

Influence of humidity and thermal decomposition on the protonic conductivity of single and polycrystalline CsH₂PO₄

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Abstract

The influence of the preparation conditions and metaphosphate secondary phase on the proton conduction and chemical stability of the single and polycrystalline CsH₂PO₄ samples was studied by the ac admittance technique. The relation between frequency dependences of the admittance plots and adsorbed water as well as a content of the metaphosphate phase was determined. It was shown that in ambient conditions the thermal decomposition reactions start on the sample's surface at temperatures above specific point, $T_1=425$ K, and the rate of the decomposition reactions on the interfaces is strongly influenced by the sample's quality. It is suggested that this reaction is initiated by the melting of the thin layer of CsH₅(PO₄)₂ on the surface of CsH₂PO₄. The variation of the contributions of the intergrain and electrode–proton conductor boundaries to the total admittance with the temperature was studied for polycrystalline CDP samples and obtained data were compared with those for nominally pure CDP single crystal samples.

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1. Introduction

Crystalline proton conductor CsH₂PO₄ (CDP) exhibits high conductivity (more than 10^{-2} S cm⁻¹) as a cubic phase ($T > T_{sp} = 503$ K) [1–5]. Recently, the possibility of using CDP in a fuel cell operating at moderate temperature was demonstrated [6,7]. Despite good cell performance, long-term stability is strongly influenced by thermal decomposition and subsequent formation of the low-conductive metaphosphate phase [5–10]. To improve performance and thermal stability, it is important to understand the origin of the physical–chemical processes and their influence on the protonic conductivity. The results of the previous studies showed that these phenomena are very sensitive to the temperature, quality of the material and preparation technique (mechanical and thermal treatment during the synthesis, atmospheric humidity) [5–11]. Thus, detailed investigations need to be completed in order to improve the CDP performance. In the first place, it demands the separation

of the bulk and surface phenomena occurring in the material at working temperatures.

It is well known that the experimentally measurable admittance $Y^*(\omega)$ consists of the bulk admittance $Y^*(\omega)_b$ and the contributions of the grain boundary $Y^*(\omega)_g$, electrode–electrolyte $Y^*(\omega)_e$ and sample's surface $Y^*(\omega)_s$. Therefore, the analysis of the frequency dependences of $Y^*(\omega)$ allows us to separate these contributions and investigate their sensitivity to the various factors outlined above.

In this study, the frequency and temperature dependences of the complex admittance were measured for low-conductive monoclinic phase of single and polycrystalline CDP. In addition, the distinctive features of the frequency dependence of the constituents $Y^*(\omega)_b$, $Y^*(\omega)_g$, $Y^*(\omega)_e$ and $Y^*(\omega)_s$ were established.

2. Experimental

The CDP single crystals were grown from water solutions by the evaporation method with slow decreasing of the temperature. The powders were prepared by grinding of the single crystals or commercial reagent (Reakhim, purity of at least

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99.9%) in agate mortar. Resulting powders were pressed at about 1000 kg/cm² with the obtained pellets having a thickness of $d=2$ mm and the square $S=70$ mm². The single crystal samples had the shape of the rectangular plates with size: $S=40$ mm² and $d=1$ mm². Silver paint was used to make the electrodes. The powders as well as the resulting pellets were treated in different ways (see Table 1) depending on whether the influence of water adsorption–desorption or annealing temperature and aging were studied. The conductance $G(\omega)$ and capacitance $C(\omega)$ were measured by automatic bridge VM 595 in the frequency range $100 \text{ Hz} \leq f \leq 20 \text{ kHz}$ and temperature range 290–480 K. The normalized complex admittance is determined as

$$Y^*(\omega) = Y'(\omega) + iY''(\omega) = G(\omega) \frac{d}{S} + i\omega C(\omega) \frac{d}{S}, \quad (1)$$

where $\omega=2\pi f$ is the angular frequency.

3. Results and discussion

In general, case frequency dependence of the experimental admittance is given by the equation:

$$\begin{aligned} Y^*(\omega) &= \sigma_{\text{dc}} + i\varepsilon_{\infty}\varepsilon_0\omega + Q(i\omega)^n \\ &= \sigma_{\text{dc}} + Q\cos(n\pi/2)\omega^n + i\varepsilon_{\infty}\varepsilon_0\omega \\ &\quad + iQ\sin(n\pi/2)\omega^n, \end{aligned} \quad (2)$$

where σ_{dc} is the bulk dc conductivity, ε_{∞} is the high-frequency dielectric permittivity, ε_0 is the permittivity of free space, Q the modulus of the complex ac conductivity, and n the exponent. The parameters σ_{dc} , ε_{∞} , Q and n are frequency independent. The term $Q(i\omega)^n$ is the complicated function of the bulk complex ac conductivity $\sigma_{\text{ac}}^*(\omega)$ and constituents $Y^*(\omega)_e$, $Y^*(\omega)_g$, $Y^*(\omega)_s$. Therefore, frequency and temperature dependences of the experimental admittance $Y^*(\omega)$ are rather difficult to analyze. Due to this fact, the representation of $Y^*(\omega)$ in log–log scale is preferable because power law frequency response is much more sensitively assessed when presented in this form.

