Dissociation of H_2 into H^+ in High-Dielectric Media for Fuel-Cell Applications

Jin MIZUGUCHI, Takahiro KANEGAE, and Hiroo TAKAHASHI

Department of Applied Physics, Graduate School of Engineering, Yokohama National University, Yokohama 240-8501, Japan

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One of the most critical issues in the development of fuel cells is the use of costly platinum as the catalyst for the dissociation of H_2 into protons (H^+). Furthermore, the reserve of platinum is also limited. We present here a non-platinum method for dissociating H_2 into protons using high-dielectric media, in which the binding energy of H_2 is greatly reduced by dielectric effects. A trial has been made in the present investigation to dissociate hydrogen in an electrochemical cell using ferroelectric materials. Currents due to the hydrogen dissociation in ferroelectric media have been observed, suggesting that our new approach can be a potential technique for forming protons in the absence of platinum. [DOI: 10.1143/JJAP.47.2262]

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Nowadays, fuel cells using H_2 have attracted much attention as a clean energy source for the future.¹⁾ However, a number of technical issues, such as electrolyte and cost problems, still remains. One of the most critical issues is probably the use of costly platinum (about \$25/g) as the catalyst for the dissociation of H_2 into protons (H^+). Furthermore, the reserve of platinum is also limited (about 70,000–80,000 tons worldwide). At the moment, one automobile uses 4–5 g of platinum as a three-way catalyst for controlling the exhaust emission. On the other hand, fuel-cell cars require approximately ten times more platinum for the dissociation of H_2 at the anode and also for the reduction of oxygen at the cathode. All together, roughly 50 g of platinum is necessary for one fuel-cell car. In view of the present situation, an alternative technology that can replace platinum is in great demand.

We present here a non-platinum method for dissociating H_2 into H^+ using high-dielectric media, such as ferroelectrics, in which the binding energy of H_2 is greatly reduced in proportion to the inverse square of the dielectric constant. Simple calculation reveals that about 4.4 eV (i.e., bond energy of H_2) is required to break the H–H bond for the formation of atomic hydrogens: $\text{H}_2 \rightarrow \text{H} + \text{H}$. In addition, an additional energy of 13.6 eV is necessary for the ionization of an atomic hydrogen: $\text{H} \rightarrow \text{H}^+ + \text{e}^-$. Altogether, we need about 18 eV for the dissociation of H_2 into protons *in vacuo*. On the other hand, we know one typical example, in which the atomic hydrogen or hydrogen-like atom dissociates easily into a proton at room temperature. This example is an impurity semiconductor, in which the ionization of donors (for example, a tetravalent Si atom is substituted by a pentavalent P atom) occurs easily even at room temperature.²⁾ For a phosphorus donor atom, four electrons are involved in the covalent bonds, and the fifth one is free. The excess electron acts approximately like the single electron of the hydrogen atom, with the modification that it is in a Si crystal ($\epsilon_r = 12$ where ϵ_r denotes the relative dielectric constant). Thus, we must consider the effect of this medium on the force between two charged bodies. The binding energy is then reduced by an amount of $1/\epsilon_r^2$ (i.e., $13.6/12^2$) in proportion to the inverse square of the dielectric constant. With further modification of the effective mass in the crystal, we obtain an impurity ionization of about 0.01 eV. This is the binding energy of the electron in a Si crystal that is much smaller than the thermal energy kT at room temperature (0.025 eV), where k and T designate the

Boltzmann constant and the absolute temperature, respectively. This indicates that the donor atom can completely be ionized even at room temperature. This is exactly the point, on which we focus our attention in order to dissociate H_2 into protons without using any platinum.

However, in our case, H_2 is not embedded in the lattice of a dielectric crystal, but is simply adsorbed on the surface of a dielectric medium. Although the effect is much smaller in our case, we still believe that the bond energy of H_2 can significantly be weakened using easily polarizable dielectric media according to Coulomb's law. As compared with the electron distribution on the nonpolarizable substrate [Fig. 1(a)], the bonding electrons are more localized near the surface of the dielectric medium owing to positively polarized charges, which appear on the surface of the dielectric medium [Fig. 1(b)]. The present polarization reduces effectively the negative charge of the bonding electrons, resulting in the weakening of the bond energy that leads to the dissociation of H_2 into protons by thermal energy (kT) at room temperature. The reduction in bond energy is obviously more enhanced by increasing the dielectric constant. In this sense, the ferroelectrics are ideal for the dissociation of H_2 .

We have carried out two kinds of dissociation experiment of H_2 into protons using an Al electrode with dielectric powders, or a Pt-sputtered Al electrode. Figure 2(a) shows a glass tube of 5 mm diameter, whose outer surface is covered with evaporated Al. On top of the tube, a sintered disc covered with sputtered Al that is made of a ferroelectric

Fig. 1. Schematic illustration of contour of electron probability for H_2 : (a) non-polarizable and (b) dielectric substrates. As compared with the electron distribution on the nonpolarizable substrate, the bonding electrons are more localized near the surface of the dielectric medium owing to the appearance of a positively polarized charge at the surface of the dielectric medium.

