

ВЛИЯНИЕ ЧАСТОТЫ ЭЛЕКТРИЧЕСКОГО ТОКА НА ЭЛЕКТРОПРОВОДНОСТЬ ТОНКИХ ПЛЕНОК ЭЛЕКТРОЛИТОВ

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В работе продолжены исследования эффекта аномально высокой электропроводности поверхности раздела воздух-электролит при электролитическом разложении воды. Эксперименты проводились как на переменном токе с помощью мостовой схемы, так и на постоянном, в четырехэлектродной ячейке. Ранее было показано, что в тонких слоях электролита, граничащих с воздухом, удельная электропроводность, измеренная в четырехэлектродной ячейке, при электролизе воды превышает соответствующую величину, измеренную с помощью мостовой схемы для растворов гидроксида натрия – в 1,5 раза, растворов серной кислоты – в 1,25 и растворах сернокислого натрия - 2,5 раза. При замене поверхности газ-жидкость на границу жидкость-твердая фаза эффект исчезал. Было показано, что аномально высокая электропроводность тонких слоев электролита на границе с воздухом зависит от температуры (при 4 °С электропроводность слоя раствора толщиной 1мм увеличивалась в 8-12 раз), ионного состава, рН (максимум увеличения электропроводности в 5 раз соответствует рН изоэлектрической точки). Это позволило предположить, что данный эффект обусловлен туннелированием заряда (без переноса массы) по упорядоченным структурам на поверхности воды – гигантским гетерофазным кластерам. Такой механизм был назван крокетным. Для проверки влияния поверхности были проведены эксперименты в слоях электролита толщиной от 1 мм до 0,1 мкм. Тонкие пленки электролита стабилизировались ПАВ ДС-10, и их толщина измерялась интерферометрическими методами. Было показано, что удельная электропроводность тонких пленок, по сравнению с электропроводностью исходного электролита, увеличивалась в 150-250 раз. Это подтверждало наши предположения о природе эффекта аномально высокой электропроводности поверхности раздела фаз газ-электролит при электрохимической генерации нескомпенсированных H⁺ и/или OH⁻ ионов. Неожиданно оказалось, что удельная электропроводность пленок электролита толщиной ниже 50 мкм при измерении на переменном токе частотой 10 кГц также превышает величины электропроводности, измеренной этим же методом в объеме исходного электролита. Величины электропроводностей тонких пленок электролита, измеренные разными методами, практически совпадали. Было предположено, что это явление связано с изменившимися усло-

виями заряжения двойного электрического слоя. Для проверки предположения были измерены величины удельной электропроводности слоя электролита толщиной 1 мм при изменении частоты переменного тока от 10 кГц до 0,1 Гц. Было показано, что эффект увеличения электропроводности начал проявляться при частотах до 1 кГц. Расчеты показали, что при этих частотах количество электричества, сообщаемое электродам, достаточно для заряжения двойного слоя и начала фарадеевского процесса. Таким образом, получено еще одно подтверждение, что крокетный механизм электропроводности проявляется при двух условиях: электролитическом генерировании H^+ или OH^- ионов и переносе зарядов по упорядоченным структурам на поверхности воды.

Ключевые слова: электропроводность, кластер, граница раздела фаз, перенос заряда

INFLUENCE OF FREQUENCY OF ELECTRIC CURRENT ON ELECTRIC CONDUCTIVITY OF THIN FILMS OF ELECTROLYTES

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In the work the investigations of the effect of abnormally high electric conductivity of surface of the air-electrolyte interface during electrolytic decomposition of water were continued. Experiments were carried out both at alternating current via the bridge circuit and at direct current in the four-electrode cell. Previously, it was shown that in thin air-bordering electrolyte layers specific conductivity measured in the four-electrode cell during electrolysis of water exceeds the corresponding value measured with the bridge circuit for solutions of sodium hydroxide by 1.5 times, for solutions of sulfuric acid by 1.25 times and for solutions of sodium sulfate by 2.5 times. When replacing the gas-liquid interface by the liquid-solid phase one the effect disappears. It was shown that the abnormally high electric conductivity of thin air-bordering electrolyte layers depends on temperature (at 4 °C electric conductivity of 1 mm thick solution layer increases 8-12 times), ion composition, pH (maximum 5 times increase of electric conductivity corresponds to pH of isoelectric point). This allowed suggesting that such effect is caused by tunneling of charge (without mass transfer) through ordered structures on the surface of water - giant heterophase clusters. This mechanism has been called croquet. To check the influence of surface the experiments in 1 mm and 0.1 mm thick layers of electrolyte were conducted. Thin electrolyte films were stabilized by the DC-10 surfactant and the thickness was measured by interferometric methods. It has been shown that specific electric conductivity of thin films increases by 150-250 times in comparison with conductivity of the original electrolyte. This confirmed our assumptions on the nature of the effect of abnormally high electric conductivity of the gas-electrolyte interface during electrochemical generation of uncompensated H^+ and/or OH^- ions. Surprisingly, it appears that specific electric conductivity of the electrolyte film of thickness below 50 μm as measured at the 10 kHz alternating current is also higher than conductivity measured with the same method in the initial electrolyte volume. The values of electric conductivity of thin electrolyte films measured by different methods were almost identical. It has been suggested that this phenomenon is related to the changed conditions of charging of the double electric layer.

