Numerical Simulation for Electrochemical Impedance of PEFC

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1. Introduction

PEFC is expected as a power supply for the mobile device, cars, and household cogeneration. However, there is still room for the improvement for practical use.

■ Research subjects for PEFC

- Low cost
- Long life
- High performance

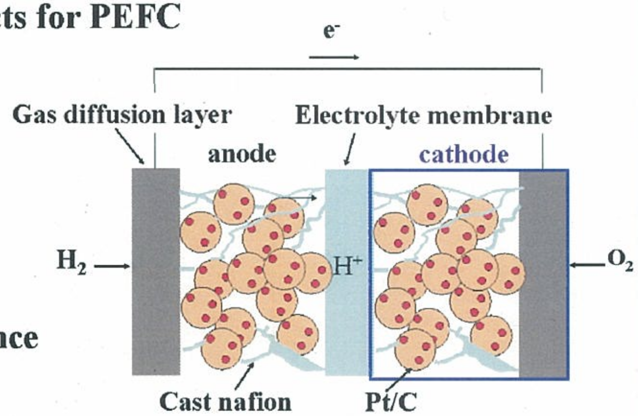


Fig. 1 Scheme of MEA

■ The purposes of present paper

- Detailed simulation of electrochemical impedance of cathode
- Clarification of the relation between impedance spectrum and electrode structure, condition and degradation
- Proposition of monitoring method for state of MEA

References

M. Eikerling, and A.A.Kornyshev,J.Electroanal.Chem.475,107,1999

Y. Bultel, L.Genies, O. Antoine, P.Ozil,R.Durand, J. Electroanal.Chem. 527,143,2002

2.1 Equivalent circuit for simulation

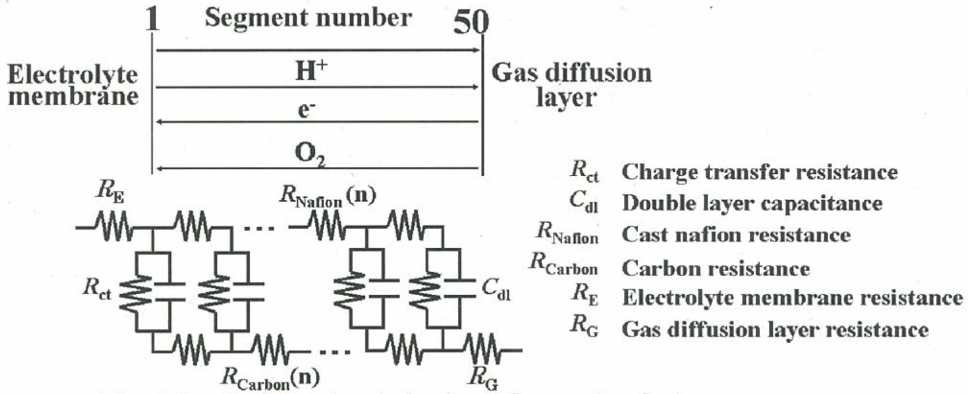


Fig. 2 Equivalent circuit for impedance simulation

Because PEFC has a porous electrode and the current is uniformly distributed the transmission line model that was the distributed constant equivalent circuit is used. In the present analysis, the catalytic layer was divided into 50 segments perpendicular to current flow direction. The time constant that involves R_{ct} and C_{dl} was assumed for each segment.

2.2 Calculation method

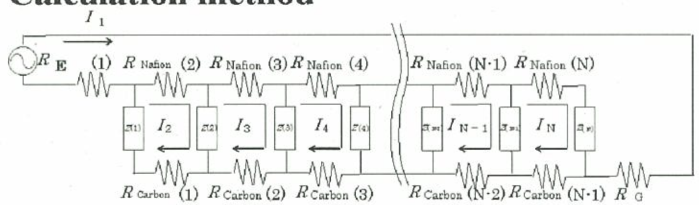


Fig. 3 Equivalent circuit of present electrode model

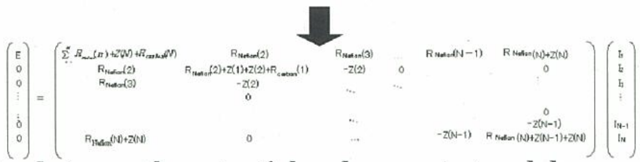


Fig. 4 Relation between the potential and current at each loop presented in Fig. 3

Impedance Z was assessed from the current I_1 obtained by the inverse matrix.

