



Silver Nanowire Catalysts on Carbon Nanotubes-Incorporated Bacterial Cellulose Membrane Electrodes for Oxygen Reduction Reaction

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Silver nanowires have unique electrical, thermal and optical properties, which support their potential application in numerous fields including catalysis, electronics, optoelectronics, sensing, and surface-enhanced spectroscopy. Especially, their application such as catalysts for alkaline fuel cells (AFCs) have attracted much interest because of their superior electrical conductivity over that of any metal and their lower cost compared to Pt. In this study, multiwalled carbon nanotubes (MWCNTs)-incorporated bacterial cellulose (BC) membrane electrode with silver nanowire catalyst was prepared. First, acid-treated MWCNTs were incorporated into BC membranes and then freeze-dried after solvent exchange to tert-butanol in order to maintain the 3D-network macroporous structure. Second, silver nanowires synthesized by polyol process were introduced onto the surface of the MWCNTs-incorporated BC membrane through easy vacuum filtration. Finally, thermal treatment was carried out to confirm the effect of the PVP on the silver nanowire catalysts toward oxygen reduction reaction. The electrode with thermally treated silver nanowire had great electrocatalytic activity compared with non-treated one. These results suggest that the MWCNTs-incorporated BC electrode with silver nanowire catalysts after thermal treatment could be potentially used in cathodes of AFCs.

Keywords: Silver Nanowires, Gas Diffusion Electrode, Electrocatalyst, Oxygen Reduction Reaction.

RESEARCH ARTICLE

1. INTRODUCTION

Recently, fuel cells have widely been considered to be an efficient and eco-friendly power source, offering much higher energy densities and energy efficiencies compared to any other current energy storage devices. Fuel cells are therefore considered to be promising energy devices for the transport, mobile, and stationary sectors.¹⁻⁴

Hydrogen oxidation reaction is thermodynamically reversible and kinetically less demanding than other reactions, implying minimal overpotential losses at the anode during fuel cell operation. On the other hand, oxygen reduction reaction (ORR) is irreversible and exhibits significant kinetic barriers. Since the kinetics of ORR is generally slow, one of the major challenges in this field is the development of high-performance cathode catalysts. Until now, the most efficient and successful catalysts used to promote ORR kinetics have been platinum (Pt)-based particle materials. However, Pt suffers from high price and

scarcity, which has motivated the development of non-Pt electrocatalysts for the ORR.

Alkaline fuel cells (AFCs) have been extensively explored due to the ability of using non-Pt catalysts. Among these, silver is a promising candidate because it has the highest electrical conductivity of any metal and is approximately 100 times less expensive than Pt. Moreover, silver catalysts have shown comparable performance to Pt.⁵

The electrodes of AFCs consist of a catalyst layer (CL) and a gas diffusion layer (GDL). The GDL should be a porous material and a good electrical conductor for two major reasons. First, the reaction gases can successfully diffuse into the catalyst layer and uniformly spread thereafter. Second, the electrons generated by the anode catalysis can be carried over an external circuit and enter into the cathode.⁶

Bacterial cellulose (BC), as one of the most abundant materials in nature, has unique properties such as high crystallinity, high chemical stability and high mechanical strength.⁷ Above all, BC membranes have macroporous 3D-inter-connected network structures.⁸ To use these

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porous BC membranes as a GDL, however, BC has to incorporate other conducting materials like multiwall carbon nanotubes (MWCNTs) since it is naturally non-conductive.^{9–11}

In this study, we fabricated MWCNTs-incorporated BC membrane electrodes with silver nanowire catalysts for ORR. MWCNTs were homogeneously introduced to the inside of the BC membranes using ultrasound treatment without any damage to the macroporous 3D-network structure. Then, silver nanowire catalysts were introduced onto the surface of the MWCNTs-incorporated BC membranes through an easy vacuum filtration method. An electrode based on the MWCNTs and the BC membranes was created through freeze-drying. The morphological and electro-chemical properties of the electrode were investigated.

