Computational Study on Fullerenes as Proton Conducting Materials

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Fullerenes possess extremely low electron affinities, e.g., 2.65 eV for C_{60}, and have attracted intense attention for semiconductors in the areas such as electronics, optelectronics, photovoltaic devices, and others in the past decade. The same unique property may be beneficial for another conductivity: ionic conductivity. Yet, their potential as ionic conductor has received little attention until recently. An ionic conductivity of fullerenes has been first observed by Stucky and cowokers[1] yet the nature of ionic conductivity was not thoroughly explored. Subsequently, Sony has developed proton-exchange membranes for polymer electrolyte fuel cell (PEFC) based on functionalized (mainly the OSO_3H and the OH groups) fullerenes.[2] It was assumed that the ion conduction was due to the proton hopping between the functional groups on the fullerene since the membrane was dry, though no detailed examination of the proton transport mechanism was reported.

Currently, intense efforts have been underway to develop high temperature proton-exchange membrane for PEFC. Proton conducting membranes based on fullerenes may be advantageous since such membranes seem to promote Grotthus proton transportation, according to Sony's claim.

Fullerenes are very unique in that they have a very low electron affinity, a high thermal stability, 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 higher volumetric density of proton conductive groups. 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. In this report, we examine C_{60}'s basic characteristics as a proton conductor: the activation barrier for proton transport and the acidity. No activation energy has been reported for C_{60}, and the experimental determination of the acidity may not be always straightforward for fullerenes in general.

Results and Discussions

Due to the size of the molecules of interest, the level for calculations of fullerenes's electronic structures was limited to low levels of theory, and in this study the PM3 method was used for all the calculations. We estimated two proton transport activation barriers for fullerenes: the intramolecular and the intermoleucle barriers. For the intramolecular H^+ transportation in C_{60}, Figure 1 shows the potential energy profiles for proton hopping with the activation energy barriers of H^+ transportation along the two paths: 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}. The distance r refers to the distance between the proton and the carbon to which the proton was originally attached in $C_{60}H^+$. 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.[3]

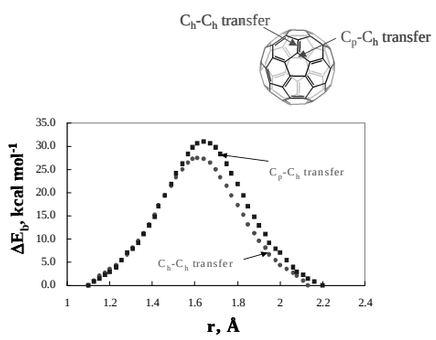
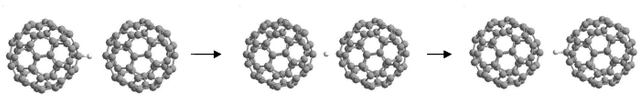


Fig. 1. Proton transport potential energies for two path ways on C_{60}.

Next, the activation barrier of H^+ transportation between two C_{60} molecules was computed for the process illustrated below (the proton shown by a white dot between two C_{60} molecules):



The calculated activation barrier was only 3.29 kcal mol^{-1}. Despite Sony's claim that the proton conductivity is due to the functional groups of fullerene, our calculations strongly suggest that C_{60} is itself highly conductive and opens up a possibility of C_{60} as proton conductive material.

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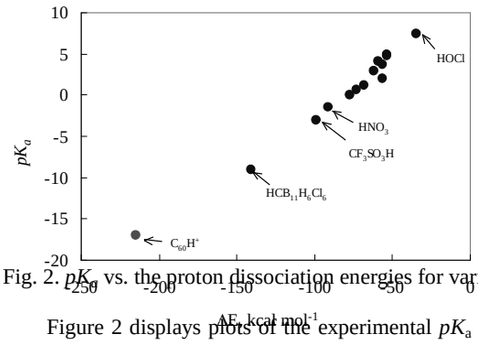

Fig. 2. pK_a vs. the proton dissociation energies for various acids

Figure 2 displays plots of the experimental pK_a values and the calculated proton dissociation energies (ΔE) for acids whose pK_a values are known, which show a clear correlation between them. The predicted pK_a values are also plotted for $HCB_{11}H_6Cl_6$, the strongest acid ever,[3] and for $C_{60}H^+$, based on the extrapolation from the assumed relationship between pK_a and ΔE.

Both the activation barriers and the acidity calculated here strongly suggest that the C_{60} molecule can be an excellent proton conducting medium. If it's dispersed in a membrane so that a percolation can be formed, proton-exchange membranes for high temperature operation can be fabricated, along with an acid.

References

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(3) C. Reed, K.-C. Kim, R. D. Bolskar, L. J. Mueller, *Science*, **289**, 101 (2000).