Fig. 1 shows typical admittance plots of different CDP samples measured at room temperature (RT). These plots strongly differ due to dependence on the preparation conditions of the samples. Nevertheless, the frequency dependences of the single and polycrystalline samples reveal a number of features. It can be seen that with the exception of the plot of sample #2 the other plots represent straight lines on the double logarithmic

Table 1
Summary of the sample's preparation

#	Sample	Technique of preparation
1	Single crystal	Single crystal plate cut parallel to (100) plane
2	Grounded commercial CDP reagent	Polycrystalline pellet pressed at RT and calcinated at 210 °C in air during 1 h
3	Grounded commercial CDP reagent	Polycrystalline pellet pressed at RT in air at 20 °C with CCl ₄ as binder
4	Grounded single crystals	Polycrystalline pellet; powder was dried at 85 °C and pressed at 70 °C and heated up to 100 °C in vacuum

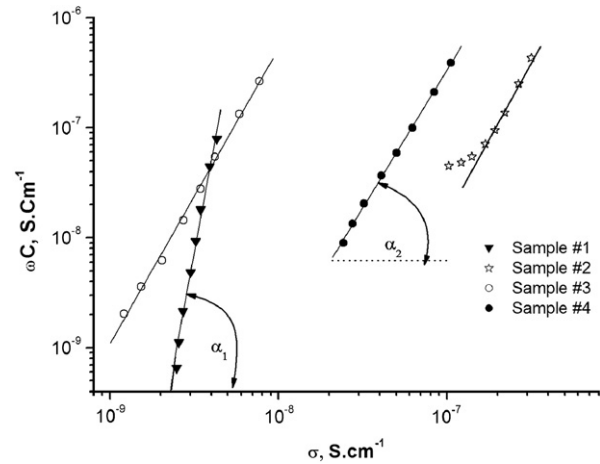


Fig. 1. Logarithmic representation of the frequency dependences of the admittances $Y^*(\omega)$ of the single crystal and powder samples prepared at different conditions and measured at room temperature before heating.

scale. For the single crystal (sample #1) this is a pronounced vertical line with a slope angle tangent $\text{tg}\alpha \approx 10$. This indicates that only two terms in Eq. (2), $\sigma_{\text{dc}} + i\varepsilon_{\infty}\varepsilon_0\omega$ (corresponding to the bulk frequency response), dominantly contribute to the measurable admittance. Moreover, in this case the condition $|\sigma_{\text{dc}}| < |\varepsilon_{\infty}\varepsilon_0\omega|$ is fulfilled. However, for the polycrystalline samples #3 and 4, the admittance plots represent inclined lines with smaller slope $\text{tg}\alpha \approx 2$. In the terms of Eq. (2), the third member $Q(i\omega)^n$ becomes progressively more significant because for polycrystals the admittance of the grain boundaries $Y^*(\omega)_g$ dominates. It should be noted that for sample #2 only high-frequency part of the admittance plot is characterized by slope 2 (Fig. 1). The deviation of the low-frequency part from linearity is due to the contribution of the electrode admittance $Y^*(\omega)_e$ caused by this sample's high dc conductivity. The change of the constituents $Y^*(\omega)_g$ and $Y^*(\omega)_e$ with the temperature, and their relative contributions to the experimental admittance $Y^*(\omega)$ are illustrated by Fig. 2. Upon heating, the frequency range of the nonlinear part of the admittance plot extends to the high-frequency region indicating the increase of

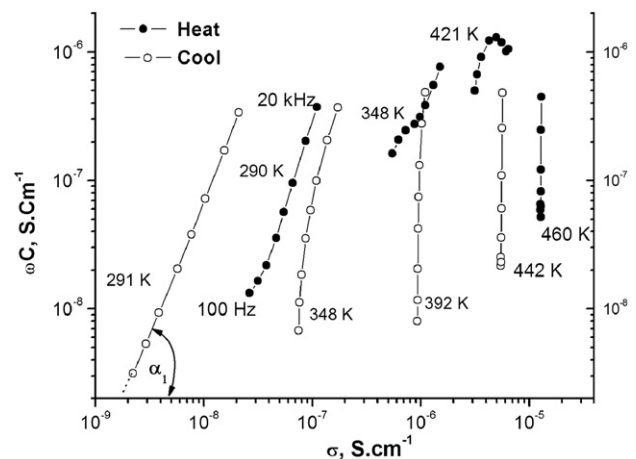


Fig. 2. Thermal evolution of the complex admittance $Y(\omega)$ in logarithmic representation for sample #2 upon heating and cooling.

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