

Experimental Study of Ice Electrolysis under UV Irradiation

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The type of photocharge carriers in ice was determined by means of an electrolysis technique. It was suggested earlier¹ that irradiation of ice by UV light above 6.5 eV generates positive H_3O^+ ions, neutral OH^\bullet radicals, solvated electrons e_s^- , D defects, and vacancies of water molecules according to the “autoionization” reaction. Is the photoconductivity (PC) observed purely “protonic”, due to motion of H_3O^+ ions and D defects, or does it have an additional electron component related to the motion of solvated electrons e_s^- or their analogies? The presence of the electron component should not produce any additional gas release near the electrodes during an electrolysis process and for that reason can be easily detected as a deviation from Faraday’s law of electrolysis. We found that the amount of gas released per coulomb of charge flow is the same with or without the UV light. Therefore, the UV light does not change the composition (the proportion) of mobile charge carriers in ice, and in 25% of our tests the PC directly demonstrates a purely protonic nature. We also concluded that solvated electrons do not participate in the dc conductivity of ice. Probable reasons are discussed for the absence of a 100% gas release rate when the density of electric currents was below $100 \mu\text{A}/\text{cm}^2$.

Introduction

It is generally accepted that ice can be considered a protonic conductor in which the charge carriers are H_3O^+ , OH^- , and L and D defects. Several experiments have been devoted to proving that ice has purely protonic conductivity with no electronic component.^{2,3} It has been shown that gaseous hydrogen and oxygen are released at the electrodes in accordance with Faraday’s law of electrolysis:

$$M = \frac{\mu}{F} Q = \frac{\mu}{F} \int_0^{t_0} J(t) dt \quad (1)$$

Here, the mass of a substance M released at the electrode is proportional to the total electric charge, Q , passed through an electrolyte, μ is its molecular mass, F is the Faraday constant, $9.648 \times 10^4 \text{ C/mol}$, and $J(t)$ is an electric current at a moment t . On that basis it was concluded that ice is a protonic conductor. Decroly et al.,² however, indicated that at low electric current densities, $j < 100 \mu\text{A}/\text{cm}^2$, an apparent deviation from Faraday’s law can be observed. They explained that a leak in their experimental cell resulted in a lesser amount of hydrogen gas being measured.

The electrolysis of ice can be used to verify the nature of photoconductivity (PC) of ice found in the optical region above $h\nu = 6.5 \text{ eV}$ (or λ below 190 nm) according to the “autoionization” reaction¹



where H_3O^+ , D, OH^\bullet , and e_s^- are respectively a positive ion, a D defect, a hydroxyl radical, and a solvated electron, and V is a vacancy in a water molecule. In principle, protonic defects (ions, Bjerrum defects) and solvated electrons can participate in PC and electrolysis. In the case of electronic PC, no additional gas should be observed as the electric conductivity increases under UV irradiation. On the contrary, if PC is purely protonic, the quantity of gas released should obey the electrolysis

law given in eq 1. The degree of deviation from Faraday’s law can be used to determine the contribution of the electronic component to the PC of ice.

Basic Electrode Reactions in Water and Ice

Electrode reactions in ice and water differ because ice has four types of charge carriers, none of which has an electric charge with an integer value, while water has two types of charge carriers with integer-value electric charges.⁴

The following consideration is not specific for a particular model of ice structure near electrodes. The electrochemical reactions on electrodes are nearly identical in water and ice, but due to the rigid network of hydrogen bonds in ice, these reactions end up with defective hydrogen bonds, L and D defects.

Thus, instead of the cathodic reaction in water⁵



we have the cathodic reaction in ice with the participation of an L defect:



This equation satisfies the requirement of electroneutrality. Indeed, $e_{\text{H}_3\text{O}^+} - e = e_{\text{L}}$, where $e_{\text{H}_3\text{O}^+} = +0.62 |e|$, $e_{\text{L}} = -0.38 |e|$, and the interstitial hydrogen atom $\text{H}_{\text{int}}^\bullet$ is neutral.

Both eqs 3 and 4 are valid in the excess of H_3O^+ ions, i.e., when $\text{pH} < 7$. This is usually the case when the electric field is applied increasing the concentration of positive ions near the cathode. For the remainder, the pH is defined as $-\log(n_+)$, where n_+ is the concentration of H_3O^+ ions in the water solution in mol/L at normal conditions ($\text{pH} < 7$ when water is doped with acid, $\text{pH} > 7$ when water is doped with base, and $\text{pH} = 7$ for pure water). In ice, the pH indicates the concentration of H_3O^+ ions in the initial water solution. The pH may be considered a good reference for the characterization of degree of ice doping.

