



## Short communication

## The influences of multi-walled carbon nanotube addition to the anode on the performance of direct methanol fuel cells

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## ABSTRACT

Different amounts of multi-walled carbon nanotubes (MWCNTs) are added to anode catalyst layer in the membrane electrode assemblies (MEAs) of direct methanol fuel cells (DMFCs). The MEA with 0.5 wt.% carbon nanotubes (CNTs) shows the best performance in DMFC. In the protonic conductivity tests, a 0.5 wt.% amount of MWCNTs results in the highest protonic conductivity. SEM and TEM observations show that a continuous and uniform distribution of Nafion ionomer layer is formed on the MWCNT surface. Therefore, the dispersed MWCNTs in the catalyst layer are considered to be helpful for developing the pathways of protons transport.

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## 1. Introduction

High-performance direct methanol fuel cells (DMFCs) require highly active catalysts and effective utilization of them in the membrane electrode assemblies (MEAs). One of the most important factors for high catalyst utilization in a membrane electrode assemblies is the building of 'triple-phase region' of reactants, electrons, protons and resultant to active catalyst sites.

Nafion ionomer in the catalyst layers of MEAs is essential to the triple-phase region, not only because of its positive effect on the protonic conductivity, but also because of its negative influence on electric conductivity and mass transport. Investigators have studied recast Nafion by optimizing its morphology [1–3], its amount [4,5], and ways of casting it [6–9]. However, no efforts have been made to adjust its distribution with other additives.

Multi-walled carbon nanotubes (MWCNTs) have been used as a conducting additive in both lithium-ion batteries [10,11] and electric double-layer capacitors [12,13]. We reason that MWCNTs possess high electric conductivity and a large aspect ratio. Apart from these qualities, the unique mechanical properties of MWCNTs also urge their applications in the MWCNT/Nafion-reinforced mem-

brane [14]. However, these approaches have not yet been applied to the MEAs of DMFC.

Nevertheless, Narayanamoorthy et al. [15] doped carbon black supported platinum catalyst with a small quantity of single-walled carbon nanotubes (SWCNTs), and evaluate the composite in a liquid electrolyte. Moreover, carbon nanotubes (CNTs) supported catalyst proved to possess better activity than a typical carbon material supported catalyst [16–19]. The reports about the subject attributed the catalytic enhancement to better dispersion of catalyst particles, increased accessibility for reagents, favorable strong interaction between catalyst and better electrical conductivity of CNTs. However, the effect of CNTs on the protonic conductivity, especially in an MEA, has not been discussed.

In this work, MWCNTs are added to the catalyst layer as an additive. In order to investigate the influences of MWCNTs on the distribution of Nafion, the MEA structure, and the single-cell performance, different characterization methods have been adopted.

## 2. Experimental

## 2.1. Preparation of MEAs

The fabrication of MEAs followed the process described in Ref. [20]. Nafion 117 membranes were pretreated through boiling in 3 wt.% H<sub>2</sub>O<sub>2</sub> solution, in 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, and finally in deionized

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water. Then, the membrane was placed between two pieces of bibulous paper under a pressure of 4 kPa upon the membrane (by putting a piece of aluminum alloy on the bibulous paper) so that we can keep the flatness and smoothness of the membrane while it is drying at room temperature. The cathode catalyst was 20 wt.% Pt/C (Hispec 3000, Johnson Matthey), and the anode catalyst was 30 wt.% PtRu/C (Hispec 5000, Johnson Matthey). Catalyst ink was prepared by mixing appropriate amount of catalyst and a 5% Nafion solution (1100 EW, Dupont), using isopropyl alcohol (IPA) as a solvent. The electrodes were obtained by spraying the catalyst slurry onto a 10-cm<sup>2</sup> carbon paper (TGP-H-090, Toray), before that a layer of carbon black (Vulcan XC-72) and PTFE (weight ratio 4:1) was sprayed on the anode carbon paper as a microporous diffusion layer. The metal Pt or PtRu loading was 1 mg cm<sup>-2</sup> for the cathode and 3 mg cm<sup>-2</sup> for the anode. The ionomer loading was 10 wt.% for the cathode and 15 wt.% for the anode, defining by the ratio that dry ionomer takes up in the catalyst layer. Cathode and anode electrodes were hot-pressed on both sides of the polymer electrolyte membrane at a temperature of 135 °C and with a pressure of 5 MPa for 120 s.

