Carbon supported Ag nanoparticles with different particle size as cathode catalysts for anion exchange membrane direct glycerol fuel cells

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Abstract
The effect of Ag particle size on oxygen reduction reaction (ORR) at the cathode was investigated in anion exchange membrane direct glycerol fuel cells (AEM-DGFC) with oxygen as an oxidant. At the anode, high purity glycerol (99.8 wt%) or crude glycerol (88 wt%, from soybean biodiesel) was used as fuel, and commercial Pt/C served as the anode catalyst. A solution phase-based nanocapsule synthesis method was successfully developed to prepare the non-precious Ag/C cathode catalyst, with LiBEt3H as a reducing agent. XRD and TEM characterizations show that as-synthesized Ag nanoparticles (NP) with a size of 2–9 nm are well dispersed on the Vulcan XC-72 carbon black support. Commercial Ag nanoparticles with a size of 20–40 nm were also supported on carbon black as a control sample. The results show that higher peak power density was obtained in AEM-DGFC employing an Ag-NP catalyst with smaller particle size: nanocapsule made Ag-NP > commercial Ag-NP (Alfa Aesar, 99.9%). With the nanocapsule Ag-NP cathode catalyst, the peak power density and open circuit voltage (OCV) of AEM-DGFC with high-purity glycerol at 80 °C are 86 mW cm⁻² and 0.73 V, respectively. These are much higher than 45 mW cm⁻² and 0.68 V for the AEM-DGFC with the commercial Ag/C cathode catalyst, which can be attributed to the enhanced kinetics and reduced internal resistance. Directly fed with crude glycerol, the AEM-DGFC with the nanocapsule Ag-NP cathode catalyst shows an encouraging peak power density of 66 mW cm⁻², which shows great potential of direct use of biodiesel waste fuel for electricity generation.

1. Introduction

The liquid alkaline fuel cells (AFCs) were one of the earliest fuel cell models that were developed in the beginning of the 1960s [1]. Because of the high output, current density and low cost of AFCs, extensive studies had been made during the 1960s to 1980s [2]. Although their popularity had been challenged by other types of fuel cells in recent years, particularly proton-exchange membrane fuel cells (PEMFCs), the resurgence of AFCs started with recent technology advances in solid anion exchange membranes (AEMs). The introduction of AEMs has brought several significant advantages over traditional AFCs and other acidic fuel cells, such as enhanced catalyst stability with negligible electro-kinetic performance losses, reduced corrosion problems associated with acid electrolyte, toleration of cheaper metal current collectors, no precipitated carbonate caused by mobile cations, reduced alcohol fuel crossover and the improvement in elimination of electrolyte leakage [2–5].

In an alkaline media, the electrocatalyst activity is higher than that in the acid media due to enhanced ion transport and facile charge transfer [6,7]. In addition, the poisoning effects on catalysts are also weak, and a wider range of metals are stable in an alkaline environment; thus, non-Platinum group metals can be used as electrocatalysts [6,7]. Ag has been found a promising cathode catalyst for a long time, because Ag shows high oxygen reduction reaction (ORR) activity at high pH, and a relatively high stability in a wide range of temperatures [8]. Furthermore, in an alkaline environment, the ORR activity on Ag is close to that on Pt [9,10]; however, the price of Ag is 100 times lower than precious metals, such as Pt and Pd. These merits make Ag a very attractive cathode catalyst. Ag-based electrocatalysts have attracted enormous research interest as an alternative to Pt for ORR in alkaline media [7,11–13]. Blizanac and co-workers have demonstrated that on Ag (111) single crystal, the ORR proceeds via a 4-electron-transfer pathway in high pH
biofuel cell can completely oxidize glycerol to CO₂, their very low performance limits their applications to environmental remediation areas. There is still room for improvement for glycerol/O₂ fuel cell techniques by increasing the performance, reducing the amount of precious metal in the electrodes, and operating fuel cells directly fed with crude glycerol fuel.