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TABLE 1: Cathodic Reaction

water	ice	pH
$\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^\bullet + \text{OH}^-$	$\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^\bullet + \text{OH}^- + \text{L}$	≥ 7
$\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}^\bullet + \text{H}_2\text{O}$	$\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}^\bullet + \text{H}_2\text{O} + \text{L}$	< 7

TABLE 2: Anodic Reaction

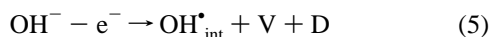
water	ice	pH
$2\text{OH}^- \rightarrow \text{O} + \text{H}_2\text{O} + 2\text{e}^-$	$2\text{OH}^- \rightarrow \text{O} + \text{H}_2\text{O} + 2\text{e}^- + 2\text{D} + \text{V}$	> 7
$3\text{H}_2\text{O} \rightarrow \text{O} + 2\text{H}_3\text{O}^+ + 2\text{e}^-$	$3\text{H}_2\text{O} \rightarrow \text{O} + 2\text{H}_3\text{O}^+ + 2\text{e}^- + 2\text{D} + \text{V}$	≤ 7

In case of pure water and ice, or in an excess of OH^- ions near the cathode ($\text{pH} \geq 7$) reactions 3 and 4 are modified:



This means that in the first stage the electrons are injected into water or ice, producing the hydrogen atoms (radicals) and OH^- ions. This may be the case when the initial surface charge accumulated causes the deviation from the electroneutrality. The particular mechanism of the cathode reaction changes as the pH changes.

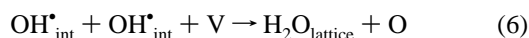
The same approach can be used for the anodic reaction, where in ice we have



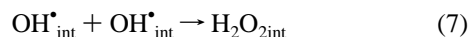
where radical $\text{OH}^\bullet_{\text{int}}$ is in an interstitial position and the $\text{pH} > 7$.

The second stage of the anodic reaction can go two different ways:

(1) The recombination of two OH^\bullet radicals and a vacancy V leads to the production of an oxygen atom O and an H_2O molecule. The latter incorporates back into the ice lattice, eliminating the vacancy V.



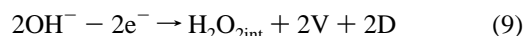
(2) Two OH^\bullet radicals form an interstitial hydrogen peroxide molecule:



Thus, the net anodic reaction has two possible variants:



and



Both variants satisfy the law of conservation of electric charge, $-2 \times 0.62|e| = -2|e| + 2 \times 0.38|e|$. Reaction 8 is considered by us to be preferable because, as will be shown in the experimental section, no hydrogen peroxide was found experimentally. Again, for the $\text{pH} \leq 7$ these reactions should be modified by adding the reaction of ionization of water molecule.

Tables 1 and 2 summarize the cathodic and anodic reactions which take place in water and ice at different pH levels.

Finally, the atomic oxygen recombines into molecular oxygen



and the atomic hydrogen recombines into molecular hydrogen



Experimental Techniques

We used a deuterium lamp (L2196, Hamamatsu Corp.) as a source of UV light for excitation of photoconductivity in ice, a multimeter (Fluke 45) to measure the electric currents, and a dc high-voltage (0–3 kV) power supply (Series 230, Bertan Corp.).

The experimental electrolysis cell is shown in Figure 1. It consists of two stainless steel flanges separated with a Teflon ring. The upper flange has a sapphire window, transparent to UV radiation for exciting photoconductivity in ice. The stainless steel mesh and the bottom flange are used as electrodes. The volume of gas released is measured with a capillary tube ($d = 1.67$ mm) containing a droplet of pure alcohol. The displacement of the droplet is proportional to the volume of gas released in accordance with reactions 10 and 11. The distance between the electrodes is 0.5 mm, and the electrode surface area is 1.5 cm^2 .

