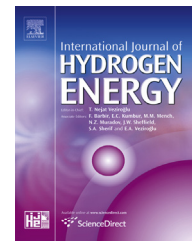




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Development of materials for anion-exchange membrane direct alcohol fuel cells

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ABSTRACT

In this paper development of anodic materials for anion-exchange membrane direct alcohol fuel cells (AEM-DAFC) using methanol or ethylene glycol as fuels is reported. In this regard, different PdM/C electrocatalysts (where M = Ag, Ni) were synthesized and characterized for both fuels. After that, it was possible to verify that the synthesized catalysts achieve high performance with both fuels in single cell tests. Finally concepts for ionomeric binders will be introduced which are supposed to allow a later operation of the cell without added bases.

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Introduction

Direct alcohol fuel cells (DAFCs) based on proton-exchange membrane fuel cell technology can offer very high energy densities and therefore are most suitable to replace or complement batteries for portable power supply or back-up power solutions. Unfortunately, problems like slow electrokinetics of alcohol oxidation in acidic media or high costs for membranes and catalysts are hindering the commercialization of DAFCs [1]. All in all, Direct Methanol Fuel Cell (DMFC), is currently closest to commercialization [2]. In the same way, other alcohols like ethanol [3], ethylene glycol [4] (EG), etc. are interesting alternative fuels under evaluation for DAFC

applications. Regarding the electrocatalytic activity of Pt/C catalyst with respect to alcohol oxidation reaction, recent studies revealed that in alkaline media higher electrocatalytic activities compared to acidic media are achievable. For the specific evaluation of the electrochemical oxidation of methanol (MeOH) and EG over Pt/C catalyst in alkaline media, the increase in activity was manifested in higher current densities and smaller overpotentials compared to those observed in acidic media [5–8]. Besides this improvement on the kinetics of anodic alcohol oxidation reaction (AOR), the kinetics of the oxygen reduction reaction (ORR), occurring at the cathodic side of the DAFC, is also enhanced in alkaline media [9]. Another advantage of Anion-Exchange Membrane Direct Alcohol Fuel Cells (AEM-DAFCs) is the possible employment of

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low-cost and more efficient electrocatalysts for AOR and ORR than Pt [10–12]. Furthermore, in alkaline media ORR electrocatalysts have also demonstrated more tolerance to alcohol crossover, because they are active for ORR but almost inactive for AOR in alkaline media [9,12].

A disadvantage of AEM-DAFCs is the carbonation of the solution by carbon dioxide (CO_2) from the air feed or even from the AOR itself. As a consequence of this process the pH is reduced and loss of reactivity for AOR is detected [13]. Because of this carbonation problem and the lack of a suitable ionomeric binder, most research groups proposed the addition of up to 5 M KOH to the fuel solution in order to maintain a high performance. As a direct result a harsh media supporting membrane degradation is observed [14]. For this reason, the use of an anion conductive polymer as binder was presented as the most promising solution for erasure of highly alkaline fuels [15].

To explain more in detail, in Fig. 1 the functionality of the binder in an AEM-DAFC assembly is shown schematically. The inset SEM picture presents a catalyst layer with a porous binder/catalyst structure being able to support the transport of reactants or products. Other required properties of the binders include the transfer of anions to the membrane and mechanical and chemical stability under working conditions.

In order to avoid the use of Pt electrocatalyst, the use of Palladium as electrocatalyst for AOR in alkaline medium has been proven, showing higher activity and better steady-state behavior than Pt [16–18]. Even more, to improve the activity and stability, diverse Pd-based catalysts including Pd-oxide composite, Pd-based binary and Pd-based ternary catalysts have been investigated by several authors.