To test the hypothesis, the values of specific electric conductivity of 1 mm thick electrolyte layer were measured at changing from 10 kHz to 0.1 Hz frequencies of alternating current. It was shown that the effect of increase in the electric conductivity begins to occur at frequencies up to 1 kHz. Calculations showed that at these frequencies the quantity of electricity transferred to the electrodes is sufficient for charging the double layer and initiation of the Faraday process. Thus, another confirmation that the croquet mechanism of electric conductivity occurs at the two conditions – the electrolytic generation of H^+ or OH^- ions and the transfer of charges through ordered structures on the surface of water – was found.

Key words: electric conductivity, cluster, water-air interface

Для цитирования:

Нефедов В.Г., Матвеев В.В., Королянчук Д.Г. Влияние частоты электрического тока на электропроводность тонких пленок электролитов. *Изв. вузов. Химия и хим. технология*. 2018. Т. 61. Вып. 2. С. 58–64

For citation:

Nefedov V.G., Matveev V.V., Korolyanchuk D.G. Influence of frequency of electric current on electric conductivity of thin films of electrolytes. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2018. V. 61. N 2. P. 58–64

INTRODUCTION

Water has physical and chemical properties that distinguish it from other liquids. The boiling and freezing points of water are the highest in the homologous series of oxides, the temperature dependences of density and dielectric constant have extremes at the temperatures of 4 and approximately 36 °C [1-5]. These properties of water are caused by the formation of associates of molecules connected by hydrogen bonds. Water also has abnormal electrochemical properties. Pure water is dielectric due to high activation energy of the reaction of its dissociation. In pure water there is no fast transfer mechanism that requires presence of an excess proton or hydroxyl ions [6]. Fast transfer and high mobility of H^+ or OH^- ions compared to other electrolyte solutions is caused by tunneling of charge between two properly oriented molecules of water. This mechanism is called a relay one. Another known fact of the conductivity anomalies is that for pure water the electric conductivity of solid phase (ice) is two orders of magnitude higher than the conductivity of its liquid phase. The abnormal electrical conductivity of water in solid state is linked to the ordered arrangement of molecules and shooting of a proton through the chain of hydrogen bonds, which cannot be divided into a multitude of proton hops between neighboring molecules [7]. Such a transfer requires existence of a long-range order in the arrangement of molecules, which is absent in liquid water [8]. In recent papers the experimental discovery of existence of ordered structures – giant heterophase clusters – is described [9-12]. The lifetime of such clusters in volume of water is about 10-12 s, which is comparable with the time of a proton tunneling between two molecules of water [7]. Probably, therefore the existence of such

structures has no effect on the electric conductivity of electrolytes. But there are indications that in the surface layer short-lived clusters become stable and their lifetime increases significantly [13,14]. Thermodynamic and kinetic stabilization of the clusters contribute to the leap of electrochemical potential on the surface of water with the gradient of about 10^6 V/cm.

As for today, there are no methods for direct investigation of the surface structure of water and water solutions, and there is contradictory information on its properties [15-20]. It is generally accepted that water molecules are oriented predominantly by the oxygen atom to the air and the OH^- ions forming a dense coat of the double electric layer are adsorbed on the H^+ ions of water molecules, that defines a negative electrokinetic potential of bubbles moving in the water.

