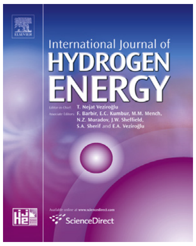

Carbon supported Ag and Ag–Co catalysts tolerant to methanol and ethanol for the oxygen reduction reaction in alkaline media

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ABSTRACT

Ag/C and Ag–Co/C catalysts with high activity towards the oxygen reduction reaction in alkaline media, different metal loadings and average sizes below 20 nm were synthesized by glycerol and borohydride reduction methods without stabilizers. Physicochemical characterization of the materials was performed by X-ray techniques (diffraction, energy dispersive and photoelectron spectroscopy) and transmission electron microscopy. Well dispersed small nanoparticles were obtained in all cases, mainly formed by Ag(0). For Ag–Co/C catalyst, it was observed that Co was not alloyed but presented as cobalt oxides. The electrocatalytic activity towards oxygen reduction reaction (ORR) in alkaline solution was evaluated by cyclic voltammetry and rotating disk techniques. A four electron transfer mechanism was established although increasing Ag loading produces a decrease of this number, indicating that hydrogen peroxide produced as intermediate in a first two electron step was not completely reduced. Alcohol tolerance of the catalysts was also established in methanol and ethanol solutions. Materials were not active for the electro-oxidation of alcohols, although it was observed that both methanol and ethanol were adsorbed on the catalyst. Highest activity and alcohol tolerance was observed for the 60 wt.% Ag loading material. Also the introduction of Co produces an increase in the activity (higher ORR limiting currents) and in the alcohol tolerance. In comparison to Pt and Pd, Ag and Ag–Co present more appropriate activities for ORR when alcohol tolerance is considered, being good candidates for the use as catalysts in alkaline direct alcohol fuel cells.

Introduction

Alkaline direct alcohol fuel cells (ADAFCs) are considered good candidates as power sources for future portable and vehicle devices owing to their high theoretical specific energy, low cost and environmental friendliness [1–3]. These systems have some advantages compared to the common polymer electrolyte membrane fuel cells (PEMFCs), such as the usage of non-precious metal catalyst, the decrease of cathode overpotential and the favorable water management. Thus, it is the

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possibility to replace Pt-based alloys by non-noble (and cheaper) metals as electrocatalysts for both electrodes the most relevant characteristic of the ADAFCs [4,5]. Previous works have shown that several metals could be used as anode catalyst [6] and silver appears as a good candidate for the cathode [7–9]. However, there are still notable challenges for ADAFCs concerning the oxygen reduction reaction (ORR), including the improvement of the low reaction rates, high overpotentials and low stabilities. Silver is a promising candidate for replacing Pt for ORRs in alkaline solution due to its high activity and comparatively low cost [10,11]. Moreover, Ag cathodes have been reported to be more stable than Pt ones during long-term operation [12]. On the other hand, Ag and its alloys show better tolerance toward methanol [7–11,13] and ethanol [14] poisoning than Pt.

It has been reported that Ag/C promotes the 4-electron pathway for ORR in alkaline solutions and increasing the content of Ag in the carbon supported catalyst produces a positive shift of the onset potential for this reaction [15]. Ying et al. [16] have reported that Ag nanoparticles supported on Co_3O_4 show large electrochemical active surface area (ESA), high catalytic activity towards ORR and also exhibit good methanol tolerance and stability in alkaline media. In a recent work Eun et al. [17] described that highly dispersed Ag nanoparticles on reduced graphene oxide (RGO) displayed higher catalytic activity than Ag/C. Tammeveskia et al. reported that Ag nanoparticle/multi-walled carbon nanotube (AgNP/MWCNT) presented a high electrocatalytic activity towards ORR, with similar specific activity to bulk Ag [18], whereas Sekol and colab. have shown that Ag@Pd/MWCNTs catalysts also presented high tolerance to methanol and ethanol [19].

