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Supported Pt, Pd and Au nanoparticle anode catalysts for anion-exchange membrane fuel cells with glycerol and crude glycerol fuels

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ABSTRACT

Carbon supported Pt, Pd, and Au nanoparticles (NPs) catalysts with small diameters (2.4–3.5 nm) were prepared through a solution-phase reduction method, and applied as the model catalysts for electro-oxidation of both high-purity glycerol and biodiesel-derived crude glycerol. The half cell investigations showed that Pt/C has the highest activity in the low potential range, which can be further facilitated at elevated temperatures. The anion-exchange membrane fuel cells (AEMFCs) investigations demonstrated no obvious drop in peak power density on Pt/C anode, when the fuel was switched from high-purity glycerol to crude glycerol, indicating a good stability of the Pt/C against poisoning/deactivation from the impurities in crude glycerol. The tests also showed that on all these three model catalysts, a volcano-type relationship exists between the fuel cell performance and crude glycerol concentration at a fixed KOH concentration, while with a given crude glycerol concentration, the performance monotonically increased with the KOH concentration increasing. The highest performances were achieved with 6.0 M KOH + 1.0 M crude glycerol at 80 °C, which are 184.2, 93.9, and 50.1 $\mathrm{mW\,cm^{-2}}$ on Pt/C, Pd/C, and Au/C anodes, respectively.

1. Introduction

The energy crisis rising from the depletion of fossil fuels has been growing up to an unavoidable concern that significantly affects the growth of the economy and the sustainability of humanity [1–4]. In 2011, the world consumed a total energy of 12274.6 million tonnes oil equivalent, 87% of which are supplied by fossil fuels [5]. The demand of energy lays a heavy burden on the dwindling petroleum resources, and raises the current crude oil price 5-fold higher than that in 1990s [6]. In addition, the current main stream energy device, internal combustion engine, is not only struggling with low efficiency (<13%) [7], but also devastating the natural environment by emitting pollutants (NO_x, SO_x, and CO) and greenhouse gas (CO_2) far more than that can be recovered in atmosphere [8]. The large concerns associated with the economy, environment, and sustainability, greatly spurred the development of more renewable energy resources and more efficient energy conversion techniques [9–11].

Recently, direct alcohol fuel cells (DAFCs) have been recognized as a promising alternative electrical power generation device to meet the humanity's energy demands [12–14]. Compared to H_2 fuel, liquid alcohol fuels are easy to store and transport, and can be derived from annually renewable biomass feedstocks. In a DAFC, the chemical energy stored in the fuel is directly converted into electrical energy without the limitation of Carnot's theorem. Therefore, the theoretical efficiency is usually >90% [15,16]. In an anion-exchange membrane – direct alcohol fuel cell, the cell performance is further improved as both the anode and cathode reactions are significantly enhanced by the better mass transfer and lower adsorption of spectator charged species [17]. In addition, the products of an AEM-DAFC remain in the aqueous solution, with zero environmental impact. Numerous studies have been carried out in anion-exchange membrane fuel cells (AEMFCs) with different biorenewable alcohol fuels, including methanol [18–21], ethanol [22–24], ethylene glycerol [25,26], and glycerol [16,27–32]. Recently, Prakash et al. reported a peak power density of 168 $\mathrm{mW\,cm^{-2}}$ on a methanol-fed PtRu anode (3 $\mathrm{mg_{PtRu}\,cm^{-2}}$) AEMFC at 90 °C [20]. Bianchini et al. also observed a peak power density of 160 $\mathrm{mW\,cm^{-2}}$ on an ethanol-fed Pd-(Ni-Zn-P)/C anode (1 $\mathrm{mg_{Pd}\,cm^{-2}}$) AEMFC at 80 °C [33]. However, the toxicity of methanol and high volatility of ethanol, along with their low flash points remain critical issues before their wide application in AMEFCs.

Glycerol has attracted great research interests as a non-toxic, non-volatile, and non-flammable biorenewable alcohol fuel.