In a former study nickel (Ni) or silver (Ag) were combined with palladium (Pd). These bimetallic Pd-based electrocatalysts were tested and according to the results it was concluded that both bimetallic electrocatalysts are suitable alternatives for usage as electrocatalytic material on the anode of anion-exchange membrane based direct ethanol fuel cell [19]. Taking these experimental results into account, in this work the synthesis of carbon supported bimetallic PdNi/C and PdAg/C catalysts with different Pd to metal ratios is described and the further electrochemical evaluation of the methanol and ethylene glycol oxidation in alkaline media over

these electrocatalyst is shown. In this sense, promising results of the electrooxidation of methanol and ethylene glycol will be described and compared to that of Pd/C electrocatalyst. As the elimination of KOH from the fuel is a fundamental issue for further applications of AEM-DAFCs, it is crucial to implement an anion conductive binder in the electrocatalyst layer. Therefore, it is important to remark that in this article the recent results on the development of ionomeric poly(*p*-phenylene oxide) (PPO) based binders for AEM-DAFC applications will be reported.

Experimental

Electrocatalyst preparation

The chemicals used in the preparation were carbon black (Vulcan XC72R, Cabot Cooperation), metal salts (PdCl_2 , Sigma Aldrich; $\text{Pd}(\text{NO}_3)_2$, Sigma Aldrich; AgNO_3 , Sigma Aldrich; NiCl_2 , Sigma Aldrich), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, Sigma Aldrich) and sodium borohydride (NaBH_4 , Sigma Aldrich). All of them were used as received without any further treatment. Solutions were prepared with deionized water.

To synthesize 100 mg of a 20 wt% electrocatalysts, 50 ml aqueous dispersion of 310 mg sodium citrate, 80 mg carbon black and metal precursor salts were prepared by ultrasonification for 30 min. During the dispersion procedure Ar was bubbled through the dispersion. After that, a 2 wt% NaBH_4 solution (freshly prepared) was slowly added to the catalyst precursor dispersion under vigorous stirring in order to reduce the metal salts. Then, the dispersion was stirred for additional 30 min in Ar atmosphere. As next step, the catalyst was filtered and washed with deionized water several times. Finally, the synthesized electrocatalyst was air dried in the fume hood.

Electrocatalyst evaluation

In a conventional three-electrode cell chronoamperometry (CA) and cyclic voltammetry (CV) experiments were conducted to study the electrocatalytic activity of the synthesised anodic materials. The electrolytes used were 0.5 M KOH + 0.5 M ethylene glycol (for the evaluation of ethylene glycol electrooxidation) and 0.5 M KOH + 0.5 M methanol (for testing the electrooxidation of methanol). In both cases Ar was used to deoxygenate the solutions.

A Pt foil of large area was used as a counter electrode and a Hg/HgO electrode (MMO) as reference electrode. The working electrode was a glassy carbon disc (5 mm in diameter with a geometric area of 0.196 cm^2) covered with a thin layer of catalyst. In order to obtain a homogeneous catalyst layer, firstly $2 \mu\text{l}$ of catalyst ink (solvent: ethanol; binder: PTFE) were pipetted on top of the glassy carbon disc. Secondly, the pipetted solution was dried in order to form the desired catalyst layer.

CA tests were carried out at an oxidation potential of $-0.2 V_{\text{MMO}}$ for 1000 s (time required to observe a steady state current). CV evaluations were carried out at 25 mV s^{-1} covering a potential window from -0.8 to $0.3 V_{\text{MMO}}$. All the

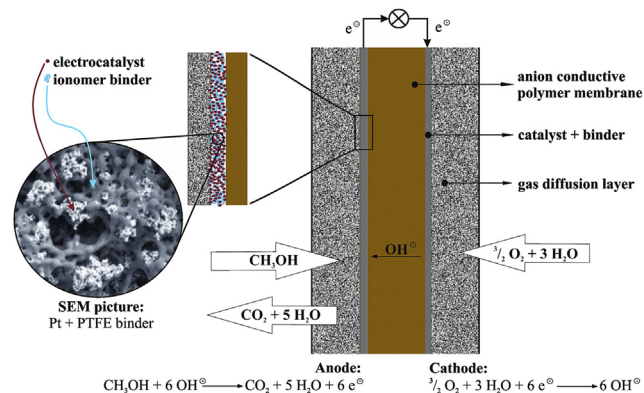


Fig. 1 – Scheme of the AEM-DMFC and the functionality of the binder in the catalyst layer.

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