

Comparative studies of polarizable dielectric fluids in yttrium-doped barium cerate by permittivity spectroscopy

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This paper presents results from studies of processes and phenomena associated with the behavior of polar dielectric liquid (water and alcohol) in the non-polar proton conducting dielectric ceramic material yttrium doped barium cerate $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\alpha}$ (BCY15). The investigation was performed by Permittivity Spectroscopy which is a branch of the Impedance Spectroscopy especially tuned for measurements and analysis of dielectrics permittivity properties. The measurements were carried out in frequency range 1 MHz down to 0.01 Hz. A gigantic enhancement of the effective capacitance was observed above a certain level of wetting. The influence of the water is stronger than that of the alcohol, which is described with difference in their polarization ability. The results are explained with the formation of absorbed dipole film in the porous ceramic matrix. This phenomenon finds application in proton conducting solid oxide fuel cells.

Key words: permittivity spectroscopy, yttrium-doped barium cerate, impedance spectroscopy, gigantic enhancement of the real part of the complex capacitance, complex permittivity.

INTRODUCTION

Permittivity Spectroscopy is a branch of Impedance Spectroscopy which is tuned for measurement and analysis of dielectrics permittivity properties. In general permittivity is the ability of a space (free or filled with dielectric) to be polarized under external electric field. For some dielectrics this ability is the ground for their property to react on alternative current.

According to the general theory [1,2], dielectrics could be classified in three categories: (i) non-polarizable; (ii) polarizable and (iii) ionic crystals. Non-polarizable dielectrics do not contain dipoles. Polarizable dielectrics contain dipoles (primary or induced) which follow the orientation of an external electric field. When such a field is applied by external electrodes, the dipoles near the electrodes are oriented correspondingly and compensate the external electric field.

The pure capacitive impedance follows the dependence:

$$Z(i\omega) = -i(\omega C)^{-1}, \quad (1)$$

where C is the capacitance. For parallel plate capacitor, it can be expressed as [1-4]:

$$C = \frac{\varepsilon \varepsilon_0 S}{d}, \quad (2)$$

where ε is the relative dielectric permittivity and ε_0

is the permittivity of vacuum, S is the surface area of the capacitor electrodes and d is the distance between them.

Taking into account the polarization losses, when A.C. signal is applied, the relative permittivity can be expressed as a complex number [1,2]:

$$\varepsilon = \varepsilon' - i\varepsilon'', \quad (3)$$

where ε' and ε'' denote the real and the imaginary (loss factor) components of the complex value of ε . Applying equations (2) and (3), the capacitance can be also presented in a complex form:

$$C = C' - iC'' \quad (4)$$

If Eqn. 1 is expressed as admittance $Y(i\omega) = 1/Z(i\omega)$, then

$$Y(i\omega) = i\omega C = i\omega(C' - iC'') = \omega C'' + i\omega C'. \quad (5)$$

The real component $\omega C''$ in Eqn.5 can be regarded as dielectric conductivity [4], which can be expressed also as equivalent resistance $R = 1/\omega C''$ directly monitored by the instrument. It involves the energy dissipative effects as ohmic conductivity, dipole's reorientation losses in electric field and others. C'' is directly related to the dielectric permittivity, i.e. to the polarization ability.

In solid oxide fuel cells (SOFC) water is produced in the porous ceramic matrix of the anode, which has high ionic conductivity at operating temperatures. In several studies on

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yttria-stabilized zirconia (YSZ) based cermet anode a hypothesis for hydroxylation of the active anode surface caused by interaction of YSZ with the produced water is proposed [5-7]. It is expected that this process should improve the conductivity of the ceramic matrix. Thus studies of water behavior as a polarizable fluid in non-polarizable ceramic matrix are important for deeper insight into the mechanisms of SOFC operation. Permittivity spectroscopy can be a useful tool for experiments performed at room temperature where the ceramic matrix will behave as non-polarizable dielectric.

Yttrium-doped barium cerate $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\alpha}$ (BCY15) is one of the best electrolytes for proton conducting solid oxide fuel cells (PCFC). Recently, it was applied in a new SOFC design known as dual membrane fuel cell (dmFC) [8-10], in which water is produced in a separate compartment. It has mixed ion (proton and oxide ion) conductivity and porous structure, which ensures water formation and evacuation. Due to the discovered mixed ionic conductivity of BCY15 [11] the so called "monolithic" design was developed. It could be also very beneficial for operation in electrolyzer mode due to the separation of the steam from the two electrodes where hydrogen and oxygen are generated and evacuated. For deeper insight into the processes at the interface BCY/water, permittivity studies were performed for a first time on porous composite samples of proton conducting $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\alpha}$ (BCY15) and oxide ion conducting $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ (YDC15) as well as on BCY15 samples [12,13]. Our experimental results [12,13], registered gigantic enhancement of real component of capacitance C' at a certain level of watering. The effect is stronger for BCY15 samples, which was explained with hemisorption of water species followed by formation and organization of dipole film that covers the pores surface. Very probably the process starts as hydroxylation of the surface [14], preferably the BCY one, for which the dissociative absorption of water is a natural property [15]. This brings to the appearance of a longer-range interaction with volumetric group effect.