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Different from biomethanol and bioethanol, which are obtained from the microorganism fermentation process of biomass, biomass derived glycerol is mainly obtained as a waste byproduct in the production of biodiesel via a transesterification reaction [34]. As a result, biodiesel derived glycerol now can be obtained at relatively lower market price (0.74–0.89 US$ gal^{-1} for crude glycerol, vs. 1.34 US$ gal^{-1} for methanol and 3.15 US$ gal^{-1} for ethanol). In addition, with the highly active triol structure, glycerol demonstrates a high volumetric energy density of 6.4 KWh L^{-1} [16,31]. Various studies have been carried out in the electro-oxidation of glycerol on Pt, Pd, and Au based catalysts. In AEMFC studies, Matsuoka et al. first reported a peak power density of ~7 mW cm^{-2} at 50 °C, using PtRu as the anode catalyst [27]. Ilie at al. investigated the membrane electrode assembly (MEA) fabrication methods and reaction condition (fuel concentration, flow rate, etc.) and obtained an optimized peak power density of ~24 mW cm^{-2} with Pt and Pt-based bimetallic anode catalysts at 60 °C [30]. Bianchini's group reported peak power densities of ~79 and 118 mW cm^{-2} on Pd/CNT [28] and Pd-(Ni-Zn-P)/C [29] anode catalysts, respectively. Recently, based on a simple nanocapsule method, our group successfully prepared highly active Pt/C and Au/C catalyst, and demonstrated exciting peak power densities of ~125 and 58 mW cm^{-2} on Pt/C and Au/C anode AEMFCs[16,31,32]. However, all of these studies were based on the high price petrochemical derived high purity glycerol (99.8%, usually ~40 US$ L^{-1} or ~150 US$ gal^{-1} from the main chemical suppliers). As the purification of crude glycerol is prohibitively expensive [35], it is usually sold with many impurities, including methanol, fatty acids (usually in the form of soaps), transesterification catalysts residues (as ash content), a variety of element such as K, Ca, Mg, Hg, P, S, As, etc. (as both dissolved and undissolved salts) [36]. Due to the concerns about the contamination and poisoning of these impurities to the fuel cell system, little investigation has been performed on the AEMFC with direct crude glycerol fuels. To directly utilize crude glycerol as a fuel for the AEMFCs, there is a clear need to first investigate the intrinsic activity of monometallic Pt, Pd, and Au catalysts toward glycerol oxidation and demonstrate their performances as the anode catalysts with crude glycerol fuel, so as to further develop more efficient multi-metallic catalysts.

In the present work, a simple organic solution-phase reduction method [37–39] was applied to prepare the carbon supported Pt, Pd, and Au nanoparticle as the model catalysts. The catalytic activities of these as-prepared catalysts toward glycerol electro-oxidation were first compared in half cell at different temperature. Based on the half cell test results, these catalysts were further applied as the anode catalysts in AEMFCs. The effects on the performance with soybean biodiesel derived crude glycerol were evaluated at 80 °C. It is demonstrated that Pt/C anode AEMFC holds the highest performance with high purity glycerol fuel, which also shows no obvious performance loss when switching to crude glycerol fuel. Fed with 6.0 M KOH + 1.0 M crude glycerol, the peak power density on Pt/C anode AEMFC can reach 184.2 mW cm^{-2}, while that on Pd/C and Au/C anode AEMFCs can also reach 93.9 and 50.1 mW cm^{-2}.

2. Experimental

2.1. Chemicals

$Pt(acac)_2$, $Pd(acac)_2$, $LiBEt_3H$ (1 M in THF), 1-octadecene, and benzyl ether were purchased from Acros Organics. Oleylamine is purchased from Aldrich Chemistry. Oleic acid and high purity glycerol (99.8%) were purchased from Fisher Chemical. $AuCl_3$ was purchased from Alfa Aesar. Crude glycerol (88%, a byproduct from soy biodiesel manufacturing) was obtained from Kingdom Bio Solutions Inc. All the chemicals were used as purchased without further purification.