## 2.2. Addition of the MWCNTs

The production of the MWCNTs was discussed in detail in Ref. [21]. In order to improve the dispersibility of MWCNTs, an acidic etching with a mixture of nitric and sulfuric acids was conducted [22]. The surface-modified MWCNTs were washed and added to the anode catalyst slurry. Samples with 0.5 wt.%, 1 wt.% and 2 wt.% MWCNTs in the anode catalyst slurry were prepared. The MWCNT amount over 2 wt.% resulted in a fragile electrode structure and thus was not included.

## 2.3. A single-cell test

The polarization curves of MEAs were obtained on a BT-2000 Fuel Cell Workstation (Arbin). While testing, 2 M aqueous methanol solution was pumped through the anode at 3 mL min<sup>-1</sup> and oxygen to the cathode at 0.5 slpm. All tests were conducted in an ambient pressure and at 25 °C. Before testing, a preconditioning process was conducted at 75 °C for 3 h, in which methanol solution passed through its anode.

## 2.4. Evaluation of protonic conductivity

The protonic conductivity of the active layer composite was investigated by the addition of an inactive composite layer, as the electrode structure presented by Boyer et al. [23]. It contained an electrically isolated inactive layer consisting of Nafion (DuPont) and

XC-72R carbon black (Cabot, without catalyst) sandwiched between two Nafion 115 membranes, as part of the electrolyte pathway. The carbon to Nafion ratio of this inactive layer was the same as that of the anode catalyst layer.

The ohmic resistance of the MEAs with the inactive layers was determined by high-frequency intercept from ac impedance measurements under a constant discharging current of 100 mA. The ohmic resistance of the sandwiched inactive layer was obtained by comparing the resistance of an MEA with an inactive layer to that of MEA with two Nafion 115 membranes and without active layer.

After the ac impedance tests, the MEAs with the inactive layers were dried and cut in liquid nitrogen for the cross-sectional characterization by SEM (S-5200) and optical microscope. The layer thickness was determined by the cross-sectional characterization. Protonic conductivity was calculated using the following equation:

$$\sigma = \frac{L}{RS} \quad (1)$$

where  $L$  is the thickness of the sandwiched inactive layer,  $R$  is the measured inactive layer resistance, and  $S$  is the geometrical area of the MEA.

## 2.5. Characterization of MWCNTs in the electrode

The anode catalyst layer with 1 wt.% MWCNTs was studied using SEM. Also, TEM and EDS were used to trace Nafion ionomer. First, a 1 μL drop of catalyst slurry was cast onto a copper mesh and oven-dried to form a mini-structure of anode catalyst layer. Then the recast Nafion was exchanged to K<sup>+</sup> form [24]. TEM (JEM2100F) and EDS (JED2200) measurements were adopted.

## 3. Results and discussion

### 3.1. Changes in electrode morphology

SEM images in Fig. 1 show the MWCNTs' morphologies in the MEA anode. It can be seen that the catalyst layer mainly consists of three-dimensional aggregates of carbon-supported catalysts. Well-dispersed one-dimensional MWCNTs have many contacts with multiple catalyst aggregates to form conductive wiring as Li et al. described [10,11]. This wiring can greatly improve protonic conductivity if they are able to conduct protons, or in other words, if they have Nafion ionomer on the surface.

Nafion ionomer in the catalyst layer tends to deposit around the bulk material of the electrode during the fabrication process. This phenomenon has been reported in different expressions. Uchida et al. [1] stated that Nafion ionomer mainly existed in the secondary pores among catalyst aggregates. Xie et al. [2] found a Nafion skin

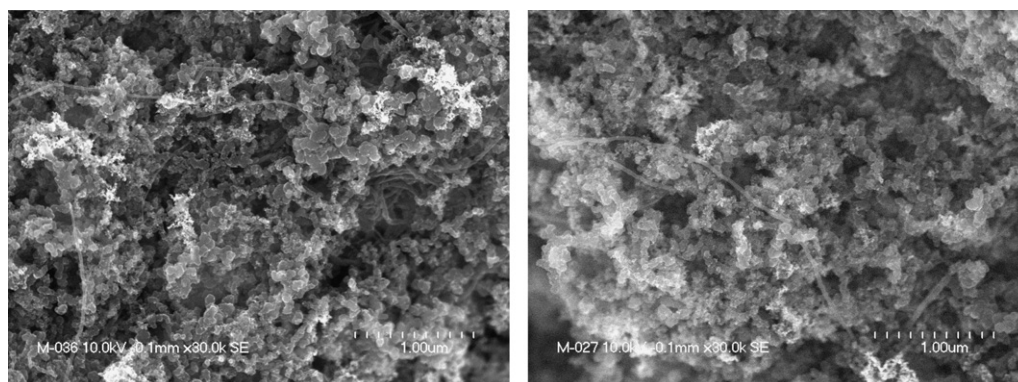


Fig. 1. SEM images of cross-section of the MEA anode with 1 wt.% MWCNTs.