The calculation was performed by Excel, and the frequency range was from 10mHz to 10KHz.

3.1 Experimental method and results

Electrode materials

- Catalyst
  (TEC10E50E, Pt ratio 46.2 %, Pt 0.4mg/cm^2)
- 5% Nafion Dispersion (DE521)
- Electrolyte (Nafion 117)
- Carbon paper (TGP-H-060)

Experimental condition

- Cell Temperature : 72℃
- Gas flow : 0.1dm^3/min (Both electrodes)
- Relative humidity : 100%

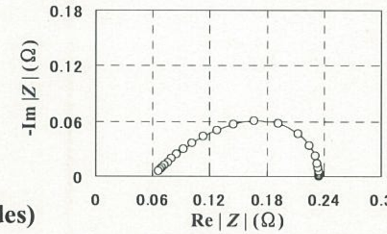


Fig. 5 Experiment result

3.2 Fitted result by TLM

Fitting Parameters

$R_{ct} = 5.2\Omega$ $C_{dl} = 1\times 10^{-2}$F

$R_{Nafion} = 5\times 10^{-3}\Omega$ $R_N = 6\times 10^{-2}\Omega$

$R_{Carbon} = 5\times 10^{-5}\Omega$ $R_G = 0\Omega$

(The values are same in all segments)

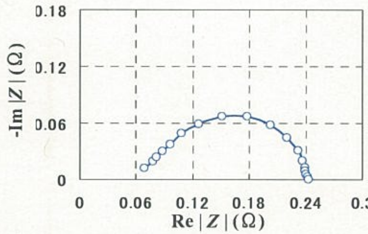


Fig. 6 Fitting result

The electrochemical impedance in Fig. 5 shows the straight line of 45 degree in the high frequency region on the Nyquist plot, and this locus is deviated from a true semicircle. This is a typical spectrum of the distributed constant type impedance. Fig. 6 shows the fitted result with the equivalent circuit of present electrode model, and the fitted result agrees with the experimental one in Fig. 5.

4 . Simulation

■ Impedance parameters and influence factor

R_{ct} : Length of three phase boundary
Concentration of reactants
Rate constant

C_{dl} : Area of two phase interface

R_{Nafion} : Ionic resistance

R_{Carbon} : Electronic resistance

■ Distribution conditions of parameters

(a) Concerning the structure
How to fabricate MEA
Amount and variety of each composition materials

(b) Concerning the statement
Degradation of electrode
Water Flooding etc..

■ Content of simulation

The following impedance simulation results are shown by using the calculation method shown by 2.Theory.

4.1 Influences of R_{ct}, R_{Nafion} and R_{Carbon}

4.2 Influence of C_{dl}

4.3 Influences of distributed R_{ct}

Impedance spectra with various parameters can be predicted by the present simulation.

4.1 Influences of R_{ct}, R_{Nafion} and R_{Carbon}

(a) Variation of R_{ct}

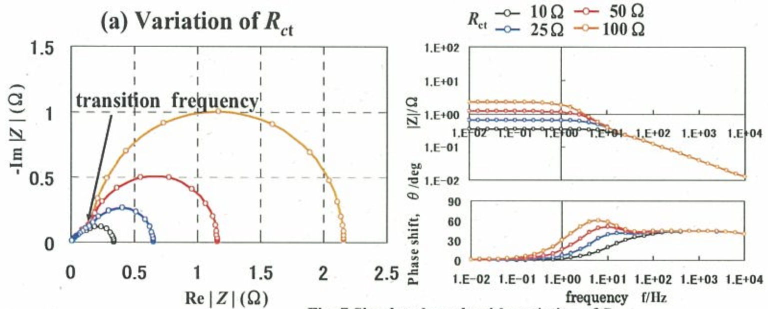


Fig. 7 Simulated result with variation of R_{ct}.

