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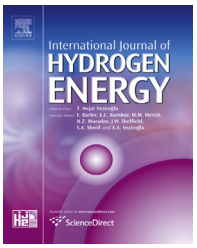

Bimetallic Pd–Mo nanoalloys supported on Vulcan XC-72R carbon as anode catalysts for direct alcohol fuel cell

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ABSTRACT

Vulcan XC-72R carbon supported Pd and Pd–Mo alloys of different Pd:Mo atomic ratios were prepared by hydrothermal synthesis method. The bimetallic nanoalloys were characterized by powder X-ray diffractometry and inductively coupled plasma-atomic emission spectroscopy to determine their crystal structures and elemental compositions. Alloy formation of the nanocatalysts was proven by energy dispersive X-ray spectroscopy line profiles using field emission scanning electron microscopy. The performance of as-prepared nanocatalysts was evaluated for the reactions of methanol, ethanol, ethylene glycol and glycerol electrooxidation in alkaline media by cyclic voltammetry, linear sweep voltammetry and chronoamperometric measurements. It was found that bimetallic Pd–Mo/VC catalysts have higher activity due to different electronic structure as compared to the monometallic palladium. Also, the Pd_3Mo/VC catalyst showed excellent catalytic activity, high durability and stability which indeed propose it to be as a promising electrocatalyst for future direct alcohol fuel cells.

Introduction

Direct alcohol fuel cells (DAFCs) have attracted considerable interest in their application to alternative power sources for portable electronic devices and electric vehicles [1–3]. Liquid fuels, such as low molecular weight alcohols (methanol, ethanol, ethylene glycol and glycerol) have several advantages compared to pure hydrogen, because they can be easy handled, transported and stored. Furthermore, they have relatively high energy conversion efficiency, high mass energy density and low-to-zero pollutant emission, comparable to that of gasoline [4,5]. The electrocatalytic reaction of alcohol oxidation in alkaline media is more facile, allowing to use low catalysts loadings and to select a wide range of catalysts [6–8]. Accordingly, Platinum is an interesting candidate for the alcohols oxidation. High costs of the Pt-based electrocatalysts and susceptibility of the catalysts against poisoning of the CO-like intermediates formed during alcohol oxidation are the main barriers to the commercialization of DAFC technology [9,10]. It is therefore

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desired to develop low cost non-platinum catalysts with comparable or improved kinetics for anodic electrooxidation and better resistance to CO poisoning. Palladium and palladium based alloys have demonstrated high activity in electrooxidation of alcohols in alkaline media, and therefore can be used as less expensive analogs of platinum [11–14]. Furthermore, it has been reported that the addition of non-noble metals to palladium can facilitate and improve alcohol electrooxidation [15–19]. In the field of heterogeneous catalysis, searching for proper support materials is another effective strategy in view of reducing noble metal loading and enhancing catalyst performance. Carbon materials with various structures and shapes, such as carbon nanofibers, active carbon and carbon nanotubes have been used as electrocatalyst supports [20–23]. No materials other than carbon have the essential properties such as electronic conductivity, corrosion resistance, and low cost required for the commercialization of fuel cells. Vulcan XC-72R carbon black (VC) provides excellent conductivity in a range of applications at relatively low loading levels and is typically easier to disperse compared to other conductive grades of carbon black [24]. Inert surface of carbon support requires suitable chemical modification in order to enhance a favorable interaction with catalyst particles such as those of noble metals. One method of chemical modification is functionalization of the carbon surface which can be carried out in both the gas and liquid phases [25,26]. Acid treatment has been shown to introduce oxygen atoms on the carbon surface which can be found as components of surface oxygen complexes or functionalities. On a relative scale, the surface oxygen functionalities such as carboxylic, anhydride, phenolic and carbonyl possess varying degrees of acidic character [27]. It has been well established in the literatures that surface oxygen groups, which form anchoring sites for metallic precursors as well as for metals, determine the properties of activated carbon as a catalyst support material. The acidic groups on the surface decrease the hydrophobicity of the carbon, leading to accessibility of the surface to aqueous metal precursors, while the less acidic groups increase the interaction of the metal precursor or the metal particle with the support and, as a consequence, minimize the sintering propensity of metal on carbon [28].

We outline herein a process for preparing Pd–Mo bimetallic nanoparticles supported on pretreatment Vulcan XC-72R carbon (Pd–Mo/VC) by hydrothermal method. The alloys containing different amounts of Mo were characterized in terms of morphology, crystal structure and chemical components. Pd–Mo alloy catalysts on multiwall carbon nanotubes have been reported previously as catalytically improved anode for methanol oxidation [29]. In this work, the performance of Pd–Mo alloy catalysts on VC was evaluated by cyclic voltammetry and chronoamperometric measurements for the reactions of methanol, ethanol, ethylene glycol and glycerol electrooxidation in alkaline media.

Material and methods

Chemicals

Vulcan XC-72R carbon powder (VC) was purchased from Cabot Corporation (USA). Palladium (II) acetate ($Pd(CH_3COO)_2$), ammonium molybdate ($(NH_4)_2MoO_4$), methanol, ethanol, glycerol, ethylene glycol (EG) and sodium citrate were purchased from Merck (Darmstadt, Germany)).

Apparatus

Product X-ray diffraction (XRD) data was recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K_α radiation. The morphology and composition of the as-prepared nanocatalysts were analyzed with field emission scanning electron microscope (FESEM) (CARL ZEISS-AURIGA 60 microscope, Jena, Germany) which was equipped with an energy-dispersive X-ray analyzer (EDX). All electrochemical measurements were carried out with an Autolab potentiostat/galvanostat (PGSTAT 101, Eco Chemie, Netherlands). The experimental conditions were controlled with Nova 2.0 software. A conventional three-electrode cell was used at 22 ± 1 °C. An Ag/AgCl/KClstd (3.0 M) electrode and a platinum wire were used as the reference and auxiliary electrodes, respectively.

Preparation of pretreated Vulcan XC-72R

Vulcan XC-72R carbon was chemically treatment to synthesize nanoparticles with the best distribution and size and, as a consequence, to maximize catalytic activity. The chemical pretreatment of Vulcan XC-72R carbon powder was carried out using Senthil Kumar method [20]. 1 g carbon powder was dispersed in a round bottom flask with 1000 mL of 5% nitric acid, 0.07 M phosphoric acid and 0.2 M potassium hydroxide in the deionized water. The mixture was refluxed for 16 h at 120 °C. Treated VC was filtered and washed several times with a continuous flow of deionized water to obtain neutral pH and then dried in vacuo at 110 °C for 12 h.

Table 1 – Data of ICP-AES and EDX compositional analyses.

Sample	Loading amount (mg)			Yield (wt.%) (ICP-AES) Pd:Mo	Atomic % (ICP-AES)	Total content wt% (ICP-AES)	Average atomic % (FESEM-EDX)
	OAc salts of		Carbon support				
	Pd	Mo					
Pd/VC	42.19	–	80.00	19.72	100:0	18.28	–
Pd-black	–	–	–	98.91	–		–
Pd_3Mo	42.19	12.28	104.04	13.65:5.28	72.6:27.4	18.93	76.6:23.4
PdMo	42.19	36.84	152.12	9.48:10.39	50.3:49.7	19.87	52.2:47.8
$PdMo_3$	42.19	110.52	296.40	4.08:14.10	25.9:74.1	18.18	25.2:74.8

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