In some cases, the electric conductivity anomalies also occur at different measurement methods. The [21] describes determination of the electric conductivity of ice crystals doped by HCl at the temperatures ranging from -10 to -150 °C and the current frequency ranging from $5 \cdot 10^{-4}$ to $5 \cdot 10^5$ Hz. It was shown that at low frequencies in the temperature range from -10 to -40 °C the activationless transfer of charge occurs, while measurements at alternating current in the same range showed higher electric conductivity due to rotational motion of the molecules.

We have suggested that if the surface of water stabilizes the existence of ordered structures (i.e. giant heterophase clusters) than thin films of water solutions of electrolytes should have high electric conductivity. In fact, our experiments have shown that specific electric conductivity measured in the four-electrode cell with 1 mm thick layer of electrolyte during the electrolysis of water exceeds the corresponding value

measured with a bridge circuit for solutions of sodium hydroxide 1.5 times, for solutions of sulfuric acid 1.25 times and for solutions of sodium sulfate 2.5 times. It was also shown that the abnormally high electric conductivity of thin layers of electrolytes at the interface with air depends on temperature (at 4°C the electric conductivity of 1 mm thick solution layer increases 8-12 times), ion composition, pH (maximum 5 times increase of electric conductivity corresponds to pH of isoelectric point) [22]. It should be noted that for the appearance of this effect the two conditions are required: 1) the presence of free gas-liquid interface and 2) the presence of uncompensated OH⁻ ions (H⁺ ions in the acid and H⁺ and OH⁻ ions in sodium sulfate solution). In the closed with a lid cell this effect was not observed. Also it was not observed in the open cell in case of usage of copper working electrodes and a solution of copper sulfate as an electrolyte, in conditions while the mentioned ions were not formed on the electrodes. This allowed suggesting that such effect is caused by tunneling of charge (without mass transfer) through ordered structures on the surface of water – giant heterophase clusters. This mechanism had been called croquet.

Previously, we had reported the increase in the electric conductivity of thin films of electrolytes as measured by alternating current [23]. The aim of this work was to determine the influence of the air-liquid interface on the value of the specific electric conductivity of electrolytes. For this purpose it was necessary to estimate the influence of thickness of electrolyte layer on the value of electric conductivity of a solution using a bridge circuit at alternating current and a four-electrode circuit at direct current.

EXPERIMENTAL

A cell with dimensions 10×10×20 mm with platinum electrodes mounted along the end walls was utilized for the experiments 1 mol/L sodium hydroxide solution with the conductivity of 19.8 S/m was used as an electrolyte. The electrolyte level during the experiments was varied from 1 to 10 mm in 1 mm increments at the constant current density in the electrolyte. During the measurements at direct current the voltage drop in the electrolyte was measured by chlorine-silver electrode probes, the distance between which was varied from 3 to 20 mm. The precise distance between the electrodes was controlled using the scale bar of the MBS-9 binocular magnifier. The current was set by the potentiostat PI-50-1 or the G6-28 generator of audio signals of specific form, the voltage drop was recorded by the S1-67 oscillograph. For the measurements at alternating current the classic bridge circuit was utilized.

The difference in the usage of circuits was that at direct current the electrolysis of water with generation of OH⁻ ions occurred on the cathode and for the bridge circuit with the frequency of alternating current of 10⁴ Hz it did not occur.

To measure the electric conductivity of less than 1 mm thick electrolyte films the Syntanol DS-10 surfactant was added to the electrolyte in concentration of 20 g/L. Insertion of the DS-10 additive leads to the decrease in electric conductivity from 19.8 to 17.4 S/m, which can be attributed to appearance of non-conducting micelles of DS-10 in the electrolyte. To measure the electric conductivity of less than 1 mm thick films we used two types of cells with different conditions of the film formation. One of them was a frame, the side walls of which were 200 μm diameter nickel wire electrodes and the end walls were thin polypropylene rods (Fig. 1, A). The width of the cells was 2 cm, the length was ranged from 2 to 7 cm. The film was formed after immersing and extracting the frame from the electrolyte with the surfactant. In the second type of cells (Fig. 1, B) the electrodes length reached 25 cm at the interelectrode distance of 2 cm. A movable fluoroplastic carriage was shifted along the electrodes. The electrolyte was fed into the gap between the carriage and the tripod member (2) by the microdoser. The film of different thickness was formed as the carriage moved away. The thickness of the films was evaluated by interferometric method.

