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Comparative electrocatalytic oxidation of ethanol, ethylene glycol and glycerol in alkaline medium at Pd-decorated FeCo@Fe/C core-shell nanocatalysts

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ABSTRACT

Electrocatalytic oxidation of alcohols in alkaline solutions is critical for the development of direct alkaline alcohol fuel cells (DAAFCs). This work investigated alcohol oxidation reaction (AOR) at a novel palladium-based core-shell nano catalyst (FeCo@Fe@Pd/C) obtained by the microwave-induced top-down nanostructuring and decoration (MITNAD) synthetic strategy. The electrocatalytic properties of the FeCo@Fe@Pd/C towards the oxidation of ethanol (EtOH), ethylene glycol (EG) and glycerol (Gly) were explored, and compared with those of the Pd/C alone. FeCo@Fe@Pd/C exhibited a remarkable performance in all three alcohols but its best electrocatalytic activity was found in the oxidation of EG where the electrocatalytic rate constant (K_{cat}) was about 2 times faster than seen in Gly and ≈ 4 times faster than in EtOH. The excellent performance towards EG was further corroborated by the low resistance to charge transport. Detailed comparison with literature reports shows that the FeCo@Fe@Pd/C is a potentially viable nanocatalyst for use in DAAFC.

1. Introduction

Direct alkaline alcohol fuel cells (DAAFC) represents one of the most promising renewable and clean energy devices found in portable, stationary and e-mobility applications. Among the alcohols used in DAAFCs, ethanol (EtOH) stands out for its many advantages such as lower toxicity, higher energy density (theoretical energy density of 8 $kWh^{-1}kg$). EtOH can be produced in large quantities by fermentation of sugar and/or cellulose containing raw materials [1–4]. Also, the polyhydric alcohols such as ethylene glycol (EG) and glycerol (Gly) have been appearing as preferable alternatives as Fuels in DAAFCs. These volatile liquids (boiling points: 198 °C–EG; 290 °C–Gly) are electrochemically oxidizable [5,6]. They display relatively high theoretical energy density (5.2 $kWhkg^{-1}$ and 5.0 $kWhkg^{-1}$ for EG and Gly, respectively). Furthermore, they are biomass-derived fuel cells. Gly is obtained from methanolysis of vegetable oils while EG is from oxidation of ethylene, thus they can be produced in renewable and environmentally friendly ways [7–9].

A number of studies have been devoted to Pd-based catalysts for the electrooxidation of alcohols in alkaline medium [10]. In comparison with monometallic Pd nanostructures, Pd-based alloy nanostructures show enhanced electrocatalytic activities. As a result, a lot of Pd-based alloy nanoparticles have been successfully prepared [11,12]. The binary systems have been quite popular; Simoes et al. [7] demonstrated the higher catalytic activities of the PdAu and PdNi alloys in the electrooxidation of glycerol over the Pd alone. Shen et al. [13] also used the latter alloy combination for ethanol oxidation and found it a promising anode catalyst for alkaline direct ethanol fuel cell (DAEFCs). Su et al. [14] showed that Pd/TiO_2 nanofibres had excellent catalytic activity for glycerol, ethylene glycol and propane 1, 2- diol, with glycerol giving the highest activity. A high potential was found to remove poisoning species. Multi-metallic Pd-based alloys have also been widely explored and have found to have great advantages as catalysts in fuel cells [15–17].

A class of promising catalysts for fuel cells applications is nanoalloys with core-shells structures, a core-shell structure being the relative enrichment of a shell by one metal than another. It could also come in the form of a pure-shell, mixed-core structure [18]. Core-shell catalysts are an attractive target of catalytic research due to their enhancing properties to substrate oxidation, such as selectivity, activity and chemical/physical stability. Core-shells are also a way of obtaining unique structures and applications via combination of characteristics of the components that are not available with their single component counterparts [19,20]. Some of the reasons for coating a core or core-shell nanoparticle with a

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precious metal such as Pd are to improve the stability, and reduce the consumption of precious materials. Some very remarkable electrocatalytic improvements have been observed in recent studies with core shell catalysts relative to their bulk monometallic counterpart [21–23].