In this article, we focused on the investigation of glycerol/O₂ AEM-DGFC using Ag/C cathode catalyst with two different particle sizes. Separated anode and cathode polarization curves were collected for the study of glycerol oxidation at the anode and oxygen reduction at the cathode. Electrochemical impedance spectroscopy was also used to analyze the reaction kinetics and internal resistance. Both high-purity glycerol (99.8 wt%) and industrial grade crude glycerol (88 wt%) were used as fuel, and considerable output power density was achieved using the crude glycerol under the test conditions.

2. Experimental

2.1. Synthesis of Ag/C catalysts with different particle size

The smaller size Ag/C catalyst with a metal loading of ca. 40 wt% was synthesized through a modified solution phase-based nanocapsule method [23,26–28]. Briefly, 83.5 mg silver acetate (0.5 mmol, Acros Organics, 99%) and 81.0 mg Vulcan XC-72R carbon black (Cabot) were mixed in 10 ml oleylamine (Aldrich Chemistry, 70%) with vigorous stirring in an inert nitrogen atmosphere. The temperature was kept at 30 °C while 0.7 ml LiBEt₃H (1.0 M THF solution, Acros Organics) was injected into the solution. After kept the temperature for an additional 30 min, the final product (named as Ag/C-nanocapsule) was collected by filtration, washed with 800 ml ethanol, and dried overnight in a vacuum oven. For comparison, larger size Ag/C sample was obtained by impregnation method. In detail, 105 mg Vulcan XC-72R carbon black (Cabot) was dispersed in ethanol by sonication, and then, the carbon black was impregnated overnight with 70 mg of commercial Ag particles (Alfa Aesar, 99.9%) dispersed in hexane. After filtration, washing and overnight vacuum drying, the product marked as Ag/C-commercial was obtained.

2.2. Analysis of catalyst structures

The morphology, structure, and metal loading of Ag/C catalysts were analyzed by X-ray diffraction (XRD, Scintag XDS-2000, Cu Kα radiation, λ = 1.5406 Å, tube current of 35 mA, tube voltage of 45 kV, 2θ angles between 15° and 90°), transmission electron microscopy (TEM, JEOL 2010, operation voltage of 45 kV, 2θ angles between 15° and 90°), transmission electron microscopy (TEM, JEOL 2010, operation voltage of 200 kV) and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.3. Membrane electrode assembly (MEA) fabrication and single fuel cell test

The MEAs were fabricated with a commercial Pt/C-based anode and a self-made Ag/C-based cathode. The cathode catalyst ink was prepared by mixing Ag/C catalyst and AS-4 anion conductive ionomer (30 wt%, AS-4, Tokuyama) with 1-propanol as solvent. The mass ratio of Ag/C and AS-4 was 7:3. Similarly, the anode catalyst ink was prepared as follows: commercial Pt/C powder dispersed in iso-propanol containing 10 wt% polytetrafluoroethylene (PTFE), was used as hydrophobic agent that gave a good mechanical stability of the active layer and also prevented the electrode from being flooded by the electrolyte during operation [29]. The mass ratio of Pt/C and PTFE was 9:1. Subsequently, the cathode catalyst ink was sprayed directly onto the anion exchange membrane (A201, BioCel, 50 mV cm⁻² at room temperature [25]. Although enzymatic
28 μm, Tokuyama) with loadings of 1 mgAg cm\(^{-2}\), and the anode catalyst was sprayed onto the carbon cloth (PTFE-treated, Fuel Cell Store) with loadings of 1.0 mgPt cm\(^{-2}\). The final MEA was fabricated by mechanically sandwiching the cathode gas diffusion layer (SGL Carbon 25CC), the anion exchange membrane with cathode catalyst and the carbon cloth with anode catalyst. After fabrication, the MEA was mounted in the fuel cell hardware, to which high purity glycerol (99.8 wt%) and 100% humidified O\(_2\) gas were supplied. A crude glycerol (88 wt%, directly obtained from soybean biodiesel production) was also directly used as anode fuel. The MEA was activated at 0.1 V until the current density got stable, and after that the polarization (\(I–V\)) curve was collected.