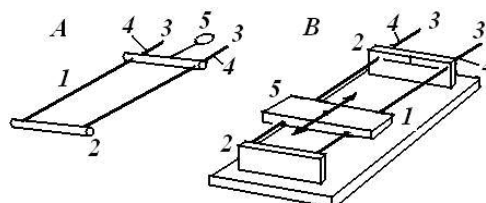


Fig. 1. Scheme of cells for investigations of conductivity of thin films A – frame-cell; 1 - electrodes 2 - polypropylene rods; 3,4 - current conductors for powering the working electrodes and connecting a measuring device; 5 - hanging loop. B - cell with movable carriage, 1 - electrodes 2 - tripod elements for securing the electrodes; 3,4 - current conductors for powering the working electrodes and connecting a measuring device; 5 - movable carriage

Рис. 1. Схема ячеек для исследования проводимости тонких пленок А – ячейка-рамка; 1 – электроды, 2 – полипропиленовые стержни; 3,4 – токоподводы питания рабочих электродов и для подключения измерительного прибора; 5 – петля для подвешивания, Б – ячейка с подвижной кареткой, 1 – электроды, 2 – элементы штатива для крепления электродов; 3,4 – токоподводы питания рабочих электродов и для подключения измерительного прибора; 5 – подвижная каретка

RESULTS AND DISCUSSIONS

1. Effect of layer thickness on the value of specific electric conductivity of electrolyte

The dependence of electric conductivity on the thickness of the electrolyte film is shown at Fig. 2,

where the ordinate axis shows the value of the coefficient of increase of electric conductivity defined as

$$K = \frac{\kappa}{\kappa_i},$$

where κ_i – value of specific electric conductivity of the initial solution; κ – value of specific electric conductivity measured at direct current or alternating current on the free electrolyte-air surface.

The figure shows that at the usage of direct current the electric conductivity of sodium hydroxide solution increases 1.05-1.5 times with the decrease of the layer thickness from 10 to 1 mm (curve 1). In the cell with the 1 mm thick layer the electric conductivity increases 1.5 times at the concentration range from 0.01 to 16 mol/L. In the layer of sodium hydroxide with DC-10 additive the increase is also observed but to a lesser extent (curve 2).

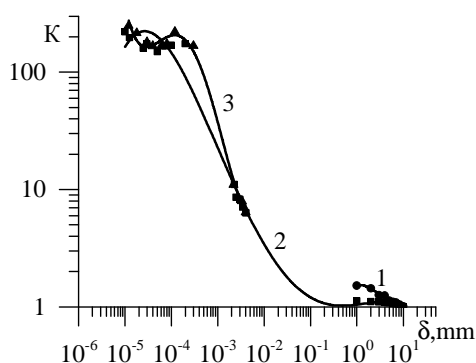


Fig. 2. Dependence of the coefficient of increase in the electric conductivity on the thickness of the electrolyte layer. 1 - measurements at the electrolysis in the 10^{-1} mm thick electrolyte layer without surfactant; 2 - measurements at the electrolysis in the electrolyte layer with the surfactant; 3 - measurements by the bridge circuit

Рис. 2. Зависимость коэффициента увеличения электропроводности от толщины слоя электролита. 1 - измерения при электролизе в слое электролита толщиной 10^{-1} мм без ПАВ; 2 - измерения при электролизе в слое электролита с ПАВ; 3 - измерения мостовой схемой

It should be noted that although the insertion of the surfactant leads to the reduction of the measured values of specific electric conductivity and the K coefficient due to transfer of the surfactant to the surface of aqueous solution and de-structuring of its surface (compare curves 1 and 2 in the range of the liquid layer thicknesses from 10 to 1 mm), the electric conductivity of 50 μm thick films increases approximately 10 times, and of 100-700 nm thick films – 200 times and remains approximately constant.

In the experiments with film thickness less than 1 μm the increase of electric conductivity was observed at the measurements at alternating current (Fig.

2, curve 3). It was assumed that this effect may be associated with such a small working surface of the electrodes being used that the quantity of electricity in the half-cycle of alternating current was sufficient for charging the double electric layer and beginning of the Faraday process.