2. EXPERIMENTAL DETAILS

2.1. Preparation of BC Membranes

Gluconacetobacter xylinum BRC-5 was cultured on a Hestrin and Schramm (HS) medium, which was composed of 2% (w/v) glucose, 0.5% (w/v) yeast extract, 0.5% (w/v) bacto-peptone, 0.27% (w/v) disodium phosphate, and 0.115% (w/v) citric acid. The cells were precultured in a test tube for seven days and then inoculated onto a 60 mm × 15 mm Petri dish containing 14 mL of HS medium. The cells in the Petri dish were statically incubated at 30 °C for five days. The BC membranes were purified in a 0.25 M NaOH solution for 48 h at room temperature in order to eliminate the cells and components of the culture liquid. Then the pH of the BCM was lowered to 7.0 through repeated washing with distilled water. The purified BC membranes were stored in distilled water at 4 °C to prevent drying.

2.2. Acid Treatment of MWCNTs

As-received MWCNTs (NCT, Japan) were treated with acid using the following procedure reported in an earlier study.¹² The MWCNTs were treated in an acid mixture (sulfuric acid/nitric acid = 3:1 (v/v)) at 65 °C for 24 h. Any impurities within the MWCNTs were removed through acid treatment and carboxylic and hydroxyl functional groups were introduced onto the surface of the MWCNTs.

2.3. Synthesis of Silver Nanowires

Silver nanowires were synthesized by reducing silver nitrate (AgNO₃) with Ethylene glycol (EG) in the presence of polyvinylpyrrolidone (PVP). In a typical experimental procedure, 10 mL of 0.1 M AgNO₃ solution in EG was heated in a three-necked flask at ~160 °C, after which 1 mL of 1.7 mM NaCl solution in EG was added quickly. After reaction for 15 min, 10 mL of 0.15 M PVP solution in EG was injected drop-wise into the reaction system by

syringes within 10 min. The reaction was kept at ~160 °C for another 2 h, and magnetic stirring was maintained during the entire procedure. After the solution was cooled to room temperature, the final dispersion was diluted with acetone and centrifuged at 4,000 rpm for 30 min. The supernatant dissolved in the residual EG was then removed by syringe, and water was added into the centrifuge tube to disperse the products and dissolve the residual PVP. Finally, the supernatant was also removed by syringe, and the process was repeated twice more. These purified products were preserved in ethanol.

2.4. Preparation of Porous MWCNT Electrode Supported by BC Membrane

The acid-treated MWCNTs were dispersed in distilled water using ultrasound treatment. The BC membrane was immersed in the aqueous MWCNT dispersion, and ultrasound treatment was applied for several days. In this process, the MWCNTs penetrated into the BC membrane. Using the filtration method, the silver nanowires were introduced onto the MWCNTs-incorporated BC membrane. Then, the BC membrane was immersed in tert-butanol for several days and freeze-dried for 48 h in order to dry it without any damage to the macroporous 3D-network.

2.5. Characterization

The morphologies of the silver nanowires, the MWCNT-incorporated BC and the silver nanowires on the MWCNT-incorporated BC were observed using field emission scanning electron microscopy (FESEM, S-4300SE, Hitachi, Japan) at an accelerating voltage of 15 kV after the samples were pre-coated with a homogeneous Pt layer through ion sputtering (E-1030, Hitachi, Japan).

X-ray diffraction (XRD) measurements for the silver nanowires were carried out using a Rigaku DMAX-2500 with CuK α radiation (wavelength, $\lambda = 0.154$ nm) at 40 kV and 100 mA.

To confirm the electrocatalytic activity, cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were carried out in N₂ or O₂-saturated 0.1 M KOH solutions at room temperature. The results were measured by a potentiostat (PGSTAT302N, Autolab). In all the measurements, Pt and Ag/AgCl were used as the counter and reference electrodes, respectively. The CV tests were performed between -1.0 and 1.0 V at a scan rate of 50 mV/s. The LSV tests were performed between -1.2 and 0.0 V at a scan rate of 20 mV/s and rotation rates ranging from 500 to 4000 rpm.