The ohmic electrodes were prepared according to the technique developed by Evtushenko et al.⁶ These electrodes use stable, electrically charged double layers at the ice–metal interface. The layers consist of thin monomolecular layers of intrinsic water ions (OH^- on the anode and H_3O^+ on the cathode), frozen into the ice–metal interface when phase transition occurs with direct current maintained through the interface. Due to leveling of electron energy levels of the ice and of the electrodes, the layer provides an effective exchange of electrons between ice and metal. Such electrodes were used for verification of the protonic nature of the conductivity of pure ice.³

Experimental Results

Figure 2 demonstrates transients in the electric current and the volume of gas (hydrogen plus oxygen) released during the process of electrolysis at $T = -10^\circ \text{C}$. At the moment $t = 0$, a bias of $V = 1$ kV was applied to the ice sample. The arrows indicate the time interval when the UV light was turned on. The illumination significantly increased the conductivity and electric current compared to the nonilluminated values. This results in an increase of the rate of gas release.

Figure 3 shows typical results for the volume of gases released versus the charge passed during the electrolysis of pure ice at $T = -10^\circ \text{C}$. The theoretical dependence (dashed line) is plotted according to Faraday's law of electrolysis, with the assumption of pure protonic conductivity of ice.

We performed measurements on 12 different samples of pure ice. Three out of 12 samples showed an experimental dependence close to that of the theoretical one. For instance, curve 1 presents one such dependence for the sample from Figure 2. The solid arrows indicate the moments when UV light was turned on and off; no change in the slope of the experimental line was observed at these moments. Two other samples that demonstrated similar behavior have deviations from the theoretical line within a 5% margin. The initial shift of curve 1 relative to the theory is explained by the initial delay in the gas release associated with the dissolving process.³

Nine of our samples demonstrated a significant deficiency in the amount of gas released. The typical “nontheoretical” behavior is shown by curve 2 in Figure 3. The average deviation from theoretical behavior was $10 \pm 0.5\%$. It varied from sample to sample and could be as high as 42%! Yet, for any particular sample during the experiment this value remained more or less constant. Again, the illumination of ice with UV light, indicated by the open arrows, did not change the slope of the experimental

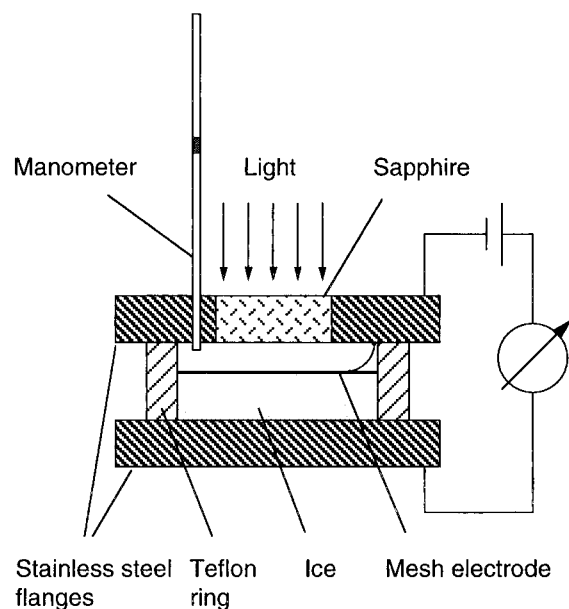


Figure 1. Experimental setup for ice electrolysis, consisting of an electrolysis cell, power supply, and an electrometer. The volume of gas released is measured with an accuracy of 1%.

