

## Fullerene-Based Membrane for Dry Operation of Polymer Electrolyte Fuel Cells

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Water management in polymer electrolyte fuel cells (PEFC) is one of the most difficult issues that require careful attention in designing a reliable fuel cell. A breakdown in water balance at the cathode side results in either drying out or water flood, while the anode side tends to get dry due to the water diffusion across the membrane. Currently dominant water-based proton-exchange membranes (PEM) require not only a humidifier which takes extra space, but also favor an even distribution of water throughout the membrane.

To eliminate the problems associated with water management, a number of efforts have been underway in the development of anhydride PEM.<sup>1-3</sup> Recently, Sony has developed proton-exchange membranes based on functionalized (mainly the OSO<sub>3</sub>H and the OH groups) fullerenes for polymer electrolyte fuel cell (PEFC).<sup>4</sup> Fullerenes are very unique in that they have a very low electron affinity and are easy to chemically functionalize; thus their performance (the conductivity, the thermal/chemical/mechanical stability,...) can be fine tuned chemically. Also, fullerenes with multiple acid groups have a high volumetric density of proton conductive groups. The Sony group suggested that the ion conduction in the functionalized fullerene was due to the proton hopping between the functional groups on the fullerene, therefore requiring no humidification, though no detailed examination of the proton transport mechanism was reported.<sup>4</sup> Still, chemical functionalization of fullerenes is well-established; thus their performance (the conductivity, the thermal, the chemical, and the mechanical stabilities) can be controlled and even fine-tuned chemically. Thus, they could be promising materials for a new type of tailored ionic conductors. Yet, so far, it is not clear whether the conductivity of Sony's fullerene membrane is due to the functional groups or C<sub>60</sub> itself is conductive. Theoretical calculations may provide an insight into the nature of C<sub>60</sub> as a proton conducting material. In this report, we examine C<sub>60</sub>'s basic characteristics as a proton conductor primarily through theoretical calculations and report some experimental results on its application in PEFC.

### Results and Discussions

The activation energy barriers for proton hopping in fullerene were calculated at the PM3 method since higher levels of calculations are computationally prohibiting due to the size of the molecules. No activation energy barrier of proton transfer has been reported for C<sub>60</sub>.

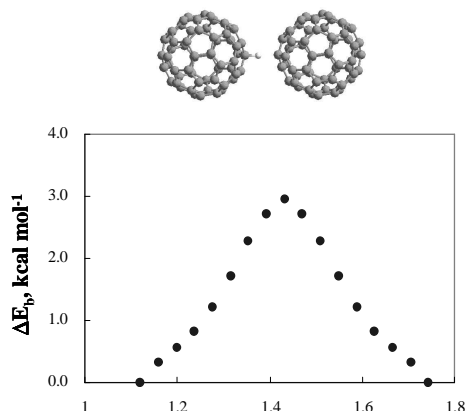


Figure 1. Inter-molecular proton transport potential energy for C<sub>60</sub>.

Figure 1 displays the intermolecular activation barrier of H<sup>+</sup>

transportation between two C<sub>60</sub> molecules, with the activation barrier of only 2.96 kcal mol<sup>-1</sup>. As to the intramolecular proton hopping, the activation energy barriers of H<sup>+</sup> transportation along the two paths were calculated: 27.8 kcal mol<sup>-1</sup> along the C-C bond dividing two hexagons (C<sub>h</sub>-C<sub>h</sub>) and 31.3 kcal mol<sup>-1</sup> along the bond dividing a hexagon and a pentagon (C<sub>h</sub>-C<sub>p</sub>) of C<sub>60</sub>. These values imply a fast movement of a proton around the C<sub>60</sub> surface, which is qualitatively consistent with the experimental observation that only a single<sup>13</sup>C-NMR spectrum was observed for the C<sub>60</sub>H<sup>+</sup> system at ambient temperature.<sup>2</sup> Our calculations of proton hopping barriers suggest that C<sub>60</sub> itself is highly conductive.

In order to verify the above theoretical results, we assembled an MEA with a C<sub>60</sub> pellet as the membrane for polarization measurements under dry condition. Although it was small, since there was no acidic proton in the pellet, the current was observed, demonstrating the proton conductivity of C<sub>60</sub> itself. Despite Sony's claim that the proton conductivity is due to the functional groups of fullerene, our result opens up a possibility of C<sub>60</sub> as possible proton conductive material.

To examine the effect of C<sub>60</sub> as an additive to PEM, a Nafion 117 membrane was doped with 1 wt% of C<sub>60</sub>, and the AC impedance was measured under dry condition. MEA's were also assembled for power measurements using dry H<sub>2</sub> and O<sub>2</sub> gases. Table 2 lists the maximum power density which was normalized by the thickness of the film, thus the unit in mW/cc both at 30 °C. Table 1 lists the proton conductivity and the maximum power density of the doped and undoped Nafion.

**Table 1.** The proton conductivity and the maximum power of doped Nafion films.<sup>a</sup>

	□, mS cm <sup>-1</sup>	mW cc <sup>-1</sup>
Nafion 117	1.7	16
Nafion 117 + C <sub>60</sub>	15	200

<sup>a</sup>Dry hydrogen and dry oxygen gases as fuel. The platinum loading of both electrodes was 0.4 mg cm<sup>-2</sup>.

Nafion doped with C<sub>60</sub> exhibits the conductivity an order of magnitude higher and the max power more than two orders of magnitude greater than Nafion 117 alone. Figure 3 demonstrates a sharp contrast in stability between Nafion doped by C<sub>60</sub> and Nafion alone under dry condition in terms of the voltage. Our finding demonstrates a strong potential of fullerene as a basic component in PEM for dry operation of polymer electrolyte fuel cells.

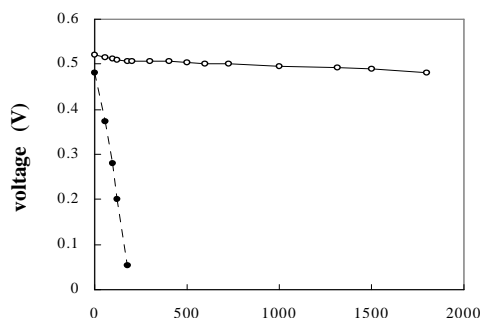


Figure 3. The voltages as a function of time at 30 °C with dry gases under 0.3 A cm<sup>-2</sup> of constant current: the Nafion doped with C<sub>60</sub> (solid line) and Nafion (broken line).

### References

1. K. Hinokuma, M. Ata, *J. Electrochem. Soc.* **150**, A112 (2003).
2. Reed, C.; Kim, K.-C.; Bolskar, R. D.; Mueller, L. J. *Science*, **289**, 101 (2000).