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Hydrogen spillover in the platinum–hydrous tin dioxide system

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The phenomenon of hydrogen spillover in the platinum–hydrous tin dioxide system leading to the growth of both protonic and electronic conductivity of the system was observed.

Hydrogen spillover is the diffusion of surface hydrogen atoms from catalyst (metal) sites, where they are produced by the dissociation of hydrogen molecules, to a support (oxide, carbon *etc.*), which has no activity for dissociative hydrogen adsorption. Hydrogen spillover was observed for the first time[1] in the 1960s, and the effect was demonstrated for various systems, mainly for platinum-coated metal oxides.[1–7] Spillover takes place in catalytic reactions[8] and often becomes a stage of catalytic processes.[9–11] The effect is accompanied by an increase in the electronic conductivity of semiconductor in the metal–semiconductor systems.[5,12,13] Hydrogen spillover effect was not described for the systems where a metal-coated substance was hydrous oxide. Hydrous oxides are usually characterized by high protonic conductivity, meanwhile the electronic conductivity of these types of oxides is negligible. The existence of hydrogen bonds in hydrous oxides gives a base to assume that spillover should be accompanied by proton migration in this system to increase the protonic conductivity. The detection and experimental observation of this phenomenon was the goal of this work. Hydrous tin dioxide (HTD) was used as a model system. It is a well-known proton conductor, and its electronic conductivity is negligible.[14,†]

The differential thermal analysis of two samples ($SnO_2 \cdot 1.5H_2O$ and $SnO_2 \cdot 1.7H_2O$) showed that the amount of water released during the temperature increase up to 100 °C (*i.e.*, the loss of physically adsorbed water[15]) equaled to the difference in total water content between these samples (see Online Supplementary Materials, Figure S1). Therefore, changes in atmospheric humidity and difference in the protonic conductivity associated with this change, are determined by different content of physically adsorbed water.

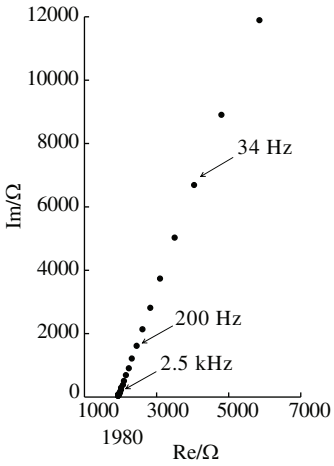

Figure 1 Impedance spectrum of the electrochemical cell Pt|$SnO_2 \cdot 1.5H_2O$|Pt in air. Thickness of the electrolyte, 1.1 mm.

The conductivity of samples in air was determined as a high-frequency cut-off on a real axis (Figure 1). Locus shape changes drastically in the presence of hydrogen and the locus shifts to a region with low resistance (Figure 2). A similar effect can be observed in a hydrogen–argon mixture. The impedance spectra in both cases can be described by an equivalent circuit in Figure 2. The low-frequency arc of a circle can be related to the processes on the electrode interface (*e.g.*, charging of a double layer and electrochemical reaction) or include the electronic conductivity. As regards high-frequency relaxational processes they can be determined by the thermoactivated conductivity of HTD volume and proton transfer on the grain surface of hydrous dioxide. Proton transfer on the surface has a diffusion nature (parameters $R_{surface}$ and $CPE_{surface}$) and equalizes the gradient of concentration induced by current flow. The parameter $CPE_{surface}$ has a type of constant phase angle element (CPA[16]). The parameters related to the electrode interface ($Z_{interface}$) can be separated from those related to the volume of sample ($R_{electronic}$, $R_{protonic}$, $R_{surface}$) by the analysis of their correlation with the sample thickness. The thickness will not have an influence on $Z_{interface}$. Relationships between the cut-offs (R_1, R_2 and R_3) determined by these parameters and the sample thickness (see Online Supplementary Materials, Figure S2) can be approximated by straight lines crossing the coordinate origin.

† HTD was prepared by precipitation from a tin tetrachloride solution with aqueous ammonia at pH 4. The precipitate was centrifuged and rinsed by distilled water several times until chloride ion tested negative. The precipitate was dried at ambient temperature in a vacuum. Thin HTD films were prepared for an optical spectroscopic study by drying a HTD–water dispersion in a vacuum. Optical spectroscopy was carried out on a Specord M40 spectrophotometer.

Water was determined by thermogravimetry (NETZSCH, STA 409C Luxx). The impedance spectra were measured on a z350m 'Elins' impedancemeter in a frequency range of 0.014 Hz–0.5 MHz in symmetrical electrochemical cells with sandwich-type gas-transparent electrodes C|HDT|C (where C is carbon black Vulcan XC-72) and Pt|HTD|Pt (Pt is platinum sponge). The electrode thickness was 0.1 mm in all cases. Samples of HTD were pressed into pellets (thickness of 0.4–3.5 mm, diameter of 3 mm) at 1 MPa. In all measurements, the pellets were kept at a constant humidity for three days before the electrodes were coated.

During the impedance measurements, the electrochemical cells were placed into a leakproof chamber, which then was filled with a mixture of air or argon with hydrogen in the specified ratio. Both of the electrodes in the electrochemical cell were exposed to the atmosphere in the chamber.

Two HTD samples were kept at 43 and 96% relative humidities (RHs). The compositions determined by thermogravimetry were $SnO_2 \cdot 1.5H_2O$ (for 43% RH) and $SnO_2 \cdot 1.7H_2O$ (for 96% RH) and the protonic conductivities were $(7.8 \pm 0.3) \times 10^{-4}$ and $(1.5 \pm 0.2) \times 10^{-3}$ Ω^{-1} cm^{-1}, respectively.