3. RESULTS AND DISCUSSION

3.1. Morphological Properties

The electrodes of AFCs consist of CL and the GDL. As mentioned above, the GDL should be a porous material

and a good electrical conductor.⁶ To maintain the macroporous 3D-network structure of the BC, some treatments were carried out. First, the solvent of the pristine BC was exchanged with tert-butanol. Then, the solvent-substituted BC was freeze-dried in order to dry the BC without damaging the macroporous 3D-network structure. The microscopic morphologies of the freeze-dried BC and the MWCNTs-incorporated BC electrode were investigated using SEM (Fig. 1). The nanosized fibrils of the freeze-dried BC were three dimensionally connected, and this structure had a large number of macropores (Fig. 1(A)). Figure 2(B) shows that the MWCNTs were well dispersed in the freeze-dried BC membrane, which is expected to be conductive. This makes MWCNT-incorporated BC an appropriate candidate for GDL because of its porous structure and conductivity.

The silver nanowire catalysts were synthesized via so-called polyol process, by reducing AgNO_3 with EG in the presence of PVP. Figure 2(A) shows the XRD patterns of the silver nanowires, and the peaks at 38.1° , 44.3° , 64.4° , and 77.8° were indexed to the {111}, {200}, {220}, and {311} facets of the face-centered-cubic phase of silver belonging to the space group $\text{Fm}\bar{3}\text{m}$ [255] (JCPDS file No. 04-0783). Figure 2(B) shows SEM image of the silver nanowires. The average length and diameter of the silver nanowires were $6.1 \pm 2.9 \mu\text{m}$ and $77 \pm 2 \text{ nm}$, respectively. The catalytic activity of the silver nanowires synthesized by this method is much lower than surfactant-free silver nanowires because of the formation of PVP layers.

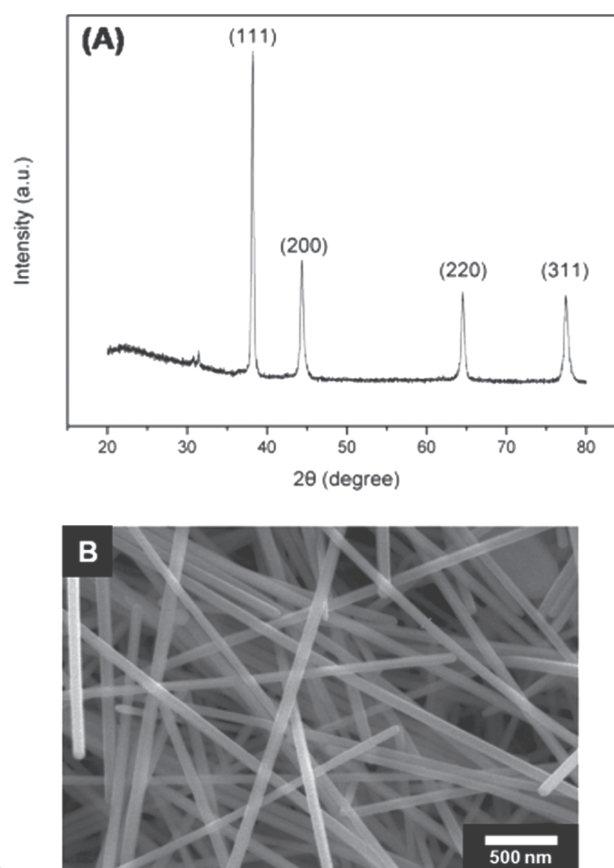


Fig. 2. (A) X-ray diffraction pattern and (B) SEM image of silver nanowire catalysts.