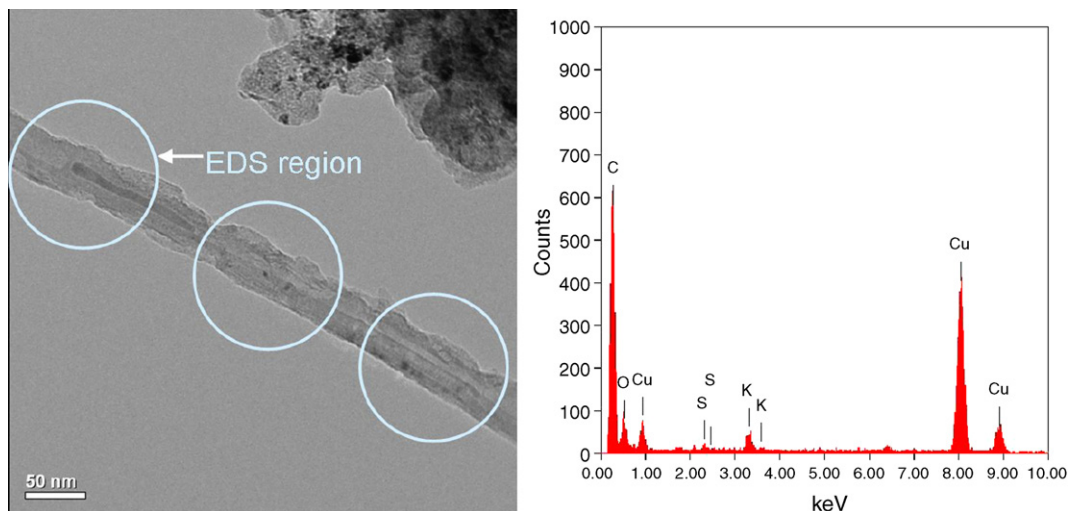


Fig. 2. TEM images (left) of a CNT after the catalyst slurry dried off, and the EDS spectrum (right) of the pointed region.

formed on the Teflon decal surface during the decal process. Their work proved that Nafion deposits around other electrode materials, instead of forming a conductive network spontaneously. In our work, therefore, Nafion’s uniform distribution among MWCNTs is expected.

To discuss the coated Nafion in our case, TEM and EDS results are presented in Fig. 2. EDS spectra of all three circled areas are the same, and only the pointed one is shown here. In Fig. 2, the EDS spectrum gives distinct kalium ion peaks within the area around the nanotube. The kalium ions can only be found in the K<sup>+</sup> form ionomer, so that the deposition of Nafion on the surface of MWCNTs is expected in the MEA anode as shown in TEM characterization. These Nafion-coated MWCNTs are able to function as pathways for protons.

### 3.2. Analysis of protonic conductivity

To evaluate MWCNTs’ effects on protonic resistance, protonic conductivity of inactive layers with and without MWCNTs are calculated and shown in Fig. 3. It is widely known that high-frequency intercepts of ac impedance spectra [25,26] represent ohmic resistance, which consists of electric resistance, protonic resistance and contact resistance. In our samples for the impedance analysis, an inactive layer is sandwiched between two Nafion 115 membranes.

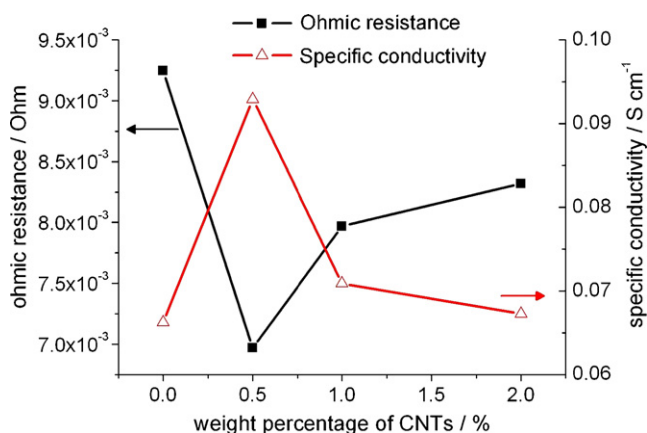


Fig. 3. Ohmic resistance and specific conductivity of the inactive layers with different percentages of CNTs additives.