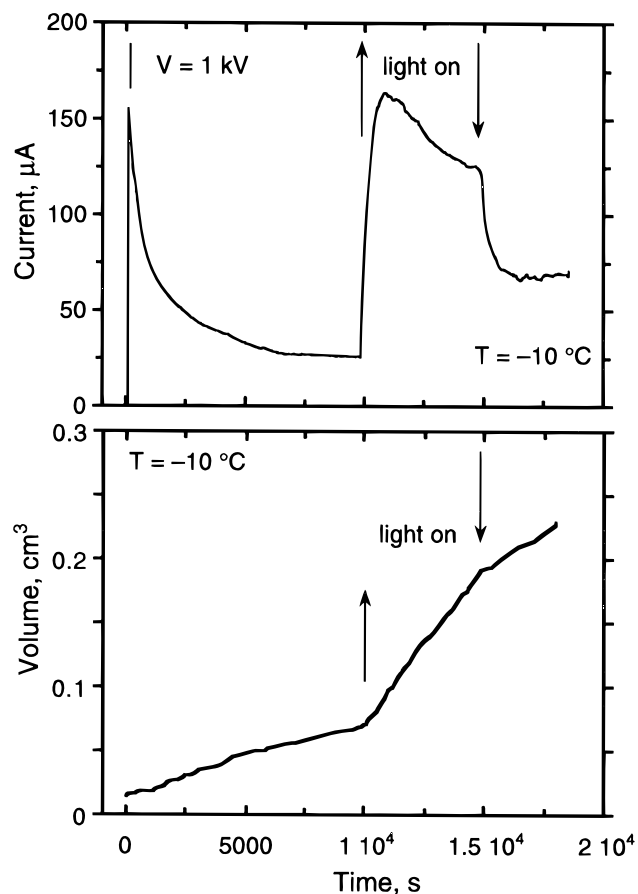


Figure 2. Transients of an electric current (upper), and the volume of gas (hydrogen plus oxygen) released (lower) during the process of electrolysis at $T = -10\text{ }^{\circ}\text{C}$. At the moment $t = 0$ a bias of $V = 1\text{ kV}$ was applied to the ice sample. The arrows indicate the time interval when the UV light was on. Illumination significantly increased the conductivity and electric current. As a result, a higher rate of gas release is observed.

curve. No leaking from the gas cell was detected. Tests with ice samples slightly doped with an acid or a base demonstrated 100% gas release in the same experimental cell used for pure ice.

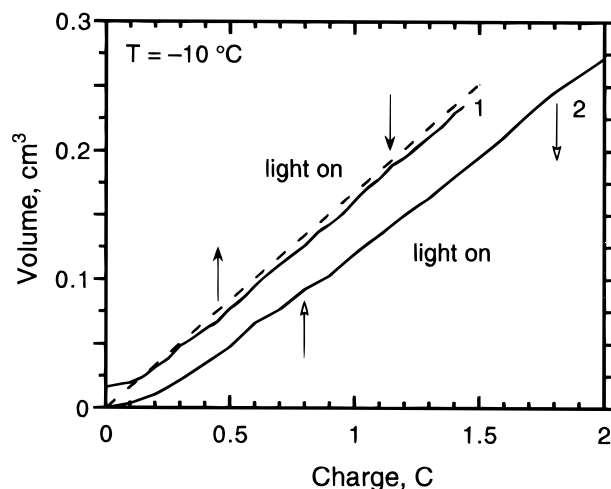


Figure 3. Electrolysis of pure ice at $T = -10\text{ }^{\circ}\text{C}$. The dashed line corresponds to 100% protonic conductivity of ice (Faraday's law). Curve 1 is the experimental dependence when a 100% rate of gas release is observed. Curve 2 is the dependence with gas deficiency. The arrows (solid for curve 1, open for curve 2) indicate the moments when UV light was turned on and off. No changes in the slopes of these curves were found.

The current–voltage dependencies I – V measured for ice samples were nonlinear and can be described as $I = \text{const} \cdot V^n$. For the sample from Figure 2, $n = 1.4$.

Discussion

It follows from the experiments that the nature of photocharge carriers in ice is closely related to the nature of intrinsic charge carriers in ice. Indeed, the illumination of ice does not change the slopes of the gas volume/charge curves. This means that illumination does not change the composition (the proportion) of mobile charge carriers, whatever it is. Indeed, if light would increase, for instance, the concentration of electron charge carriers compare to the protonic ones, then for the same amount of charge passed lesser amount of gas released is observed, resulting in the change of slope in Figure 3. Hence, if ice is a protonic conductor, its photoconductivity is protonic as well.

Thus, we need to answer the following questions: (1) Is ice really a protonic conductor? (2) If it is, then what is the reason for the observed deficit of gas released during electrolysis?

First of all, in 25% of our tests, gas release coincided with theoretical predictions for purely protonic conductivity of ice, both in darkness and under illumination. We can interpret this as proof that *both conductivity and photoconductivity of ice are of a protonic nature*. This means that solvated electrons e_s^- generated by UV light according to the reaction of “autoionization” do not participate in dc conductivity. Only protonic defects are mobile.

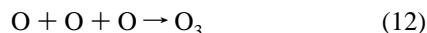
What happened to the other 75% of the tests? Where has the gas gone? Below are some possible reasons for the gas deficit.