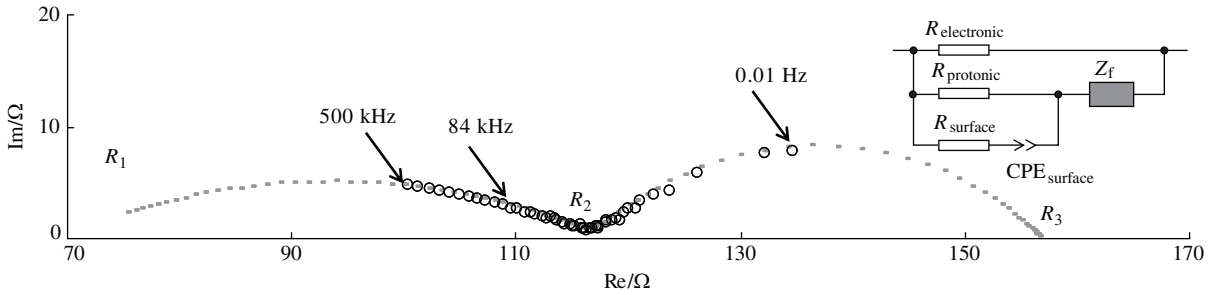

Figure 2 Impedance spectrum of the electrochemical cell $Pt|SnO_2{\cdot}1.5H_2O|Pt$ in an air–hydrogen (1:1) mixture. Thickness of the electrolyte, 0.4 mm. $1/R_1 = 1/R_{electronic} + 1/R_{protonic} + 1/R_{surface}$; $1/R_2 = 1/R_{electronic} + 1/R_{protonic}$; $R_3 = R_{electronic}$.

Therefore, these parameters are associated with the volume of the material and the effect of the electrodes is insignificant. Current-voltage characteristics of the sample (in the hydrogen–air mixtures, Pt-electrodes) were obtained to control the adequacy of the proposed equivalent circuit. The electronic resistance calculated from these characteristics equaled to the resistance obtained from impedance spectra. It can be concluded that the presence of hydrogen leads to the appearance of electronic conductivity and to the growth of protonic conductivity of HTD.

Measurements of impedance spectra in the atmosphere with different humidity have shown that the protonic conductivity of $SnO_2{\cdot}1.5H_2O$ (RH 43%) in hydrogen–air mixtures is considerably higher than that of $SnO_2{\cdot}1.7H_2O$ (RH 96%) in the absence of hydrogen (Figure 3). This fact testifies that the effect of the growth of protonic conductivity is not associated with water formation on the surface of platinum. Note that the observed effect is reversible. The growth of electronic conductivity in hydrogen–air mixtures was also observed for the dry $Pt–SnO_2$ system (see Online Supplementary Materials, Figure S3).

The increase in the sample conductivity in a hydrogen-containing atmosphere was not observed when carbon black electrodes were used instead of platinum. Therefore, the processes responsible for the effect originate at the platinum–HTD boundary and do not arise from the interaction of hydrogen with HTD on a whole surface.

HTD is a protonic conductor.[14] The study of HTD films by UV spectroscopy (fundamental absorption edge measurements) was carried out. The energy gap width of HTD is 3.6 eV and equaled to that of anhydrous SnO_2. The presence of semiconducting properties in HTD leads to the following assumed mechanism of the increase in electronic and protonic conductivity. First, the dissociative adsorption of hydrogen molecules on the surface of platinum takes place. Second, the migration (spillover) of hydrogen atoms to the surface of HTD occurs. The oxidation (electron transfer) of hydrogen atom takes place on the Pt|HTD interface. Not only experimental data demonstrating the reversible migration like this for some systems such as platinum–semiconducting oxide but also the computational study of capability of such a process were reported.[17,18] Note that, besides hydrogen atom, a solvated proton can also migrate.[19] The most probable process on the platinum–HTD interface is proton migration followed by diffusion into the bulk of the material due to a concentration gradient, which leads to an increase in the protonic conductivity of the system. It is impossible to determine definitely whether the proton is localized on the grain surface or penetrates into the crystalline cell. An electron in such a system goes to the conduction band of HTD.

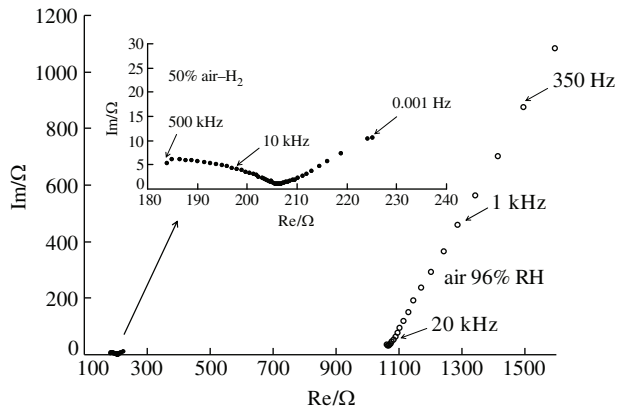

Figure 3 Impedance spectra of the electrochemical cells $Pt|SnO_2{\cdot}1.5H_2O|Pt$ in an air–hydrogen (1:1) mixture and $Pt|SnO_2{\cdot}1.7H_2O|Pt$ at 96% relative humidity. Thickness of electrolyte, 1.1 mm.

Thus, it was experimentally demonstrated that hydrogen spillover in the platinum–HTD system is accompanied by a significant increase in both protonic and electronic conductivities, and a probable mechanism of these phenomena was described.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2009.09.022.

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