### 2.4. Electrochemical impedance spectroscopy (EIS) measurement

To measure the electrochemical behavior of MEAs with different sizes of Ag catalysts, the electrochemical impedance spectroscopy (EIS) was employed. A small AC signal was generated from the frequency analyzer and then applied to an electronic load to manipulate the DC load current. The current and voltage provided a connection between the electronic load and the fuel cell in order to monitor the current and voltage responses. Those AC voltage and current outputs from fuel cell were analyzed by the frequency response analyzer (880 impedance analyzer, Scribner-Associates, USA). The scheme of EIS set-up is illustrated in Fig. 1. In the test, the frequency of AC signal was varied from 10 mHz to 10 kHz, with amplitude of 5% DC current.

### 3. Results and discussion

The crystalline structure of two different particle sizes Ag/C catalysts (Ag/C-nanocapsule and Ag/C-commercial) was investigated by X-ray diffraction (XRD), as shown in Fig. 2. All of these diffraction patterns exhibit the characteristic peaks of the planes (111), (200), (220), (311) and (222) at 2\(\theta\) angles of 39\(^\circ\), 44\(^\circ\), 65\(^\circ\), 77\(^\circ\) and 83\(^\circ\), respectively. These numbers are assigned to the face centered cubic (fcc) crystalline structure of Ag (JCPDS card, 04-0783). It also indicates that Ag is in metallic state, because no characteristic peaks of silver oxide were found in their XRD patterns. The Debye–Sherrer equation (Equation (1)) was used to estimate the average crystal grain size, where \(\tau\) is the mean size of the ordered (crystalline) domains, \(\lambda_0\) is the X-ray wavelength (1.5406 Å), \(\beta\) is the line broadening at half the maximum intensity (FWHM) in radians, \(\theta\) is the Bragg angle and \(K\) is the shape factor (typical \(K\) value of 0.9 is used in here). From the calculation based on (220) peak, the particle sizes of Ag/C-nanocapsule and Ag/C-commercial are 4.2 nm and 29.0 nm, respectively.

\[
\tau = \frac{K\lambda_0}{\beta \cos \theta}
\]

The morphology of as-synthesized catalysts was characterized by TEM. Images of Ag/C-nanocapsule and Ag/C-commercial catalysts are shown in Fig. 3(a) and (c). It is easy to note that the Ag particles are well dispersed on the surface of carbon black in the Ag/C-nanocapsule, and the particle size of Ag/C-nanocapsule is much smaller than that of Ag/C-commercial. The Ag/C-commercial is not only poor dispersed but also has a larger particle size. The corresponding particle size histograms evaluated from 100 random particles in an arbitrarily chosen area are shown in Fig. 3(b) and (d). The mean particle size of Ag/C-nanocapsule catalyst and commercial Ag nanoparticles are 5.4 nm and 27.4 nm, respectively, which agrees well with XRD results.

The polarization (\(I–V\)) and current density-power density curves of glycerol–O\(_2\) AEM-DGFC are shown in Fig. 4(a). The cell operating temperature was set at 80 °C in order to facilitate the reaction kinetics and fuel diffusion [32]. From the \(I–V\) curve, it is observed that the open circuit voltages of the fuel cells with different cathode catalysts are 0.73 V (Ag/C-nanocapsule) and 0.68 V (Ag/C-
commercial), respectively. Due to higher reaction rates and better oxygen diffusion, the peak power density of 86 mW cm\(^{-2}\) is achieved at the Ag/C-nanocapsule cathode-based AEMFC. By using the Ag/C-commercial as the cathode catalyst, the peak power density of AEMFC is only 45 mW cm\(^{-2}\). Based on the analysis of the \(I-V\) curve, the fuel cell with Ag/C-nanocapsule cathode has over-performed the one with Ag/C-commercial cathode in both the kinetic dominated regime (current density is \(<50\) mA cm\(^{-2}\)) and the ohmic resistance controlled regime (\(>50\) mA cm\(^{-2}\)), which implies that higher activity and less performance loss due to the resistance to ionic current\[33\] were achieved on the Ag/C-nanocapsule catalyst. There’s no obvious transport controlled regime on the \(I-V\) curve, and the possible reason is that both fuel cells cannot reach a very high current density (i.e. \(>600\) mA cm\(^{-2}\)). The better ORR activity on Ag/C-nanocapsule can be attributed to its smaller particle size\[34,35\] and uniform particle distributions\[17,18\]. It has been proven in a three-electrode system that through both the direct and indirect ORR pathways, the oxygen goes through the 4 steps, including O\(_2\) adsorption, O-O bond breakage, and desorption of products, to complete the ORR\[10,36\]. The Ag/C with a smaller size has a higher surface area, thus leading to more catalytically active sites exposed, which can facilitate the oxygen reduction. Our fuel cell test confirms that this will facilitate ORR kinetics on Ag in single AEMFC. In addition, the results also show the particle size effect on ohmic loss in the fuel cell operation: the performance of fuel cell with the smaller cathode catalyst particle size dropped slowly during the test, which implies that using small size cathode catalyst can lead to less ohmic loss.