Wang and Johnson [24] did some extensive studies on the general trends of core-shell preferences in transition metals in binary alloy particles using the density functional theory. It was discovered that core-shell preferences from segregation energies are described largely by only two independent key factors - the *Cohesive energy* and the *Wigner-Seitz radius* (atomic size), and the interplay between them. For core-shell nanoparticles formed from different groups, the metal with the largest cohesive energy (the primary factor) goes into the core. For core-shell nanoparticles formed by atoms within a group, the metal with the smallest Wigner-Seitz radius (the secondary factor) determines core-shell preference, where the smallest atom goes into the core to relieve compressive strain. Some exceptions were found for systems composed of 4d and 5d components, which are then dominated by cohesive energy, as the difference between the radii is too small. Core-shell structures containing inexpensive non noble core surrounded by a noble metal shell can bring about further improvements in producing low- cost catalysts for fuel cell applications. Ideally, only the noble catalytic material is located at the surface, where the reactions take place and the reaction rate should not suffer as a result if the inactive core.

Based on the above principle, a novel ternary Pd-based nanocatalysts has been synthesized with an inner Fe-based alloy core, FeCo@Fe/C (a core-shell structure) decorated with a Pd shell, FeCo@Fe@Pd/C, using a facile technique we called *“microwave-induced top-down nanostructuring and decoration”* (abbreviated as ‘MITNAD’). The MITNAD synthetic strategy simply involves the use of fast microwave irradiation for a one-step top-down nanosizing of large-sized soft magnetic FeCo@Fe/C core-shell material (0.21–1.5 μm) to sub-10 nm sized Pd-decorated structure, FeCo@Fe@Pd/C (*ca.* 3–7 nm). Considering that for practical applications, core-shell nanocatalysts with sub-10 nm sizes are preferred [25], the FeCo@Fe@Pd/C could serve as a viable electrocatalyst for the oxidation of small organic molecules such as alcohols. In this work, we studied the electrocatalytic properties of this novel core-shell nano catalyst for EtOH, EG and Gly electrooxidation in alkaline medium. The results obtained, compared with literature show that the FeCo@Fe@Pd/C nanocatalysts is an effective catalyst in DAAFCs especially in direct ethylene glycol fuel cells (DEGFCs).

2. Experimental

2.1. Synthesis of Pd-coated FeCo@Fe/C core-shell nanocatalysts

The Pd-coated FeCo@Fe/C core-shell nanoparticles (FeCo@Fe@Pd/C) were prepared as we recently reported [26,27]. Briefly stated, the FeCo/C was first obtained by simple reduction method using chloride salts solutions of Co and Fe (equimolar mixture) dispersed in Vulcan XC-72 carbon. The suspension was ultrasonicated for about 30 min, and then subjected to heating under continuous magnetic stirring until the solvent was completely evaporated to give smooth, thick slurry. The slurry was oven-dried at 60 °C, and then ground in an agate mortar to give a fine dark and free-flowing powder. The obtained FeCo/C powder was heated in a tube furnace at 300 °C under flowing H_2/Ar for 2 h, and then annealed at 500 °C for 2 h, and then cooled to room temperature under Ar atmosphere to achieve the core-shell structure (FeCo@Fe/C). The FeCo@Fe@Pd/C was obtained from the mixture of the as-prepared FeCo@Fe/C and $PdCl_2$ (1:3mole ratio) in ethylene glycol solution containing polyvinylpyrolidone and subjected to rapid microwave irradiation (using the Anton Parr Synthos 3000 microwave reactor) at 500 W, 80 bars, and ~198 °C for 15 minutes. The resulting product was repeatedly washed with acetone and deionised water to remove traces of ethylene glycol and other impurities, and then dried at 100 °C. For comparison, Pd/C nanoparticles of same mass loading as the core-shell were also synthesized using the same microwave procedure. Due to its larger cohesive energy (4.5 eV) and a smaller atomic size (1.40 Å), Co will prefer the core region while Fe (4.3 eV and 1.47 Å) will migrate to the surface forming the shell, giving rise to the FeCo@Fe/C alloy. The primary factor for core shell preferences, cohesive energy, also comes into play between the Fe and Pd atoms. Pd with a smaller cohesive energy (3.5 eV) will prefer the shell while Fe with a larger cohesive energy will occupy the core of the catalyst, thus forming the Pd-decorated core-shell FeCo@Fe@Pd/C.

