Theory of Interfacial Proton Transport in Polymer Electrolyte Membranes

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Outline

- Importance of surface proton transport
- Model of the surface (interface)
- Mechanism of surface proton transport
- Mathematical description and results
- Conclusion/Prospective
Our main research focus is on polymer electrolyte membrane (PEM) fuel cells. Operation relies on the proton conducting PEM which conductivity is mainly due to a network of water filled pores. At T>90 °C the water starts to evaporate which leads to a significant decrease of PEM conductivity. Since the bulk water transport is out of game, one has to count on the surface proton transport.

**Aim:** to understand the mechanism of surface proton transport and, based on that, link surface structure with proton mobility.
Can the surface transport provide high enough mobility? Yes!

Experiments at Langmuir films show a diffusion coefficient values close to that of bulk water: (BW $9.3 \cdot 10^{-5} \text{cm}^2 \text{s}^{-1}$):


Conductivity measurements at nanosheet assemblies give conductivity of $\sim 10^{-2} \text{ S cm}^{-1}$ at T=70°C

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Surface group separation distance \(\sim 7\text{Å} \)

Conductivity measurements at nanosheet assemblies give conductivity of \(\sim 10^{-2} \text{S cm}^{-1} \) at \(T=70^\circ\text{C} \)

Model Surface

Activation energy of a single hop is 0.6 eV
Such a large value is due to uneven distribution of hydrogen bonds

Solution: to keep the number of HB at each surface group constant

Concerted Motion (Soliton)

Hydrogen bonds distributed evenly

Activation energy is 0.3 eV

S. Vartak, A. Roudgar, A. Golovnev, and M. Eikerling, submitted to the Journal of Physical Chemistry C
Hydronium ions move in the potential created by surface groups

\[ H = \sum_i m \left( \frac{du_i}{dt} \right)^2 + \frac{k}{2} (u_{i+1} - u_i)^2 + V(u_i) \]

\( u \) is the hydronium ion displacement

What should \( V(u) \) look like? \( V(u_i) = ? \)

- Periodic
- Harmonic for small displacement
- Steep ascending and descending flanks; plateau between wells
- Asymmetric

Exact potential profile is unknown. How to model it then?
Potential Profile

How does the hydronium motion depend on the potential profile?

Two extreme cases of the considered potentials

Different potentials offer different behaviour of hydronium ions. But what about soliton energy and mobility?

\[ V_1(u) = -\varepsilon \cosh^{-2}(\lambda u) \]  
(Strong HB)

\[ V_2(u) = -\varepsilon \cos^2\left(\frac{\pi}{a} u\right) \]  
(Weak HB)
Consider a soliton travelling with a velocity $v$

$V_1(u)$

steep wells, large plateau

$E^{(1)} = \sqrt{\frac{2\varepsilon ka^2}{1 - \frac{v^2}{v_0^2}}} \frac{1}{b} \sqrt{\frac{ka^2}{2\varepsilon}}$

$\mu^{(1)} = \frac{1}{b} \sqrt{\frac{ka^2}{2\varepsilon}}$

$b$ is the viscous friction coefficient introduced to derive mobility

$V_2(u)$

slanting wells, minor plateau

$E^{(2)} = \frac{2}{\pi} \frac{\sqrt{2\varepsilon ka^2}}{\sqrt{1 - \frac{v^2}{v_0^2}}} \frac{1}{b} \sqrt{\frac{ka^2}{2\varepsilon}}$

$\mu^{(2)} = \frac{\pi}{2} \frac{1}{b} \sqrt{\frac{ka^2}{2\varepsilon}}$

$v_0^2 \equiv \frac{ka^2}{m}$ is the maximal soliton velocity

$\frac{\mu^{(2)}}{\mu^{(1)}} = \frac{E^{(1)}}{E^{(2)}} = \frac{\pi}{2}$

$\frac{N^{(2)}}{N^{(1)}} \approx 100$

Soliton size ratio
Consider a soliton travelling with a velocity $v$

$V_1(u)$

steep wells, large plateau

$$E^{(1)} = \sqrt{2\varepsilon ka^2} \sqrt{1 - \frac{v^2}{v_0^2}}$$

$$\mu^{(1)} = \frac{1}{b} \sqrt{\frac{ka^2}{2\varepsilon}}$$

$V_2(u)$

slanting wells, minor plateau

$$E^{(2)} = \frac{2}{\pi} \frac{\sqrt{2\varepsilon ka^2}}{\sqrt{1 - \frac{v^2}{v_0^2}}}$$

$$\mu^{(1)} = \frac{\pi}{2} \frac{1}{b} \sqrt{\frac{ka^2}{2\varepsilon}}$$

Only two (three?) parameters define the dynamics:

$\varepsilon$ - potential well depth. Already calculated!

$ka^2$ - hydronium ion – hydronium ion interaction.

$b$ - viscous friction coefficient

S. Vartak, A. Roudgar, A. Golovnev, M. Eikerling, submitted to the Journal of Physical Chemistry
Conclusion

- A mechanism of soliton proton transport on a surface
- The particular potential profile has a minor influence on soliton’s energy and mobility
- A complete description of single soliton properties

Prospective

- Numerical calculation of the constants to evaluate mobility
- The step from a single soliton to soliton statistics to find conductivity
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3-Step Mechanism

In 2D one can avoid overcoming large potential barriers

At \( l = 6.4 \text{ A} \) all the structures have the same energy
To evaluate results one has to calculate the constants used

\[ H = \sum_i \frac{m}{2} \left( \frac{du_i}{dt} \right)^2 + \frac{k}{2} (u_{i+1} - u_i)^2 + \frac{\varepsilon}{q^2} \left\{ 1 - q^2 - \text{dn}^2 \left( \frac{2K(q)}{a} u, q \right) \right\} \]

\( \varepsilon \) - potential well depth. Already calculated!

S. Vartak, A. Roudgar, A. Golovnev, M. Eikerling, Collective proton dynamics at highly charged interfaces studied by Ab Initio Metadynamics, submitted to Chemistry of Materials.

\( b \) - viscous friction coefficient. Where does it come from?

\( k \) - hydronium ion – hydronium ion interaction.
Quest for Conductivity

\[ \sigma \equiv q n \mu \]

\[ n = ? \]

A step from one soliton consideration to a soliton statistics

probability density for creation of a soliton

\[ W(\nu; \nu + dv) = \frac{\omega}{2\pi} \exp \left( -\frac{E_d + E(\nu)}{k_B T} \right) dv \]

\[ E_T(\delta) \equiv \exp \left( -\frac{E(\delta) - E(0)}{k_B T} \right) \]

\( E(0) \) is the energy of a static kink
Narrow potential wells correspond to narrow solitons with a smaller number of participants but a higher level of collectiveness of the motion.