

Highly conductive and Non-leached  
polybenzimidazole/carbon nanotube-based membrane  
electrode assembly with remarkable durability

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High temperature-polymer electrolyte membrane fuel cell (HT-PEMFC) that works without humidification has become a market requirement because it offers several advantages over the currently available Nafion-based FCs. For example, the problem of water management becomes unnecessary, leaching of the electrodes decreases and the activity of Pt based-electrode improves (1).

Phosphoric acid-doped polybenzimidazole membrane (PA-PBI) seems so far the most successful candidate to achieve a high performance PEMFC at elevated temperatures and non-humidified conditions (2, 3). However this system showed a leaching process of the membrane free PA molecules during the FC operation, leading to a decline in the performance, and consequently a low durable FC (4). Recently, it was reported that doping PBI with solid polymeric phosphoric acids is achieving a high proton conductivity of the membranes due to the highly ordered hydrogen bonding network and the fast proton transfer process at the anhydrous state (5, 6). Of course, the use of non-leached membranes in FCs will be advantageous from the leaching point of view (7), but at the same time their use is expected to reduce the proton migration between the electrodes and the membrane, because the electrodes of PEMFC requires not only redox reactivity and electron conductivity but also proton conductivity to advance smooth reactions (8).

Two years ago, our group reported a new functionalization process of FC catalyst support in which carbon nanotubes (CNT) is  $\pi$ -stacked with unique proton conducting polymers e.g. pyridine based-PBI; PyPBI (Fig.1), and then the prepared composites were used as precursors for the deposition of Pt particles (9-11). This method showed a good catalytic activity of CNTs towards oxygen reduction reaction and a good FC performance. During that time, there was a belief that proton conduction of the electrodes were activated by PA molecules that leached from PA-doped PBI membrane. Therefore, we think that introducing non-leaching FC electrodes with activated proton conduction properties can help to assemble a non-leaching MEA with enhanced proton conduction properties, and also such a non-leaching MEA is expected to provide a highly durable FC.

Here, we offer a new platform of FC technology by activating the proton conductivity of the electrocatalyst by using a non-leaching dopant. In this report, we functionalize the basic PyPBI-wrapped CNT composite by a highly proton conducting acidic polymer; poly(vinylphosphoric acid) (PVPA; Fig. 1). PVPA is known to form a strong dynamic hydrogen bonding network and thermally stable at elevated temperatures (12, 13). Therefore, the new formulated electrocatalyst composite will serve not only as a redox site and an

electron conductor but also as a proton conductor, leading to an accelerated proton migration process through the MEA which is homogeneously assembled by using a PVPA doped-PBI membrane.

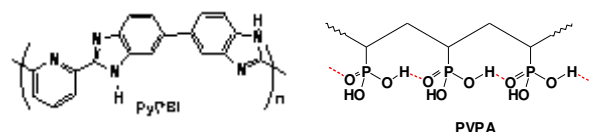


Fig. 1 The chemical structure of PyPBI and PVPA.

The resultant electrocatalyst is subject to a characterization process including X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), Infrared spectroscopy (IR) scanning electron microscopy (SEM) and transmittance electron spectroscopy (TEM) to confirm the composite structure and the dispersion of Pt nanoparticles. The cyclic voltammetry (CV) is measured to determine the electrochemical surface area (ECSA) of the electrocatalyst. Subsequently, we measure the FC performance of the assembled MEA at non-humidified operating conditions by using hydrogen and air as fuel and oxidant, respectively. Furthermore, we analyzed the FC performance by means of electrochemical impedance spectroscopy (EIS) to understand the role of PVPA on the proton conductivity of the MEA. At the end of this report, we stress testing the durability of the assembled MEAs in order to evaluate the non-leaching formulation technique on the FC life time.

The electrochemical surface area of the electrocatalyst was measured to be  $40.2 \text{ cm}^2/\text{mg}_{\text{Pt}}$ . The power density of the PVPA-based MEA was recorded to be  $252 \text{ mW}/\text{cm}^2$  at non-humidified operating conditions. The impedance spectra showed an enhancement in proton conduction through PVPA-based MEA, and indicated a lower polarization resistance for oxygen reduction reaction after PVPA functionalization. The accelerated durability testing of PVPA-based MEA showed a high number of cycles compared to the PA-based MEA.

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