Fig. 2. (a) Al electrode with ferroelectric powders and (b) cylindrical Al electrode with sputtered Pt (about 500 Å) on both inner and outer surfaces.

material (height: 1 mm; $\epsilon_r = 1000$) was fixed. The disc was then made to be electrically in contact with the evaporated Al electrode of the glass tube. In the tube, ferroelectric powders based on BaTiO_3 ($\epsilon_r = 3500$ or 10000) were encapsulated up to a height of 30 mm. Ferroelectric powders were prepared by pulverizing the sintered ceramics up to a diameter of 5 μm . Figure 2(b) shows the cylindrical Al electrode (about 4 mm in diameter) with sputtered Pt on both the inner and outer surfaces of the electrode in the island form (thickness: about 500 Å). This serves as the reference sample for the Al/dielectric electrode. Figure 3 shows the electrochemical cell filled with deionized water for measurements of the dissociation current due to H_2 dissociation, where an Al electrode is used as the counter electrode and the Al/dielectric electrode is shown as an example of the working electrode. As soon as the Al/dielectric electrode was immersed, in the absence of H_2 , into the electrochemical cell including deionized water and the counter electrode, an electromotive force of about 45 mV appeared between the Al/dielectric electrode ($\epsilon_r = 3500$) and the Al counter electrode. At this moment, the dielectric powders were slightly soaked into deionized water through the dielectric

Fig. 3. Electrochemical cell filled with deionized water for measurements of current due to H_2 dissociation, where Al electrode is used as counter electrode and Al/dielectric electrode is shown as example of working electrode. The polarities of the electrodes are Al/dielectric electrode (+) and Al counter electrode (−) before H_2 introduction, and Al/dielectric electrode (−) and Al counter electrode (+) upon H_2 introduction.

disc at the Al/dielectric electrode. Nearly the same potential was also observed when the Al/dielectric electrode was replaced by another electrode with $\epsilon_r = 10000$. The present potential is attributed to the difference in electrochemical potential between the Al/dielectric electrode (i.e., mostly Al) and the deionized water, as well as between the deionized water and the Al counter electrode.³⁾ Since both electrodes are nearly entirely made of Al, a small electromotive force of 45 mV appeared in the experiment, and this value seems to be reasonable. On the other hand, an electromotive force of about 188 mV appeared between the Pt-sputtered electrode prepared on the cylindrical Al and Al counter electrodes, and this value increases with increasing thickness of the sputtered Pt. Since the above potential works as an internal battery, no external voltage was applied in the present experiment. The potential thus generated is sufficient for separating the ionized protons and electrons into free charge carriers. Therefore, we measured the current with an ampere meter placed in series with the electrochemical cell.

Figure 4 shows the current as a function of time before and after H_2 introduction. In the case of the Al/dielectric electrode with $\epsilon_r = 3500$ or 10000 in the absence of H_2 , a current of 0.18 $\mu\text{A}/\text{cm}^2$ was observed to flow from the “Al/dielectric” electrode (+) to the Al counter electrode (−). This is the current due to the deionized water as induced by a potential difference of 45 mV. The moment H_2 was introduced at a flow rate of 2 ml/min, the current direction was suddenly reversed: −0.04 and −0.12 $\mu\text{A}/\text{cm}^2$ for $\epsilon_r = 3500$ and 10000, respectively [Al on glass tube (−) and Al (+)]. This indicates that the dissociation of H_2 into protons ($1/2 \text{H}_2 \rightarrow \text{H}^+ + \text{e}^-$) occurs at the Al/dielectric electrode and the released electron is transferred, through the external circuit, to the Al counter electrode, whereas the protons are transferred to the electrolyte and diffuse toward the counter electrode owing to the difference in H^+ concentration. Thus, the reaction of ($\text{H}^+ + \text{e}^- \rightarrow 1/2 \text{H}_2$) will presumably occur at the Al counter electrode. The present elementary reaction is similar to the process found in a concentration cell. It is also important to note that the total current due to H_2 with $\epsilon_r = 10000$ is about 1.4 times higher than that with $\epsilon_r = 3500$, although the current is not exactly proportional to the dielectric constant.

Fig. 4. Currents before and after H_2 introduction for Al/dielectric or cylindrical Al electrode with sputtered Pt. The direction of the current flow is reversed by H_2 introduction in both cases.

In parallel, we have also carried out the same experiment in the absence of ferroelectric materials. A slight increase in forward current by less than 2% [Al/dielectric electrode (+) and Al counter electrode (-)] was observed upon H₂ introduction. However, this is obviously not due to H₂ dissociation, as determined from the direction of the current.

In the reference experiment with the sputtered Pt electrode, the current direction before H₂ introduction was the same as that of the Al/dielectric electrode and the current was 0.25 $\mu\text{A}/\text{cm}^2$. Then, H₂ introduction generated the reverse current ($-0.23 \mu\text{A}/\text{cm}^2$), as exactly observed in the case of the Al/dielectric electrode. However, the increases in current due to H₂ are about 1.6 and 2.2 times higher than that of the Al/dielectric electrode with $\epsilon_r = 3500$ and 10000, respectively.

The above results are clearly indicative of the dissociation of H₂ into protons through the ferroelectric media at room temperature. However, our interpretation is not entirely complete. An alternative explanation other than ours can also be possible. For this reason, further research is necessary for detailed analysis of the dissociation mechanism of H₂.

In summary, we have shown that H₂ dissociates into protons in high dielectric media, such as ferroelectrics, in the absence of platinum. This opens up a new horizon for the dissociation technology of H₂ into protons for fuel-cell applications. Further research should be directed, with practical application in mind, toward the improvement in contact efficiency (i.e., area and frequency) between the H₂ gas and the ferroelectric material.

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- 1) M. L. Perry and T. F. Fuller: *J. Electrochem. Soc.* **149** (2002) S59.
- 2) C. Kittel: *Introduction to Solid State Physics* (Wiley, New York, 1986) 6th ed., Chap. 8.
- 3) H. Gerischer: *The Surface Chemistry of Metals and Semiconductors* (Wiley, New York, 1969).