Other parameters ［ C_{dl} 1×10⁻²F R_{Nafion} 1×10⁻³Ω R_{Carbon} 1×10⁻⁵Ω ］

The R_{ct} is the functions of amounts of catalyst and electrolyte, humidity and oxygen concentration. The value of R_{ct} influences the locus in distributed constant region.

(b) Variety of R_{Nafion}

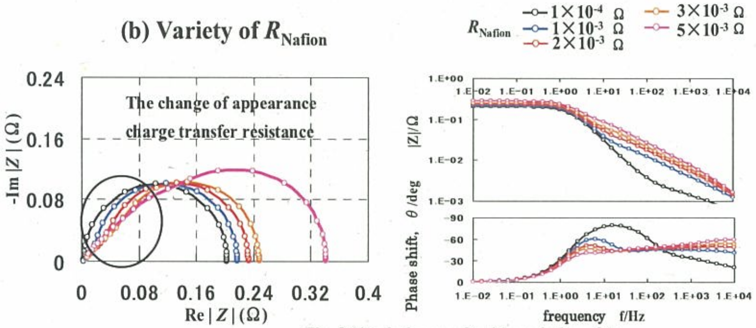
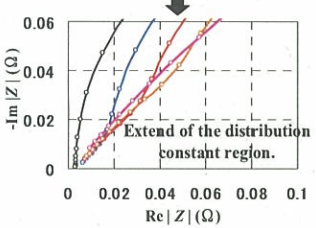


Fig. 8 Simulation result with variation of R_{Nafion}

Other parameters ［ R_{ct} 10Ω C_{dl} 1×10⁻²F R_{Carbon} 1×10⁻⁵Ω ］



The R_{Nafion} is related to the ionic resistance which is influenced by the amount of cast nafion and water content. When R_{Nafion} is small, current flows uniformly to all segments in the equivalent circuit. The value of the apparent charge transfer resistance is 1/50 of the distributed constant region becomes large and a break point corresponding to transition frequency becomes obvious, when $R_{Nafion} = 1\times10^{-4}\,\Omega$, is 0.2 Ω since R_{ct} is 10 Ω.

(c) Variation of R_{Carbon}

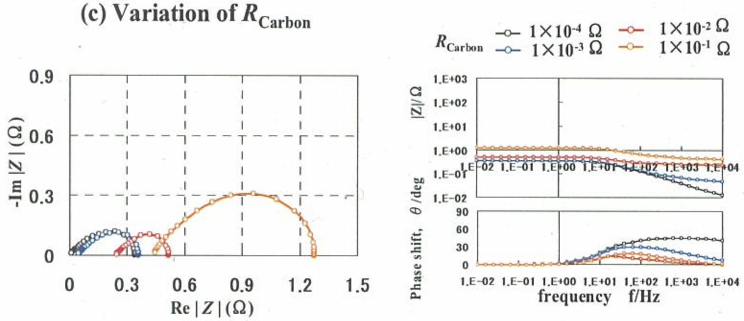


Fig. 9 Simulated result with variation of R_{carbon}.

Other parameters ［ R_{ct} 10Ω C_{dl} 1×10⁻²F R_{Nafion} 1×10⁻²Ω ］

4.2 Variation of C_{dl}

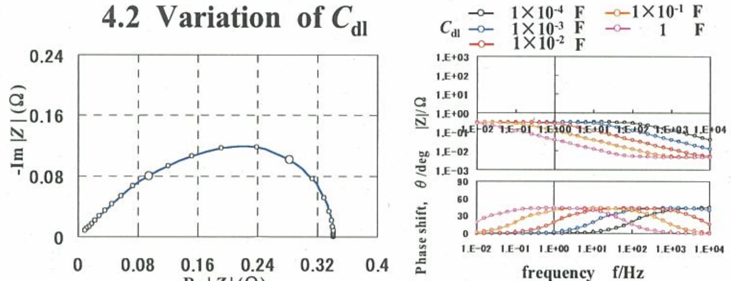


Fig. 10 Simulated result with variation of C_{dl}

Other parameters ［ R_{ct} 10 Ω R_{Nafion} 1×10⁻³Ω R_{Carbon} 1×10⁻⁵Ω ］

The C_{dl} is the function of the area of two phase interface.

