A quantum dynamics study on the H^+ transmission in a Pt-Nafion interface

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(Received 13 September 2006; Accepted 25 October 2006; Published 31 October 2006)

We performed a quantum dynamics study on the proton-like hydrogen (H^+) transmission from the platinum (Pt) electrode to the Nafion side chain. In particular, we calculated the transmission probability (T_p) for H^+ from the Pt side to the Nafion side using the coupled-channel method via the local reflection (LORE) matrix scheme and plotted T_p as a function of the H^+ initial translational energy. Our results showed that without quantum effects, H^+ transmission across the Pt-Nafion interface will be impossible to proceed at the operating temperatures (i.e. 353-373 K) of conventional fuel cells. We also found that the asymmetric nature of the barrier in the system we considered enhances the transmission. [DOI: 10.1380/ejsnt.2006.640]

Keywords: quantum dynamics; transmission; tunnelling; activation energy; hydrogen; interface

I. INTRODUCTION

Polymer electrolyte membrane (PEM) fuel cells –also called proton exchange membrane fuel cells– deliver high power density and offer the advantages of low weight and volume, compared to other fuel cells. Using a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst, PEM fuel cells need only hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids like some fuel cells. Typically fueled with pure hydrogen supplied from storage tanks or onboard reformers, they operate at relatively low temperatures, around 80°C (176°F or 353 K), which allows them to start quickly (less warm-up time) and results in less wear and better durability on system components. PEM fuel cells are used primarily for transportation applications and some stationary applications. Due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio, PEM fuel cells are particularly suitable for use in passenger vehicles, such as cars and buses.

Water in Nafion continues to be the preferred media for proton transfer in hydrogen fuel cells because water is non-toxic and this media offers relatively good conductivities, is self-regenerating, and is non-poisonous towards the catalyst. However, since higher temperatures are necessary to achieve greater conductivities, a major drawback is its relatively low boiling point which prevents the use of water in open fuel cells above 100°C (373 K). Thus, it is important to understand proton conductivity in aqueous environments so that new media can be designed that can operate at higher temperatures. In addition, owing to the small mass of the proton, the low energy barriers involved in proton transfer in water, and the relatively large zero point energies, theory indicates that quantum effects are dominant in aqueous proton transfer events. Unfortunately, theoretical investigations on proton conductivity in aqueous environments such as those that deal with the quantum effects on the proton transfer across the catalyst-Nafion interface have not been conducted, while related investigations on quantum effects on others systems are quite limited. Molecular quantum dynam-

ics studies on proton diffusion in perovskites [1, 2] and a quantum-mechanical first-principles study of the influence of different trivalent impurities on the oxygen-vacancy formation and migration properties in doped ceria [3] reveal remarkable correspondence between atomic and macroscopic properties. Furthermore, some theoretical studies have shown that the inclusion of zero point energy can reduce free energy barriers by 2-3 kcal/mol for enzyme reactions [4–6].

As an initial and important part of understanding photon conduction in aqueous environments, we aim to investigate thoroughly and systematically the various processes involved above. We begin our study on the H^+ transmission across the Pt-Nafion interface using available potential energy curves as functions of the H^+ reaction path coordinate. This study focusing on simple and ordered systems is our first step toward the modeling of more complex H^+ and interface reactions, such as those involving the Pt-Nafion interface and inter-atomic vibrational degrees of freedom. Some co-authors of these works have already obtained results for higher dimensions in separate but related studies [7–15] which will be used as references in our future works. Here, we employ a numerically stable method for solving coupled-channel problems [16] co-developed by our group, based on a quantity called the *local reflection matrix* which allows us to determine most quantities of physical interest such as transmission and reflection probabilities.

Using DFT (density functional theory)-based *ab initio* calculations, Tsuda, *et. al.* [17] recently reported a mechanism depicting a hydrogen atom's migration from a platinum catalyst to a Nafion membrane. They found that a H atom initially adsorbed on Pt is extracted by the sulfonate group ($-SO_3-$) on the side chain of Nafion, accompanied by partial electron transfer from the H atom to the Pt. The electron-poor H atom conducts in Nafion, while the partial electron transfer from the H atom results in the generation of electric power in polymer electrolyte fuel cells (PEFCs).

II. THEORY

In this study, we investigate the quantum dynamics of the proton transfer across the Pt-Nafion interface by calculating the transmission probabilities T_p for H^+ from the

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FIG. 1: Transmission probability (T_p) plots for the proton-like hydrogen atom (H^+) from the Pt electrode (initial state) to the Nafion side chain (final state) for the $CF_3SO_3-Pt_2+H$ (original) system and the hypothetical system, as functions of the hydrogen's initial translational energy (in eV). The inset shows the corresponding potential energy curves for H^+ transfer for the $CF_3SO_3-Pt_2+H$ (original) system having an asymmetric barrier and for a hypothetical system with a symmetric barrier, as functions of the hydrogen's reaction path coordinate (in angstrom). The height of the barriers is approximately 0.507 eV.

Pt side to the Nafion side. Using the calculated potential energy profiles for the migration of the H atom from the Pt to the trifluoromethane sulphonate ion ($-SO_3-$) for different $CF_3SO_3-Pt_2+H$ systems [17], we employed the coupled-channel method *via* the local reflection matrix scheme (LORE) [16] to obtain the transmission probabilities (for an elaborate description of the system and details of the potential energy calculations, please refer to Ref. [17]). During transmission, the Pt atoms as well as the various atoms that compose the ($-SO_3-$) group were assumed to be fixed as the H^+ atom travels across the Pt-Nafion interface. Thus, the potential energy curve (PEC) used in the actual calculations of T_p did not include zero-point vibrational energies. The energy reference for the PEC corresponds to that of the initial state, i.e. when the H atom is adhered to the Pt atom. The PEC for the $CF_3SO_3-Pt_2+H$ systems investigated was asymmetric (i.e. the system's energy in the Nafion side approaches a value that is significantly lower than zero).