To further investigate the cathode and anode behaviors, a constant (cell) voltage test was conducted in order to get cathode and anode polarization curves. In this test, the anode and cathode overvoltage at constant fuel cell operation voltage of 0.5 V (near the OCV), 0.3 V (near the peak power density) and 0.1 V (near the limiting current) were measured. The test was performed at the setting potential, by looping 55 ml of 1.0 M glycerol + 2.0 M KOH from the anode fuel vessel into the anode plate channel, with the same cathode O\(_2\) flow rate under 30 psi back pressure for 0.5 h. The anode potential was measured using an electronic load during the test: a Hg/HgO (1.0 M KOH) reference electrode was dipped into the anode fuel vessel, the electronic load was connected between the reference electrode and the fuel cell anode to make a closed loop. The potential could be read from the load, and this obtained potential value can be converted to a reversible hydrogen electrode (RHE) by
\[
V_{\text{RHE}} = V_{\text{measured}} - 0.098 - 0.059 \times (\text{pH of electrolyte solution})
\]
The cathode potential can be calculated using the equation below:
\[
E_{\text{cathode}} = E_{\text{apply}} + E_{\text{anode}} + E_{\text{resistance}}
\]
Where \(E_{\text{cathode}}\) is the cathode potential (vs. RHE), \(E_{\text{apply}}\) is the constant voltage applied on the test, \(E_{\text{anode}}\) is the measured anode potential and \(E_{\text{resistance}}\) is the ohmic lost during the test, which can be calculated from measured average current density multiplied by fuel cell internal resistance (directly tested by the Scribner fuel cell stand). The \(I-V\) curves of cathode and anode are shown in Fig. 4(b).
At the anode, all of the fuel cells (with different cathode catalysts) share a same trend, which can be fitted into a single curve, suggesting the polarization properties of both anodes are similar, and the electro-oxidation of glycerol under tested conditions is a fast process (compared with the sluggish ORR at the cathode). However, at the cathode, the cells show a different \( I-\) \( V \) trend. Because of the higher ORR activity on Ag/C-nanocapsule, the polarization on Ag/C-nanocapsule cathode is higher than that on Ag/C-commercial. In addition, the AEMFC with the Ag/C-nanocapsule catalyst can reach a higher limiting current density. These results confirm that the Ag/C-nanocapsule with small, uniformly dispersed nanoparticles is a better cathode catalyst compared to the commercial Ag/C with larger particle size.

It is very interesting to study crude glycerol as a fuel for the AEM-DGFC. The components of crude glycerol include 88 wt% of glycerol, 5.42 wt% of matter organic non glycerol, 4.16 wt% of moisture, 2.37 wt% of ash and 628 ppm of methanol. The fuel was used without any further treatment. Again, the fuel cell with Ag/C-nanocapsule cathode catalyst demonstrated a superior performance. The peak power density under the same operation conditions (same to the high purity glycerol AEMFC, Fig. 4) are 66 mW cm\(^{-2}\) and 38 mW cm\(^{-2}\) for Ag/C-nanocapsule and Ag/C-commercial catalysts, respectively, as shown in Fig. 5. By keeping the other test conditions identical, the catalyst particle size is still the dominant factor in governing the crude glycerol AEM-DGFC performance. Although the crude glycerol fuel cell performance (66 mW cm\(^{-2}\)) is lower than that of the high purity counterpart (86 mW cm\(^{-2}\)), it is still acceptable. The performance of these fuel cells (in terms of power density) is higher than that of glycerol–\( O_2 \) biofuel cell in magnitude orders [37,38]. This result demonstrates great potential of direct use of industrial-grade crude glycerol to generate electricity. However, the catalyst stability and operation stability associated with direct crude glycerol fuel cells should be investigated [33], and they are still underway in our lab.

