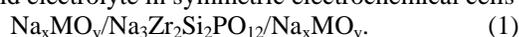


Electrochemical Behavior of Na⁺-Oxide Bronze/Na⁺-Solid Electrolyte Interface

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Sodium-oxide bronzes of the general formula Na_xMO_y are non-stoichiometric compounds having the mixed ion-electronic conductivity. In consequence of this property the bronzes can be used as reversible electrodes in contact with sodium-conducting solid electrolytes (Na⁺-SE). The certain compositions of these bronzes - Na_{0.5}WO₃, Na_{0.6}CoO₂ and Na_{0.33}V₂O₅ - were studied as reference electrodes in the solid-state potentiometric gas sensors [1]. Analogous bronzes were chosen as electrode materials for impedance spectroscopy investigation. The compound Na₃Zr₂Si₂PO₁₂ ("true" NASICON) was used as a solid electrolyte in symmetric electrochemical cells



The cells of type (1) were prepared by consecutive pressing (at 250 MPa) of the powders of corresponding bronze and a solid electrolyte between two platinum discs in a cylindrical mold made of PMMA.

The impedance of the cell was measured in the frequency range $f=0.07 - 100$ kHz. Analysis of the frequency dependence of the electrode impedance components $Z_e=R_s-j(\omega C_s)^{-1}$ has shown that ac behavior of the Na_xMO_y/Na⁺-SE interfaces corresponds to the model of adsorption relaxation of the electrical double layer [2, 3]. It can be described by both the equivalent electric circuit (Fig.1) and the impedance equation in the form

$$Z_e = \{j\omega C_{dl} + R_F^{-1} + [R_A + (j\omega C_A)^{-1} + (1-j)W_A\omega^{-1/2}]^{-1}\}^{-1}, \quad (2)$$

which indicates quick adsorption of solid electrolyte conductivity ions (C_{dl}), the discharge \leftrightarrow ionization reaction of these ions at the interface (R_F), and also the slow process of diffusion (W_A) and adsorption (R_A and C_A) of rigid lattice ions (possibly O^{2-} ions for NASICON [4]). The parameters of equation (2) were determined in compliance with the previously proposed algorithm [3]. The ion reversibility of the Na_xMO_y/Na⁺-SE interface is characterized by both a charge transfer resistance (R_F) and an exchange current (i_0) for the Faraday reaction $\text{Na}^+ + e^- \leftrightarrow \text{Na}$ that can be calculated according to the relation

$$i_0 = RT/zFR_F. \quad (3)$$

Fig.1 demonstrates the graphical method of determination of charge transfer resistance (R_F).

As seen in Table 1, the values of both R_F and i_0 for the interfaces with such bronzes as Na_{0.6}CoO₂, Na_{0.5}WO₃ and Na_{0.33}V₂O₅ are the same order. The certain increasing i_0 with decreasing the content of sodium ions in the bronze structure (x) is observed. Analogous phenomenon was observed for the Na_xCoO₂/NASICON interface with x equals to 0.6 (β -phase), 0.8 (α' -phase) and 1 (α -phase) [1]. As supposed in [5], electron holes are dominant charge carriers in the cobalt bronze structure. Their concentration in elementary cell is $1-x$. The higher initial concentration of electron holes is, the greater is the amount of sodium that can be injection into the structural space between the layers of the CoO₆-octahedra. Perhaps this supposition is applicable for an explanation of more high ion reversibility of the interface with oxide bronzes having less in content of Na⁺-ions in spite of a various nature of M-ions in their structures.

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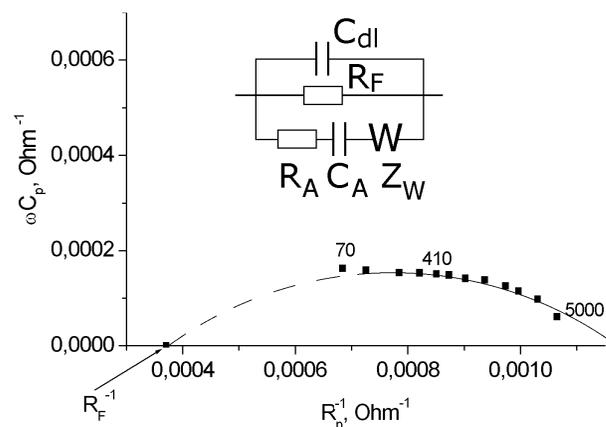


Fig.1. Equivalent electric circuit and complex admittance plane plot for the Na_{0.5}WO₃/NASICON interface at T=20°C, H=52% rel. The numbers at the points are frequencies in Hz.

Table 1. The values of charge transfer resistances (R_F) and exchange currents (i_0) at T=(22±2)°C.

Bronzes	R_F , Ohm*cm ²	i_0 , μA*cm ⁻²
Na _{0.6} CoO ₂	733	35
Na _{0.5} WO ₃	400	63
Na _{0.33} V ₂ O ₅	280	90