2.2. Preparation of Pt/C, Pd/C, and Au/C catalysts

All catalysts were synthesized through a modified organic solution phase reduction method [15,31,32,40]. For the preparation of Pt/C (40 wt%), 196.7 mg of $Pt(acac)_2$ (0.5 mmol), 200 μL of oleylamine, and 200 μL of oleic acid were first dissolved in a mixture of 146.3 mg Vulcan XC-72R carbon black and 40 mL of benzyl ether at 60 °C under a N_2 protection. As the temperature was increased to 120 °C, 1.0 mL of $LiBEt_3H$ was quickly injected into the system. The temperature was held for 30 min, and then slowly increased to 180 °C and held for an additional 30 min. Pd/C (40 wt%) was prepared through a similar procedure. 152.3 mg of $Pd(acac)_2$ (0.5 mmol) and 79.8 mg of carbon black were mixed in 40 mL benzyl ether solvent, and was rapidly heated to 100 °C in a N_2 atmosphere. As the temperature reached 100 °C, 200 μL of oleylamine and 200 μL of oleic acid were injected into the system, followed by quick injection of 1.0 mL $LiBEt_3H$. The temperature was held for 20 min, and then slowly raised to 180 °C and held for an additional 30 min. To prepare Au/C (40 wt%), 151.7 mg of $AuCl_3$ (0.5 mmol) was mixed with 16 mL of 1-octadecene and 4 mL of oleylamine under a nitrogen blanket. The system was then rapidly heated to 80 °C, subsequently followed by a quick injection of 1.5 mL $LiBEt_3H$. After holding the temperature for 10 min, the solution was cooled down to room temperature and mixed with 148.0 mg of carbon black. All the final products were collected by filtration, washed with copious ethanol, and dried in vacuum oven at 50 °C overnight.

2.3. Physical characterizations

The morphology, nanostructure and metal loading of the catalysts were analyzed by transmission electron microscopy (TEM), X-ray diffraction (XRD), and induced couple plasma-atomic emission spectroscopy (ICP-AES). The TEM characterizations were performed on a JEOL JEM-4000FX with an operation voltage of 200 kV. The XRD patterns were collected on a Scintag XDS-2000 θ/θ Diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å), with a tube current of 35 mA and a tube voltage of 45 kV. The ICP-AES was performed after dissolving 10 mg of the catalyst into freshly prepared aqua regia (a strong corrosive acid formed by mixing concentrated nitric acid and hydrochloric acid with the volume ratio of 1:3), in order to analyze the metal loading.

2.4. Half cell tests

Half cell tests were conducted in a conventional three-electrode-cell setup (electrolyte cell AFCELL3, Pine Instrument), with a glassy carbon working electrode, a Hg/HgO/1.0 M KOH electrode, and a Pt wire counter electrode. The cell is covered by a water jacket, which enables the system to be thermostated at 25, 50, or 60 °C during the test. Prior to tests, all the electrolytes were deaerated by purging with high purity N_2 for 30 min. All potentials in the present study were given vs. Hg/HgO/1.0 M KOH electrode (0.140 V vs. NHE) [41] unless otherwise mentioned. Before each test, 2.0 mg of catalyst was dispersed in 1.0 mL of isopropanol by bath ultrasonication until no aggregation was visible to the eye. The working electrode was prepared by dropping 20 μL of the ink on the glassy carbon electrode, which yielded a catalyst loading of ~40 μg_{metal} cm^{-2}. 10 μL of 0.05 wt% AS4 (Tokuyama) ionomer solution was added on top to affix the catalyst. A 10-cycle cyclic voltammetry (CV) test was performed on each catalyst in 1.0 M KOH with a sweep rate of 50 mV s^{-1}, 25 °C. The stable polarization curve obtained from the last cycle was used to calculate the electrochemical surface area (ECSA). For Pt/C catalyst, the ECSA was evaluated based on hydrogen desorption peak with the Pt pseudo-capacity of 0.210 mC cm^{-2}. The ECSA of Pd/C was obtained from the PdO reduction peak to avoid the multilayer hydrogen adsorption/absorption