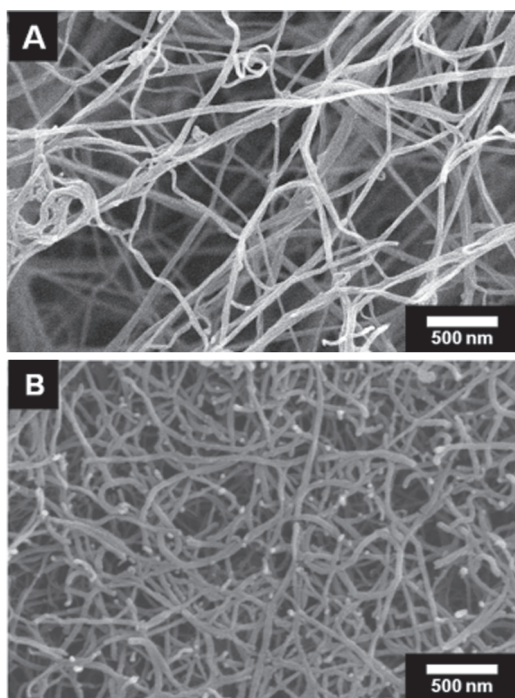


Fig. 1. The SEM images of (A) the freeze-dried BC membrane in tert-butanol and (B) the MWCNTs-incorporated BC membrane electrode.

To increase the catalytic activity of the silver nanowires and to raise the electroconductivities of the silver nanowires through decomposition of the PVP, the silver nanowire catalysts on the MWCNTs-incorporated BC membrane electrodes were annealed at 180°C for 20 min in an oxygen atmosphere.¹³ The adhesion between silver nanowires and MWCNTs-incorporated BC membrane as well as the catalytic activity is one of the important factors for the performance of electrodes made using these materials. The adhesion of the electrode synthesized by the easy filtration method is evaluated by mechanical tape testing,¹⁴ as shown in Figure 3. Figures 3(A) and (B) show photographic images of the silver nanowires on MWCNTs-incorporated BC membrane before and after peeling the 3 M Scotch tape, respectively. The silver nanowires on the MWCNTs-incorporated BC membrane electrode after adhesion test did not exhibit any changes compared with the electrode before the adhesion test. This simple experiment indicates the strong mechanical adhesion of the synthesized electrodes. The morphology of the electrode surface is shown in Figure 3(C). As expected, the BC membranes are holding the silver nanowires well. This is undoubtedly further evidence of the mechanical adhesion between the catalysts and GDL.

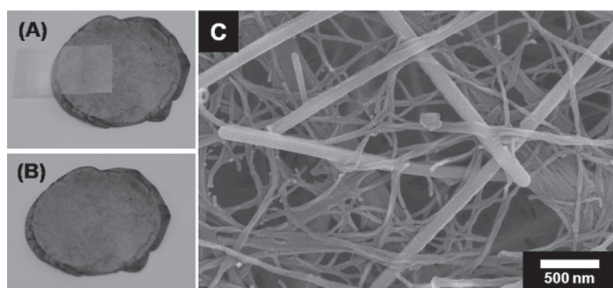


Fig. 3. The photo images of the silver nanowires on MWCNTs-incorporated BC membrane (A) before and (B) after peeling the 3 M Scotch tape. (C) The SEM image of the silver nanowires on MWCNTs-incorporated BC membrane surface.

3.2. Electrochemical Properties

The electrocatalytic activity of the silver nanowires towards oxygen reduction was then examined by cyclic voltammetry (CV). Figure 4 shows the representative CV curve of the silver nanowires on MWCNT-incorporated BC membrane electrode in 0.1 M KOH that was saturated with N_2 , at a potential sweep rate of 50 mV/s. In the CV curves measured within the potential range of -1.0 to 1.0 V (vs. Ag/AgCl), three anodic current peaks were clearly observed at $+0.26$, $+0.42$ and $+0.46$ V, respectively. The small peak A_1 is due to silver dissolution and formation of a surface monolayer of Ag_2O films. The peaks A_2 and A_3 are attributed to the formation of bulk phases of $AgOH$ and Ag_2O , respectively.¹⁵