2.2. Equipment and procedure

The Pd/C, FeCo@Fe/C and FeCo@Fe@Pd/C were thoroughly characterized using XRD (PANalytical X’Pert powder diffractometer with Co Kα radiation), HRTEM and selected area electron diffraction (SAED) (Tecnai F-20 instrument equipped with Gatan HAADF-STEM operated at an accelerating voltage of 200 kV, Gun extraction voltage was 4500 V). Energy dispersive spectroscopy (EDS) line scan was also performed using this instrument in the STEM mode. Samples for TEM analysis were prepared by dispersing the nanoparticles in methanol, sonicating for 1 min in order to ensure adequate dispersion of the nanostructures, evaporating one drop of the solution onto 300 mesh Cu grid, coated with a lacey carbon film. SEM images were obtained utilizing a field emission scanning electron microscope (FESEM Zeiss-Leo DSM982). All electrochemical experiments were carried out at room temperature with a conventional three-electrode configuration using an Autolab potentiostat PGSTAT 100 (Eco Chemie, Utrecht, Netherlands) driven by the General Purpose Electrochemical Systems data processing software (GPES and FRA software version 4.9). The working electrode was a modified glassy carbon disk electrode (GCE, Autolab Netherlands, diameter = 3.0 mm). A Pt rod and Ag|AgCl, saturated (3 M KCl) were used as a counter and reference electrode, respectively. Electrochemical impedance spectroscopy (EIS) measurements were performed with Autolab Frequency Response Analyser (FRA) software between 100 kHz and 10 mHz with the amplitude (rms value) of the AC signal of 10 mV. All solutions were de-aerated by bubbling pure nitrogen prior to each electrochemical experiment. Before each measurement the GCE was polished to a mirror finish using Alumina slurry (nanopowder Aldrich) and then cleaned by ultrasonic stirring in ethanol and acetone for 3 min, respectively. To prepare the catalyst ink, 1.0 mg of the nanoparticle was dispersed in 1.0 ml of ethanol containing 100 μL of 5% Nafion solution (DuPont). The mixture was ultrasonicated for about 3 min to make a uniform ink. The GCE was modified by dropping 6 μL of the catalyst ink on its surface and allowing it to dry in an oven at about 60 °C. The Pd loading on each electrode was maintained at 1.3 ± 1 μg. Every electrochemical experiment on methanol oxidation was performed in high purity N_2 saturated KOH or KOH containing methanol solutions. The Cyclic voltammetry (CV) and Linear sweep voltammetry (LSV) tests were performed from 0.4 V to -0.1 V (vs. Ag/AgCl, KCl) on the catalysts in high purity N_2 saturated 0.1 M KOH. Chronoamperometry tests were performed for up to 1200seconds at a constant voltage of -0.2 V (vs. Ag/AgCl, KCl). Solutions of 0.5 M C_2H_5OH in 0.5 M KOH, 0.5 M $C_2H_4(OH)_2$ in 0.5 M KOH and $C_3H_5(OH)_3$ in 0.5 M KOH were used as electrolyte solutions. Electrochemical measurements were performed after degassing the solutions with high ultra-pure N_2 gas.