The purpose of this work is a deeper insight into the processes and phenomena in the system BCY/polar dielectric liquid combined with further improvements of the complex permittivity analysis. The study stresses on the influence of the polarizable dielectric on the behavior of the system. This investigation is an important step in the

optimization of the "monolithic" dmFC design for operation in reversible mode.

EXPERIMENTAL

The complex permittivity measurements were carried out on porous BCY15 sample with diameter and thickness respectively 2cm and 1,14mm and 33% porosity obtained with graphite as pore former and evaluated by mercury porosimetry and hydrostatic weighing.

BCY15 pellets stability in water has been tested by Differential Thermal Analysis and Thermogravimetry combined with Mass Spectroscopy in the temperature range 20-600°C. A good chemical stability has been observed [16]. The reproducibility and reversibility of the permittivity measurements confirmed the stability of the samples in the selected experimental conditions.

The complex permittivity measurements were performed on Solartron 1260 FRA in frequency range 1 MHz – 0.1 Hz at room temperature with amplitude of the signal 1V and density 5 points/decade. The experimental cell consists of two coaxial brass cylindrical electrodes with coplanar working surface.

The permittivity measurements were carried out first on dry membranes (with humidity equal to that of the ambient atmosphere), followed by a series of measurements with increasing quantity of the liquid introduced in the volume of the samples with a micropipette. Preliminary calibration measurements of pure liquid (water or ethanol) in spacer with the dimensions of the sample showed lack of frequency dependence [12].

The measured data are presented in C'/f or R/f plots, where f is the frequency [12]. The plot is very illustrative for registration of the investigated phenomena. It is used by other authors for studies of permittivity enhancement in ceramic dielectrics [14,17,18].

RESULTS AND DISCUSSION

The results from permittivity measurements of BCY15 sample with 33% porosity at different quantities of ethanol and water are presented in Fig.1. For dry samples a small increase of C' is observed below 1Hz. Having into account the strong affinity of BCY15 towards water, this increase could be caused by the ambient humidity. The effect of water on the enhancement of C' is stronger than that of ethanol – for one and the same sample the sharp increase of C' starts at 20 μ l water with enhancement of 3 orders, while for ethanol it

is observed at 60 μ l and the enhancement is only 10 times. This result is in agreement with the dielectric constant of the two fluids (82 for water and 25,5 for ethanol)[19], which reflects their polarization ability. The additional quantity of the two liquids increases slightly C' (Fig.2).

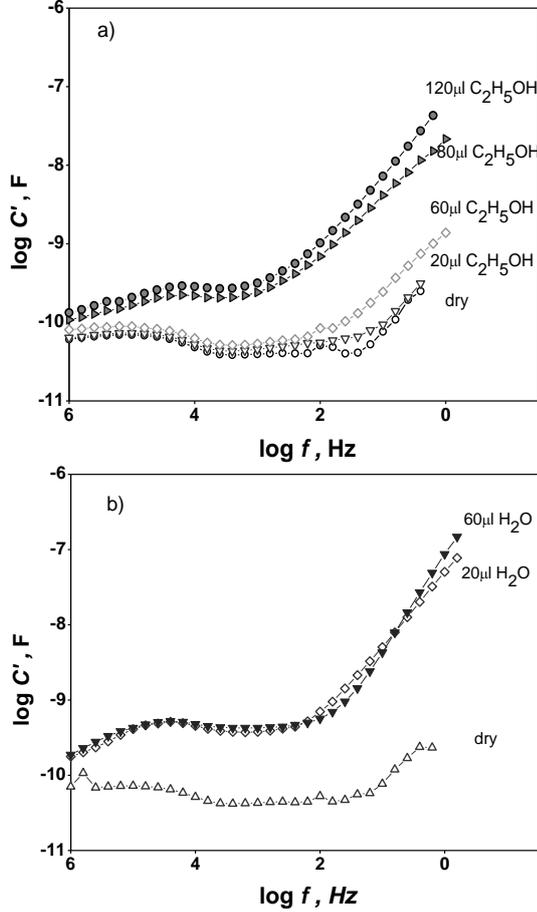


Fig.1. Permittivity measurements of BCY15 sample: a) frequency dependence of C' at different quantities of ethanol; b) frequency dependence of C' at different quantities of water

For elimination of the sample geometry and the influence of the experimental set-up, a dimensionless parameter, named coefficient of enhancement γ_i , was introduced:

$$\gamma_i = \frac{C'_i}{C'_0}, \quad (5)$$

where C'_i is the capacitance at a given frequency ω_i and C'_0 is the capacitance at the highest measured frequency (Fig. 2). Its frequency dependence for the measurements presented in Fig. 1 is given in Fig. 2.

For better presentation of the relation between the enhancement of C' and the microstructure of the ceramic the so called single-frequency analysis was introduced (Fig.3), where the quantity of the liquid is recalculated as percentage of the pores filling in

respect to the measured porosity; the coefficient of the enhancement is calculated at one and the same frequency - the lowest one where reliable results are observed for all the measurements. Results for γ_{4Hz} are presented in Fig.3.