To confirm the electrocatalytic activity of the silver nanowires with and without PVP layers, the reaction kinetics of oxygen reduction at the silver nanowires with and without PVP layers were studied with rotating disk voltammetry.¹⁶ As mentioned above, the PVP layers were removed through thermal annealing treatment at 180 °C for 20 min. The ORR polarization curves obtained for the silver nanowire catalysts before the annealing treatment (Fig. 5(A)) and after the annealing treatment (Fig. 5(B))

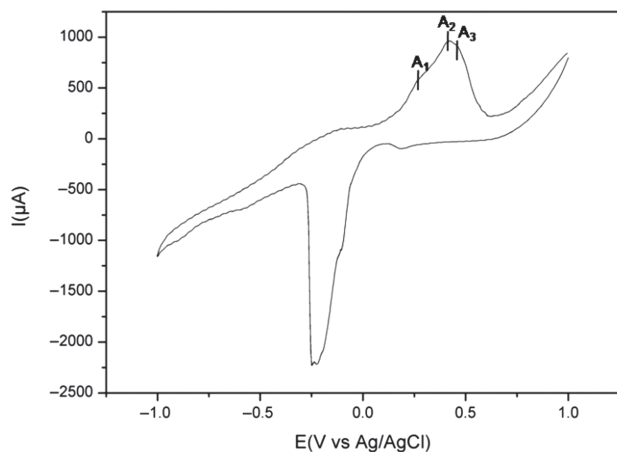


Fig. 4. The cyclic voltammogram of the silver nanowires on MWCNTs-incorporated BC membrane electrode in N_2 -saturated 0.1 M KOH solution. Potential scan rate 50 mV/s.

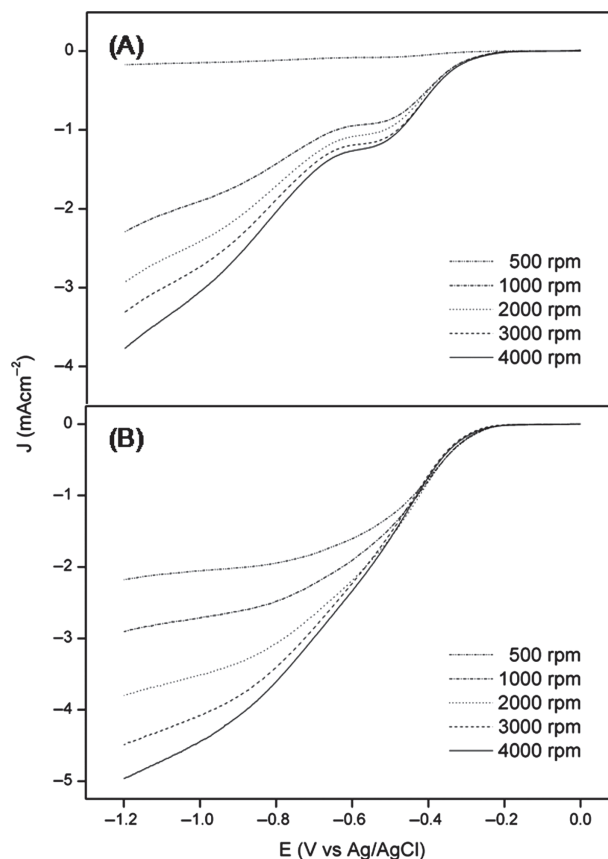
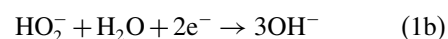
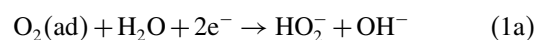
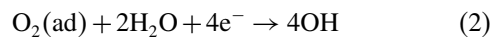


Fig. 5. The ORR polarization curves obtained on the silver nanowire catalysts before the annealing treatment (A) and after the annealing treatment (B) at rotation rate from 500 to 4000 rpm in an O_2 -saturated 0.1 M KOH solution.