➡ Nyquist plot — The locus doesn't change.

Bode plot — The amplitude and phase shift move in parallel with log f.

4.3 Influence of distributed R_{ct}

- Influence of oxygen concentration
- Length of three phase boundary changes

➡ **Impedance simulation when R_{ct} is distributed**

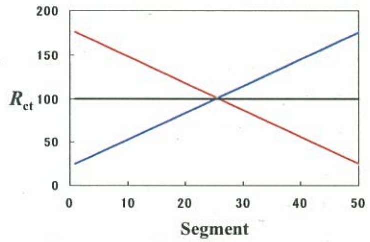


Fig. 11 Distribution of R_{ct}

Total catalyst revitalization area is same

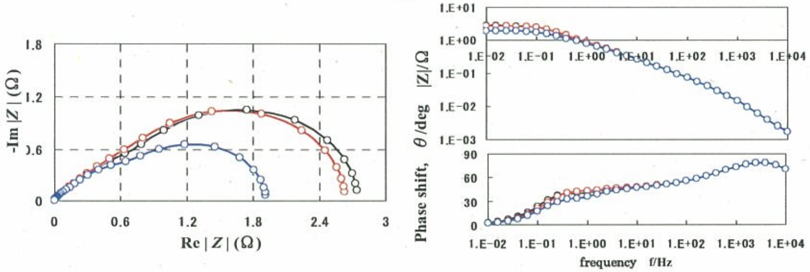
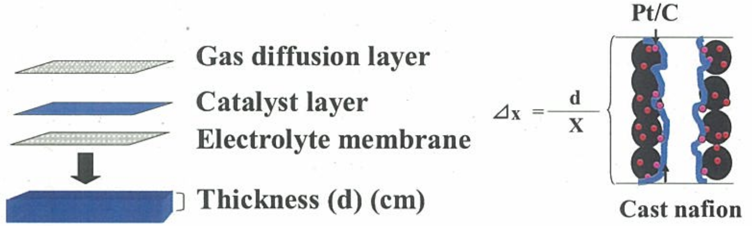


Fig. 12 Simulated result variation of *Rct*

Other parameters (C_{dl} 1×10^{-2}F R_{Nafion} $5\times10^{-2}\Omega$ R_{Carbon} $1\times10^{-5}\Omega$)

The spectrum changes significantly by the state of distribution.

5. The electrode model by distribution of the composition materials



$$\Delta x = \frac{d}{X}$$

Fig. 13 Scheme of simple electrode model

For example each impedance parameter can be calculated from the relation of equations (1) to (4) with following factors.

Equation of impedance parameter

$$R_{ct}(n) = \frac{R_{ct}^{*}}{A_{tp}\Delta x} \quad (\Omega) \quad (1)$$

$$C_{dl}(n) = \frac{C_{dl}^{*}A_{t0}}{\Delta x} \quad (F) \quad (2)$$

$$R_{Nafion} = \frac{\rho_{Nafion}\Delta x}{\beta_1} \quad (\Omega) \quad (3)$$

$$R_{Carbon} = \frac{\rho_{Carbon}\Delta x}{\beta_2} \quad (\Omega) \quad (4)$$

- A_{tp} Length of three phase boundary (cm)
- A_{t0} Area of two phase interface (cm^2)
- β_1 Influence factor of cast nafion
- β_2 Influence factor of carbon
- Δx Thickness of catalyst layer (cm)
- ρ_{Nafion} Specific resistance of Nafion
- ρ_{Carbon} Specific resistance of Carbon

Simulation by this calculation ⟷ Comparison ⟷ Experimented result in real cell

⬇

Useful analyses of electrode structure and electrodes degradation

6. Summary

The equivalent circuit for cathode of PEFC was expressed by using the transmission line model.

The relation between the various parameters and impedance spectrum was summarized theoretically.