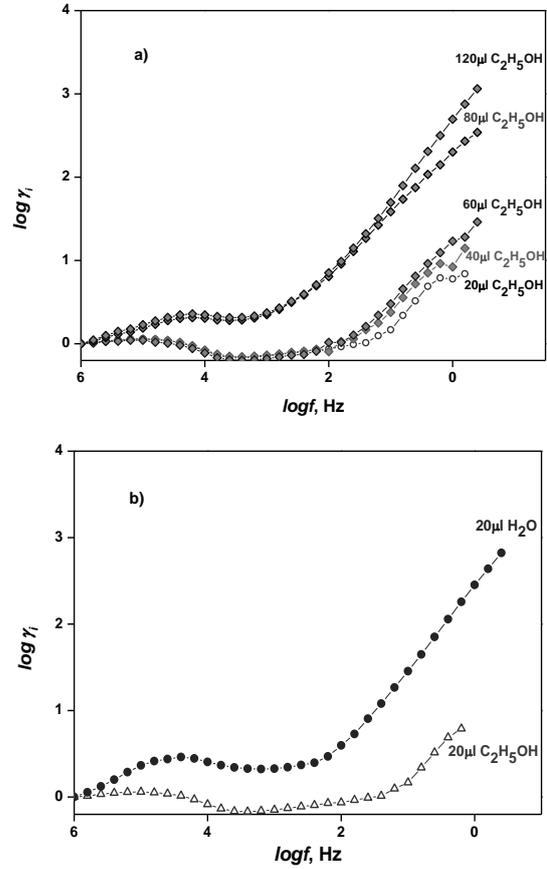


Fig.2. Frequency dependence of the coefficient of enhancement γ_i for BCY15 sample: a) frequency dependence of γ_i at different quantities of ethanol; b) frequency dependence of γ_i for one and the same quantity of water and ethanol

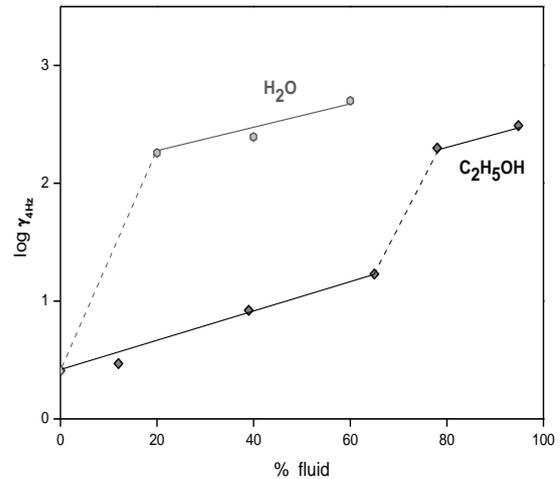


Fig.3. Single-frequency analysis of γ_i at $i = 4Hz$ for water \circ and ethanol \diamond .

CONCLUSIONS

The observed results confirm that the phenomenon gigantic enhancement of C' 's related to the interaction of the well developed hydrophilic ceramic surface with the polar dielectric liquid, which brings to the formation of liquid dipole layer (at elevated temperatures – semiliquid). The effect is stronger for the fluid with higher dielectric constant. This phenomenon should increase the conductivity of the ceramic matrix, which explains the enhanced oxide-ion conductivity of porous BCY15 in wet oxygen registered by impedance spectroscopy. The formation of electrochemically active volumetric hydroxylated layer can be of big importance for operation in electrolyzer mode.

In classical SOFC the water is produced in the porous anode. The developed methodology of complex permittivity could be a new tool for elucidation of water behavior in SOFC anodes. Some experiments on YSZ/Ni cermet are in progress.

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СРАВНИТЕЛНИ ИЗСЛЕДВАНИЯ НА ДИЕЛЕКТРИЧНИ ПОЛЯРНИ ФЛУИДИ В ИТРИЕВО ДОТИРАН БАРИЕВ ЦЕРАТ ЧРЕЗ ДИЕЛЕКТРИЧНА СПЕКТРОСКОПИЯ

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(Резюме)

Представени са резултати от изследвания на процеси и явления, свързани с поведението на полярни диелектрични течности (вода и алкохол) в неполярен протон провеждащ керамичен материал - итриево – легиран бариев церат $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\alpha}$ (BCY15). Изследването е извършено с Диелектрична спектроскопия, която е клон на Импедансната спектроскопия, използвана за измервания и анализ на свойствата на диелектричната проникваемост. Измерванията се провеждат в честотен диапазон от 1 MHz до 0.01 Hz. Наблюдавано е гигантско нарастване на ефективния капацитет над определено ниво на омокряне на образците. Влиянието на водата е по-силно от това на алкохола, поради различната им поляризационна способност. Резултатите са обяснени с образуването на диполен абсорбционен филм в пористата керамичната матрица. Това явление намира приложение в протон-проводящи оксиди за твърдооксидни горивни клетки.