at rotation rates ranging from 500 to 4000 rpm in an O_2 -saturated 0.1 M KOH solution are shown in Figure 5. As shown in Figure 5(A), two plateaus of limiting current can be observed at around -0.6 and -1.0 V, suggesting that electrocatalytic reduction of oxygen proceeds via two-step processes:



However, from the rotating disk voltammograms (RDVs) of oxygen reduction recorded for the silver nanowires without PVP layers (Fig. 5(B)), there was only one plateau with higher current density than those obtained for the silver nanowires with PVP layers (Fig. 5(A)). These RDVs indicate that the ORR on the silver nanowires without PVP layers proceeds via the most efficient four-electron process:



The voltammetric results suggested that the PVP layers on the silver nanowire surfaces evidently reduce the electrocatalytic activity towards oxygen reduction. Therefore, the silver nanowire without PVP layers after thermal treatment

is promising candidate to replace Pt for use as catalysts of AFC cathode.

4. CONCLUSIONS

A MWCNTs-incorporated BC membrane electrode with silver nanowire catalyst was prepared. To form the GDL, 0.1 wt% acid-treated MWCNTs were made to penetrate into BC membranes, which were then freeze-dried after solvent exchange to tert-butanol in order to maintain the 3D-network macroporous structure. Then, silver nanowires synthesized by polyol process were introduced onto the surface of the GDL through easy vacuum filtration. To examine the effect of the PVP on the silver nanowire catalysts toward ORR, thermal treatment was carried out. The electrode with thermally treated silver nanowires had higher electrocatalytic activity than those not treated, because the PVP layers, which interrupt electrochemical activity, were removed from the thermally treated silver nanowires. These results suggested that the MWCNTs-incorporated BC electrode with silver nanowire catalysts could be potentially used AFC cathodes.

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References and Notes

1. N. Sannes, *Fuel Cell Technology: Reaching Towards Commercialization*, Springer, London (2006).
2. M. M. Mench, *Fuel Cell Engines*, John Wiley and Sons, Ltd., London (2008).
3. J. Larminie and A. Dicks, *Fuel Cell Systems Explained*, Second edn., John Wiley and Sons, Ltd., Chichester (2003).
4. A. Hermann, T. Chaudhuri, and P. Spagnol, *Int. J. Hydrogen Energy* 30, 1297 (2005).
5. F. Bidault and A. Kucernak, *J. Power Sources* 196, 4950 (2011).
6. J.-H. Lin, W.-H. Chen, Y.-J. Su, and T.-H. Ko, *Energ. Fuel* 22, 1200 (2008).
7. P. Chen, S. Y. Cho, and H.-J. Jin, *Macromol. Res.* 18, 309 (2010).
8. Y. S. Yun, H. Bak, and H.-J. Jin, *Synthetic Met.* 160, 561 (2010).
9. D. Kim, L. Zhu, J.-H. Kim, C.-S. Han, and S. Baik, *J. Nanosci. Nanotechnol.* 12, 3408 (2012).
10. H.-S. Jang, S. K. Jeon, O.-H. Kwon, S. C. Lee, C. S. Kim, and S. H. Nahm, *J. Nanosci. Nanotechnol.* 12, 3242 (2012).
11. P. Nayek, S. K. Roy, and R. Dabrowski, *J. Nanosci. Nanotechnol.* 12, 6216 (2012).
12. S.-M. Kwon, H.-S. Kim, and H.-J. Jin, *Polymer* 50, 2786 (2009).
13. A. R. Madaria, A. Kumar, F. N. Ishikawa, and C. Zhou, *Nano Res.* 3, 564 (2010).
14. R. Zhu, C.-H. Chung, K. C. Cha, W. Yang, Y. B. Zheng, H. Zhou, T.-B. Song, C.-C. Chen, P. S. Weiss, G. Li, and Y. Yang, *ACS Nano* 5, 9877 (2011).
15. J. Guo, A. Hsu, D. Chu, and R. Chen, *J. Phys. Chem. C* 114, 4324 (2010).
16. Y. Lu, Y. Wang, and W. Chen, *J. Power Sources* 196, 3033 (2011).

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