The electrochemical impedance spectroscopy (EIS), which is also known as AC impedance technique, is capable of distinguishing the influences (voltage drop caused by charger transfer, membrane or mass transfer resistance) of the different processes (kinetic, ohmic or mass transport dominated) in the whole electronic system [39,40]. Herein, EIS is used to investigate the causes of the performance differences between the two fuel cells with different silver cathode catalysts. The resistance in high frequency regions could be attributed to the combined behavior of internal ohmic resistance and contact capacitance, the intercept of real component in \( x \)-axis is the reflection of the sum up of contact resistance and ohmic resistance (from cell components such as membrane and catalyst layer and the contact between each of them); the resistance in low frequency is charge transfer issue dominated, and the arc diameter in that location is inversely proportional to the ORR rate [41].

In our test, Nyquist diagrams obtained from the two fuel cells are shown in Fig. 6. In the spectra, although not that clear (due to the two arcs overlapping), one high frequency arc and one low frequency arc can still be observed. In the high frequency arc, the semicircle of Ag/C-nanocapsule is obviously smaller, which proves the fast kinetic process of ORR obtained on this catalyst. The higher surface area and more exposed catalytically active sites will definitely endow Ag/C-nanocapsule with higher ORR rate. Those results are in consistence with the \( I-\) \( V \) curves and the electrode polarization curves. In the high frequency regime, the spectrum of fuel cells using Ag/C-nanocapsule catalyst has relatively smaller intercept in real axis \( (Z_{Re}) \) than that of Ag/C-commercial, which means the cell has low contact and ohmic resistances. Since there’s no difference in the MEA and cell assembly between the two cells, the lower resistance of Ag/C-nanocapsule cell can be attributed to the catalyst layer. In the Ag/C-nanocapsule coated layer, small catalyst particle size can allow sufficient humidifying water to be held in the
Fig. 6. EIS plots measured with the fuel cells using different particle size Ag/C cathode catalysts.

electrode, and the uniform particle distribution can prevent the agglomeration effect, which may lead to the boundary resistance increasing. Furthermore, the small particle and uniform distribution can decrease the migration path of ions, which can further reduce the distributed resistance. The high frequency EIS results provide the information that in the real fuel cell operation, the smaller cathode catalyst particle size will not only facilitate the ORR performance of 66 mW cm⁻².

4. Conclusions

A solution phase-based nanocapsule method was developed to prepare the Ag/C-nanocapsule catalyst. The XRD and TEM characterizations reveal that Ag nanoparticles prepared by the nanocapsule approach have a small diameter of around 5.4 nm and narrow size distribution of 2–9 nm. To serve as control sample, the commercial Ag-NPs with a size of distribution 20–40 nm were deposited on carbon support using the impregnation method. Results of glycerol–O₂ anion exchange membrane fuel cells (AEM-DGFC) with Ag/C-nanocapsule and Ag/C-commercial cathode catalysts show that the fuel cell with smaller Ag particles has a higher ORR activity: the peak power density of 86 mW cm⁻² was achieved on Ag/C-nanocapsule at 80 °C. In the constant voltage tests, with the same anode behavior, the AEMFC with the Ag/C-nanocapsule cathode can reach a higher current density and maintain less cathode overvoltage, as compared with the one with the Ag/C-commercial cathode. In the impedance test, the Ag/C-nanocapsule cathode-fuel cell shows a smaller arc and a smaller intercept in the real axis, which indicates a smaller kinetics resistance and a smaller contact/ohmic resistance, respectively. A crude glycerol was also served as fuel, and the AEMFC shows a promising performance of 66 mW cm⁻².

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