III. RESULTS AND DISCUSSION

In order to investigate any quantum mechanical behavior of H^+ transmission from the Pt electrode to the Nafion side chain, we obtained the transmission probability plots for H^+ as functions of its kinetic energy when it is incident on the Pt-Nafion interface from the Pt side. Figure 1 (solid, heavy line) shows that the transmission probability T_p of H^+ is close to zero at low initial kinetic energies E_k (approximately below 0.333 eV) but rises to unity at ca. $E_k = 0.623$ eV as E_k increases. The transition region,

described by the S-shaped region in the plot, is centered about 0.478 eV (less than 0.507 eV which corresponds to the barrier height for this reaction). Note that even with an energy E_k smaller than the barrier height (0.507 eV), H^+ transmission may still occur. Conversely, transmission may still not happen even if the particle's energy is higher than the barrier. These are clear indications of the presence of quantum mechanical effects in the reaction that we attribute to the very small mass of the H^+ particle. These results conform well with the quantum effects that we also observed in the dissociative adsorption of H_2 molecules and the subsequent diffusion of dissociated H atoms on the Pt surface [18, 19]. We also found that the center of the transition region is significantly lower than the barrier peak of the PEC (potential energy curve) for the reaction (see inset, solid line). To verify this, we considered a hypothetical reaction characterized by a symmetric PEC about a barrier of height 0.507 eV (see inset, broken line) and obtained the corresponding T_p vs. E_k plot. As shown in Fig. 1 (broken, light line), the center of the transition region for this case is 0.505 eV which is almost equal to the barrier height.

Figure 2 gives us the plot of the energy distribution $f(E_k) = (1/k_B T_s) \exp(-E_k/k_B T_s)$ for different surface temperatures $T_s = 250, 300,$ and 400 K. These temperatures roughly represent the operating temperatures of polymer electrolyte membrane (PEM) fuel cells, i.e. $80-100^\circ C$ ($353-373$ K). Also shown are the plots for the transmission probability $T_p(E_k)$ and for the quantity $T_p(E_k) \times f(E_k)$ at $T_s = 250, 300,$ and 400 K, which determines the thermal average $T(T_s) =$

FIG. 2: Plots for the transmission probability (T_p), the energy distribution f and the product $T_p \times f$, at $T_s = 250, 300$ and 400 K, for the $\text{CF}_3\text{SO}_3\text{-Pt}_2\text{+H}$ system, as a function of the hydrogen's initial translational energy E_k (in eV). The inset shows a magnified version of the plots for $T_s = 250, 300$ K.

$\int_0^\infty (1/k_B T_s) T_p(E_k) \exp(-E_k/k_B T_s) dE_k$ for the proton in the membrane. The non-zero values for $T_p(E_k) \times f(E_k)$ in Fig. 2 and the subsequent finite values for the thermal averages within the energy range we considered show that protons are transmitted across the Pt-Nafion interface. Aside from the low activation barrier for this system, we find that the asymmetric nature of the barrier also contribute in the transmission process. This is a very encouraging result as reports have shown that the activation barrier for proton transfer to the Nafion membrane is lowered when placed in an aqueous environment. We also performed similar calculations for a less accessible channel for H migration in the $\text{CF}_3\text{SO}_3\text{-Pt}_2\text{+H}$ system characterized by a high activation barrier. Although the barrier in the PEC for this case is likewise asymmetric, evidence of quantum mechanical effects that are responsible for the proton transmission were greatly reduced due to the height of the barrier, making the proton transfer practically impossible to proceed.

IV. SUMMARY

Using available potential energy profiles for the migration of the H atom from the Pt to the $-\text{SO}_3-$ of Nafion for the $\text{CF}_3\text{SO}_3\text{-Pt}_2\text{+H}$ system, we calculated the transmission probabilities for H^+ across the Pt-Nafion interface. These were plotted as functions of the H^+ atom's initial translational energy E_k for $0 < E_k < 2$ eV. Our study showed that without quantum effects, H^+ transmission across the Pt-Nafion interface will be impossible to proceed at the operating temperatures

(i.e. 353-373 K) of conventional fuel cells. In addition, we found that the asymmetric nature of the barrier enhances the transmission. Finally, further calculations are currently in progress to investigate the effects of other degrees of freedom (e.g. vibrational) in the system.

Acknowledgments

This work is partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (Developing Next Generation Quantum Simulators and Quantum-Based Design Techniques) from the Ministry of Education, Culture, Sports, Science and Technology; the 21st Century Center of Excellence (COE) Program "Core Research and Advance Education Center for Materials Science and Nano-Engineering", supported by the Japan Society for the Promotion of Science (JSPS); and the "Research and Development of Polymer Electrolyte Fuel Cell Systems" project of the New Energy and Industrial Technology Development Organization (NEDO). The calculations presented here were carried out using the computer facilities of the Institute for Solid State Physics (ISSP) Supercomputer Center (University of Tokyo), the Yukawa Institute Computer Facility (Kyoto University), the Japan Atomic Energy Research Institute (ITBL, JAERI), the Center of Computational Physics (Tsukuba University), the Cyber Media Center (Osaka University), and the High Performance Computing Laboratory of the De La Salle University, Manila, Philippines.

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