C_{60} and Its Composites for Proton Conducting Membranes in Polymer Electrolyte Fuel Cells

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Currently, intense efforts have been underway to develop high temperature proton-exchange membrane for PEFC in light of an enhanced CO tolerance of the catalyst, an ease of the heat management, increased catalytic activities, and overall improvements in the cell polarization.

Recently, Sony has developed proton-exchange membranes based on functionalized fullerenes for polymer electrolyte fuel cell (PEFC).[1] Through optimization of functionalization to C_{60}, mostly with the OSO_3H and the OH groups, they have achieved the best performance of the fullerene-based membrane, which was a compressed pellet, with 10^{-2} S cm^{-1} of ionic conductivity. It was suspected that the ion conduction was due to the proton hopping between the functional groups on the fullerene, though no detailed examination of the proton transport mechanism was reported. Still, chemical functionarization 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_{60} itself possesses a conductive nature or whether the conductivity can be further improved from the Sony's membrane. In this report, we examine C_{60}'s basic characteristics as a proton conductor.

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_{60}.

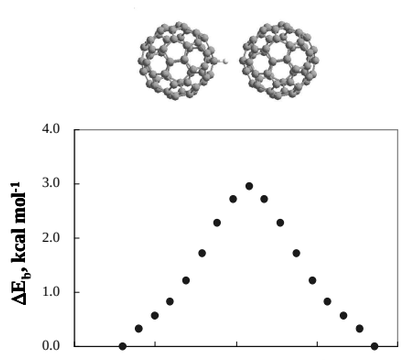
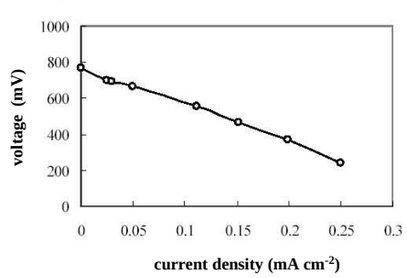


Figure 1. Intermolecular proton transport potential energy for C_{60}.

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

In order to verify the above theoretical results, we assembled an MEA with a C_{60} pellet as the membrane for polarization measurements under dry condition. Figure 2 presents the polarization curve for the cell measured at 30 ºC with dry hydrogen and oxygen as the fuels under atmospheric pressure. Though the current density is small since there is acidic proton in the pellet, this is a direct evidence of C_{60}'s proton conductivity. Despite Sony's claim that the proton conductivity is due to the functional groups of fullerene, our result opens up a possibility of C_{60} as possible proton conductive material.

Figure 2. The polarization curve for a fuel cell with a C_{60} membrane.



To examine the effect of C_{60} as an additive to PEM, a Nafion 117 membrane was doped with 1 wt% of C_{60}, and the AC impedance was measured under dry condition. MEA's were also assembled for power measurements using dry H_2 and O_2 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 ºC. 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 Nadion films.[a]

	σ, mS cm^{-1}	mW cc^{-1}
Nafion 117	1.7	16
Nafion 117 + C_{60}	15	200

[a]Dry hydrogen and dry oxygen gases as fuel. The platinum loading of both electrodes was 0.4 mg cm^{-2}.

Nafion doped with C_{60} 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_{60} 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.

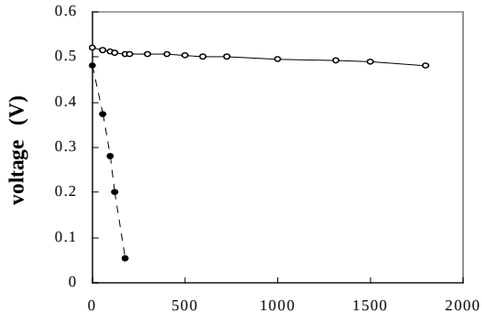


Figure 3. The voltages as a function of time at 30 ºC with dry gases under 0.3 A cm^{-2} of constant current. the Nafion doped with C_{60} (solid line) and Nafion (broken line).

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).