1. There may be a leak in the experimental cell. However, no leak of our gas cell was detected using the standard procedures of vacuum technology. We observed 100% gas release for some samples. Declory et al.² also observed an apparent deviation from Faraday's law when they used low current densities, $j < 100\text{ }\mu\text{A}/\text{cm}^2$, working with pure ice; a lesser amount of released gas was measured. They concluded that there was a leak in their experimental cell. Our measurements confirm the fact of gas deficit at low current densities (less than $150\text{ }\mu\text{A}$ per 1.5 cm^2 for pure ice), but we do not relate it to a leak.

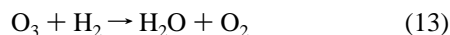
2. The released gas may be dissolving in ice, resulting in the deficit observed. The solubility of molecular hydrogen H_2 and oxygen O_2 in ice is limited by the value $\xi = 0.02 \text{ cm}^3/\text{cm}^3$ at atmospheric pressure.⁷ The corresponding amount of electric charge required to obtain these volumes is $Q = (3-10) \times 10^{-3} \text{ C}$. This value is at least 2 orders of magnitude less than the typical charges of 2 C passed through ice samples in our experiments. Thus, accumulation of the gases in ice cannot account for the discrepancy between theory and experimental results.

3. Charge carriers of an electronic type may exist in ice in addition to protonic carriers. The generation of such "electron" carriers could be limited by various factors; it could depend nonlinearly on specific conditions at the electrodes or on the purity of ice. When the concentration of intrinsic protonic carriers is higher than the concentration of electronic carriers, we observe the "100%" gas release. When ice is so pure that the concentration of protonic carriers is less than the concentration of generated electronic carriers, we see a deviation from Faraday's law. This mechanism can hardly explain the fact that the gas deficit was the same in the dark and under illumination that increased ice conductivity by 1 order of magnitude. It is very unlikely that UV light generates mobile electrons (or any charge carriers electronic in nature) and ions in precisely the same proportion as thermal generation does. Thus, we can reject the idea of participation of electrons in dc conductivity and photoconductivity.

4. When a strong electric field is applied to a sample, it is possible that the anodic reaction forms ozone, O_3 :



This ozone reacts with the molecular hydrogen released at the cathode



thus decreasing the volume of gas observed in the experiment.

5. Hydrogen peroxide, H_2O_2 , can be formed at the anode according to reaction 7. If this is the case, it will diminish the quantity of gas released.

We performed a series of tests for the presence of ozone, O_3 , or hydrogen peroxide, H_2O_2 , in the experimental cell. A colorimetric technique described in detail by Hochanadel⁸ was used for this purpose. We did not find either of these substances within the accuracy of the method, $5 \times 10^{-7} \text{ mol/L}$. Taking into account the large electric charges passed (up to 2 C) and the large molar concentrations of the substances presumed to be released (up to 10^{-1} mol/L), we should consider reactions 7 and 12 improbable.

6. When a strong electric field is applied, the metallic electrodes could serve as catalysts for a recombination reaction:



This process can be very sensitive to the electric field strength. Reaction 14 may explain the missing amount of gas. It may also explain why the volume of gas does not change after the experiment is done. Indeed, the experimental cell can remain for a few days without any displacement of the alcohol droplet in the capillary tube (i.e., a change in gas volume); see Figure 1. Probably the catalytic property of the metal surface is activated only by the applied voltage. This subject requires further investigation.

The current-voltage dependence $I = \text{const} \cdot V^n$, with $n = 1.4$, indicates that some kind of injection of charge carriers from electrodes into ice occurred. The injection of carriers of one sign, for instance, H_3O^+ ions, should give the dependence $I = \text{const} \cdot V^2$. To explain the factor $n = 1.4$, a more complex process should be considered. One of the possibilities is ambipolar diffusion of both H_3O^+ and OH^- ions, discussed by Petrenko and Chesnakov.⁹

Conclusion

We found, first, that the illumination of ice by UV light does not change the composition of charge carriers. The nature of photocharge carriers in ice is the same as that of intrinsic charge carriers. This means that photoconductivity in ice is protonic. Any solvated electrons generated by UV light do not participate in dc conductivity.

Second, at low current densities ($I < 100 \mu\text{A}/\text{cm}^2$) a deviation from Faraday's law is observed for electrolysis of ice. This deviation needs to be explained and requires further investigation.

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