Therefore the inactive layer is electrically isolated [23]. Consequently, when we modify the composition of inactive layer by adding MWCNTs, changes of its protonic resistance are expected to be recorded in the high-frequency intercepts of ac impedance spectra, and hence to reflect on the protonic conductivity.

As is revealed in Fig. 3, when 0.5 wt.% MWCNTs are added to the inactive layer, it may possess the highest protonic conductivity. This effect is attributed to the pathways for protons formed by Nafion-coated MWCNTs, which are discussed in Section 3.1. However, when more (1 wt.% and 2 wt.%) MWCNTs are added, a reduction in protonic conductivity was observed. This phenomenon is probably due to the limited dispersibility of MWCNTs. When MWCNTs take up a relatively large fraction in the dry weight of the layer, they are expected to aggregate and become inefficient or even destructive to the layer structure. Therefore, a 0.5-wt.% MWCNT addition appears to have the most positive effect on the protonic conductivity.

### 3.3. Single-cell performance

The single-cell polarization curves are shown in Fig. 4. Increases of power densities are observed in all the samples with MWCNT addition. The addition of MWCNTs is not able to affect the inner activity of catalyst or the electrical conductivity (because the catalyst support is high-conductivity XC-72R carbon black), and

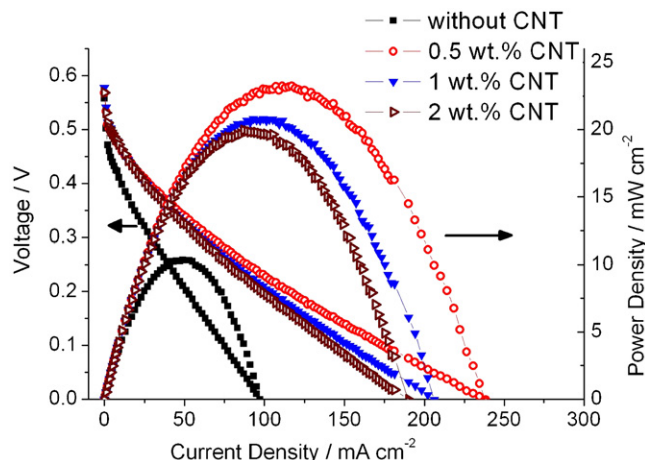


Fig. 4. Polarization curves of MEAs with and without MWCNTs at 25 °C.

thus the performance differences observed in the low-current and middle-current regions may be attributed to the change of protonic conductivity.

A ratio of 0.5 wt.% appears to possess the most appreciable effect on the activity or utilization of anode catalyst. This is attributed to the enhancement of protonic conductivity in the anode catalyst layer. However, MEAs with 1 wt.% and 2 wt.% MWCNTs exhibit lower performances than the 0.5 wt.% sample. This decrease is ascribed to the same reason discussed in Section 3.2. Over-dosed MWCNTs tend to become aggregates, and thus could result in structural instability, such as delamination, which was perceived in the samples with 3 wt.% MWCNTs in the anode catalyst layer and in the inactive layer.

In addition to the proton-conducting pathways formed by MWCNTs, our work offers a new angle for the Nafion optimization in MEAs, in which the relation between Nafion distribution and the structure of bulk materials (carbon-supported catalyst in our case) is revealed. The optimization of Nafion content often faces the conflict that too little Nafion leads to poor protonic conductivity, and that too much of it becomes a barrier for mass transport [2,27]. The conflict over the Nafion content is relatively eased in our work. It is accepted that Nafion's distribution relies on the electrode material on which it deposits. The three-dimensional shape of ordinary catalyst particles and their aggregates often results in an inefficient distribution of Nafion. In order to obtain an effective and temperate distribution of Nafion, we use one-dimensional MWCNTs to function as pathways for protons. In that case, the enhancement of protonic conductivity would not necessarily demand a higher proportion of Nafion, and thus would not lead to the blocking of mass transport.

#### 4. Conclusion

Different amounts of MWCNTs were added to anode catalyst layer in the MEAs of DMFCs. Well-dispersed one-dimensional MWCNTs have contacts with multiple catalyst aggregates. Nafion ionomer deposits on the MWCNTs, thus making the MWCNTs in the anode form pathways for protons. Measurements of protonic resistances revealed that protonic conductivity was enhanced after the addition of MWCNTs. The MEA with 0.5 wt.% carbon nanotubes showed the highest specific conductivity and the best single-cell performance. When more MWCNTs were added, structural instability was detected.

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