If we assume that the capacity of the double electric layer per unit of surface area is $C_S = 20\text{--}40 \mu\text{F}/\text{cm}^2$ [24], and the electrode area in the frame-cell is determined by the length of the electrode $l_e = 7$ cm and the thickness of the electrolyte layer $\delta = (0.01\text{--}3.00) \cdot 10^{-4}$ cm, the charge that must be gained by the electrode for charging of the double electric layer C_{DEL} and beginning of the electrochemical decomposition of water $\Delta E = 1$ V, can be estimated as

$$Q_e = C_{DEL} \cdot \Delta E = (c_e l_e \delta) \cdot \Delta E \approx (0,01 \div 8,40) \cdot 10^{-8} \cdot C$$

On the other hand at the generator frequency of $f = 10$ kHz during the half-cycle of $\tau_{1/2} = 1/(2 \cdot f) = 0.5 \cdot 10^{-4}$ s for the mean value of the measured current $I = 1$ mA = $1,0 \cdot 10^{-3}$ A the electrode may gain the charge of

$$Q = I \tau_{1/2} \approx 5 \cdot 10^{-8} C$$

that does not contradict the made assumptions.

To check the conditions under which it is possible to realize the Faraday process at alternating current the following experiment was conducted.

2. Effect of alternating current on abnormally high electric conductivity of surface.

The experiments were performed in a cell with dimensions $10 \times 20 \times 1$ mm with platinum electrodes of approximately 0.078 cm² surface area placed at the end walls. The current was set by the G6-28 generator of signals of specific form, the voltage drop in the electrolyte was measured by auxiliary electrodes, as described above.

The measurements have shown that with the decrease of pulses frequency the value of current in the cell increases from 1.08 to 2.06 mA, which indirectly indicates a decrease of resistance of the cell. Specific electric conductivity was calculated on the basis of the Ohm law from the voltage drop in the electrolyte. The dependence of conductivity on the current frequency is shown at Fig. 3. As it follows from the figure in the frequency range of 300-10000 Hz the electric conductivity is constant and approximately equal to 15 S/m, and at the decrease of the frequency from 300 Hz to 0.1 it increases to about 23 S/m, i.e. 1.5 times, as previously observed.

Let's define the quantity of electricity required for charging the double electric layer and starting the Faraday process. For the electrode area of about 0.1 cm², the voltage in the half-cycle of 2 V and the current of about 1.5 mA the quantity of electricity should be

about $(8-4) \cdot 10^{-6}$ C and the current frequency about 1000 Hz, which satisfactorily coincides with the dependence at Fig. 3.

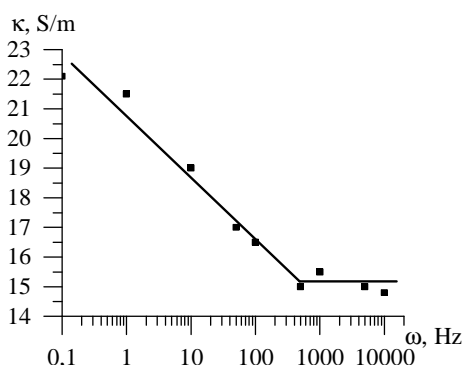


Fig. 3. Dependence of the specific electric conductivity on the frequency of alternating current

Рис. 3. Зависимость удельной электропроводности от частоты переменного тока

The obtained results suggest that for the $5 \cdot 10^{-3}$ mm thick films and the area of the electrodes of $3,5 \cdot 10^{-4}$ cm² at the frequency of 10 kHz the transferred quantity of electricity is enough for charging of the double electric layer and starting of the Faraday process. Thus, the abnormally high electric conductivity of surface can be also observed at alternating current, when during the half-cycle of current oscillations, the

transferred quantity of electricity is sufficient for charging the double electric layer and decomposition of water.

CONCLUSIONS

It was experimentally recorded more than two orders of magnitude increase of the specific electric conductivity in thin films of electrolytes bordering the air.

The increase of electric conductivity at the decrease of thickness of electrolyte film indicates significance of the gas-liquid interface for the abnormally high rate transfer of charges.

The cause of the abnormally high electric conductivity can be the transfer of charges through giant heterophase clusters (ordered structures of water molecules connected by hydrogen bonds) localized on the surface of the solution – the so-called croquet mechanism.

At measurements at alternating current this effect occurs when the current frequency decreases and depends on the type of the measuring system. Possible cause of the effect is related to the necessity to generate the OH⁻ ions. At the high frequency the double electric layer may not have enough time to keep charging up to the level required to start the Faraday process of ions generation.

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Поступила в редакцию 28.04.2017
Принята к опубликованию 27.09.2017

Received 28.04.2017
Accepted 27.09.2017