On the other hand, it was evidenced that the presence of a second metal also improved the Ag activity. Lima et al. have studied Ag–Co/C as cathode catalyst for ORR in AFCs and found that Co, in the form of $Co_3O_{4,}$ contributed to the 4-electron pathway with respect to Ag/C [20]. Bard et al. have proposed a simple mechanism to illustrate the electroactivity enhancement of Ag-based binary catalysts for ORR: the O–O bond first breaks down on one metal-atom of the binary Ag-based catalyst to form an adsorbed O atom (O_{ad}), and then the O_{ad} transfers into another metal-atom (usually Ag) to be reduced. Ag–Pt, Ag–Au and Ag–Pd have been extensively studied as effective Ag-based binary electrocatalysts for ORR [21,22]. In addition, Lima et al. have prepared a low cost carbon supported binary Ag–Co catalyst, with high electroactivity for this reaction, by a chemical reduction procedure [20]. Finally, other no-noble metals have been used for the preparation of bimetallic Ag electrocatalysts. Thus, it was observed that the increment of the amount of Ni in the Ag–Ni alloy and the heat treatment at 500 °C decreases the ORR overpotential and increases the limiting current density for this reaction [23]. Alternatively, it has been reported that Ag–Ni catalyst can be used in borohydride fuel cells exhibiting higher discharge voltage and capacity [24].

In this work, Ag/C materials with low nanoparticle sizes were synthesized by the glycerol reduction method to be used as catalyst at the cathode of alkaline fuel cells, varying the Ag loading between 10 and 60 wt.%. On the other hand, carbon supported Ag–Co catalysts have been prepared using $NaBH_4$ as reduction agent with 20 wt.% metal content. The composition, morphology, particle size and metal loading of the catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) and photoelectron spectroscopy (XPS) analysis. The electrocatalytic activity towards the ORR was studied applying two electrochemical techniques: cyclic voltammetry and rotating disk electrode, in the presence of different methanol or ethanol concentrations. Finally, the catalytic activity of 20 wt.% Ag/C and Ag–Co catalysts was compared to the performances for 20 wt.% Pd/C and Pt/C materials.

Material and methods

Preparation of Ag/C catalysts

Ag/C catalysts with different Ag content were synthesized following the glycerol reduction method reported in the literature [25]. Briefly, an appropriate amount of Vulcan XC-72R (Cabot Corp.) in a known volume of Milli-Q water was sonicated and a certain quantity of $AgNO_3$ (Aldrich, 99.9999%) was added under stirring to promote the homogenization of the mix. Afterward, another solution containing glycerol (Sigma–Aldrich, 99%) and NaOH (Sigma–Aldrich, 99.99%) was added to give the following concentrations: 0.82 mM $AgNO_3$, 1 M glycerol and 0.1 M NaOH. The mixture was kept during 24 h under stirring at room temperature and then washed, filtered and dried at 80 °C during 12 h. Three Ag/C catalysts with silver loadings of 10, 20 and 60 wt.% were prepared with this method.

Preparation of Ag–Co/C, Co/C and Pd/C catalysts

Pd, Co, Ag and Ag–Co catalysts dispersed on carbon Vulcan XC-72R with 20 wt.% metal content were prepared using $NaBH_4$ as reduction agent. A stronger reduction agent was used to guarantee metal reduction in all cases. The bimetallic particles were obtained with different nominal atomic ratios, ranging from pure Ag and Co (for a comparative purpose) to Ag:Co (3:1). Materials were prepared by simultaneous reduction of the precursor metal salts Ag $(NO_3)_2$ and $Co(NO_3)_2 \cdot 6H_2O$ (Sigma–Aldrich, 99%). The reduction process was carried out at room temperature by drop wise addition of the precursor solution onto a carbon black dispersion, which was prepared by suspending carbon powder in ultrapure water ultrasonically blending for 10 min and then 12 h under magnetic agitation. This is followed by drop wise addition of an excess of $NaBH_4$ solution for reduction and precipitation of the precursor metal particles. The mixture was kept during 12 h under stirring at room temperature and then washed, filtered and dried at 60 °C during 12 h. Similar procedure was applied for preparation of Pd/C material using $PdCl_2$ (Sigma–Aldrich, p.a.) as precursor. Commercial E-TEK 20 wt.% Pt/C catalyst was also employed for comparison.

Physicochemical characterization

The real Ag content and the atomic composition of the electrocatalysts were determined by energy dispersive X-ray analysis (EDX) coupled to a scanning electron microscopy (SEM) Jeol JEM Mod. 6300 with a silicon doped with lithium

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