EQUIVALENT CIRCUIT ANALYSIS OF A THREE-CARRIER ELECTROLYTE/ELECTRODE SYSTEM

Tatsuya Kawada, Graduate School of Environmental Studies, Tohoku University
kawada@ee.mech.tohoku.ac.jp
Keiji Yashiro, Graduate School of Environmental Studies, Tohoku University
Yuta Kimura, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
Kotaro Okuyama, Graduate School of Environmental Studies, Tohoku University
Arthur Bourdon, Graduate School of Environmental Studies, Tohoku University
Koji Amezawa, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

Key Words: Proton conductor, multi carrier, equivalent circuit, transient response, impedance

Perovskite type proton conductors are known to show non-monotonous transient responses due to non-ignorable contributions of holes and oxide ions as minor carriers. Efforts have been made to simulate the behavior of the three-carrier systems by numerical calculations[1-4]. In most cases, however, the calculation assumes reversible electrodes, and the results are not directly applicable for analyses of experimental results such as impedance spectra. The purpose of this study is to develop an equivalent circuit model of a three-carrier conductor as a simple but theoretically feasible tool to be used for practical analyses. In the modeling, charge carriers were assumed to be $H_i^{\bullet}$, $V_O^{\bullet\bullet}$, and $h^{\bullet}$, for which the gradients of respective electrochemical potentials were taken as the driving forces in the following continuity equations,

$$C_H\left(\frac{1}{F}\frac{\partial\eta_{H_i^\bullet}}{\partial t}-\frac{1}{F}\frac{\partial\eta_{h^\bullet}}{\partial t}\right)+C_W\left(\frac{1}{F}\frac{\partial\eta_{H_i^\bullet}}{\partial t}-\frac{1}{2F}\frac{\partial\eta_{V_O^{\bullet\bullet}}}{\partial t}\right)=\nabla\cdot\left(\frac{\sigma_{H_i^\bullet}}{F}\nabla\eta_{H_i^\bullet}\right)+J_{\mathrm{exch},H_i^\bullet}$$

$$C_W\left(\frac{1}{2F}\frac{\partial\eta_{V_O^{\bullet\bullet}}}{\partial t}-\frac{1}{F}\frac{\partial\eta_{H_i^\bullet}}{\partial t}\right)+C_O\left(\frac{1}{2F}\frac{\partial\eta_{O_V^{\bullet\bullet}}}{\partial t}-\frac{1}{F}\frac{\partial\eta_{h^\bullet}}{\partial t}\right)=\nabla\cdot\left(\frac{\sigma_{V_O^{\bullet\bullet}}}{2F}\nabla\eta_{V_O^{\bullet\bullet}}\right)+J_{\mathrm{exch},V_O^{\bullet\bullet}}$$

$$C_O\left(\frac{1}{F}\frac{\partial\eta_{h^\bullet}}{\partial t}-\frac{1}{2F}\frac{\partial\eta_{O_V^{\bullet\bullet}}}{\partial t}\right)+C_H\left(\frac{1}{F}\frac{\partial\eta_{h^\bullet}}{\partial t}-\frac{1}{F}\frac{\partial\eta_{H_i^\bullet}}{\partial t}\right)=\nabla\cdot\left(\frac{\sigma_{h^\bullet}}{F}\nabla\eta_{h^\bullet}\right)+J_{\mathrm{exch},h^\bullet}$$

where C_H, C_W and C_O are the chemical capacitances. A source term, $J_{exch,I}$, takes non-zero value at a gas-solid interface. The above equations are equivalent to an electrical circuit shown in Fig.1, which has three conduction lines connected by chemical capacitances. The potentials on the conduction lines represent the electrochemical potentials of corresponding carriers, and the difference between two of them is chemical potential of oxygen, hydrogen, or water. The circuit is terminated with dc voltage sources which represent the chemical potentials in the gas phase. The electrode reaction resistances are inserted in series to the termination voltage assuming that the polarization loss is due to the chemical potential shift from the equilibrium. Numerical calculation of the circuit was made with a general-purpose circuit simulator LT-spice. Figure 2 shows calculated EMF over $Sr(Ce,Yb)O_3$ with reversible electrodes upon sudden increase of water vapor pressure on one side. The transport parameters were taken from the report by Yoo and Martin[1], in which they predicted the time dependence of EMF. The experimental results by the same group[2] was successfully reproduced with a certain electrode resistance. Figure 3 shows the simulated three-terminal impedance responses of a cathode on the same material when it is placed under fuel cell condition. Reference electrode potential was taken from the potential on the proton conduction line in the middle of the circuit. Variation of the cathode resistance was found to cause unexpected change of the impedance spectra on the Nyquist plot.

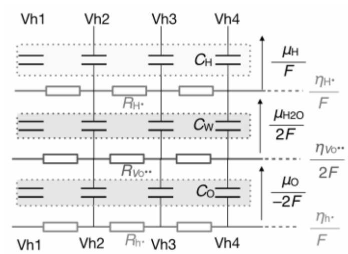

Figure 1 Main part of equivalent circuit of three-carrier conductor.

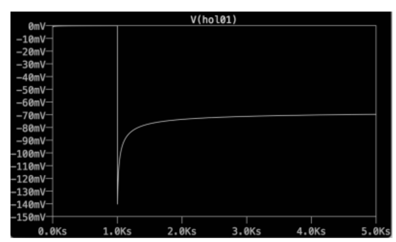

Figure 2 Transient EMF over $Sr(Ce,Yb)O_3$ at 700˚C, $p(O_2)=10^{-4.5}$ bar, upon step change of $p(H_2O)$ from $10^{-4.5}$ bar to $10^{-2.3}$ bar.

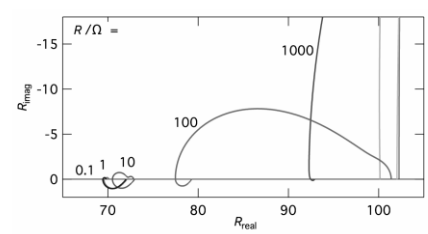

Figure 3 Simulated impedance response of a cathode with various resistance on $Sr(Ce,Yb)O_3$ placed under a fuel cell condition.

References
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