

OPTIMIZATION OF A REVERSIBLE FUEL CELL OXYGEN ELECTRODE COMPOSITION AND STRUCTURE

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Abstract: The optimization of the structure and composition of the oxygen electrode catalytic layer in polymer electrolyte membrane (PEM) unitized regenerative fuel cell (URFC) is described. The theoretical model described the transfer processes in catalytic layer is modified which allows to consider the Pt and Ir content influence on the catalytic layer performance at different URFC operating modes. The model calculations are verified through the URFC cell testing.

Keywords: reversible fuel cell, polymer electrolyte membrane, catalytic layer, oxygen electrode

Introduction

Unitized regenerative fuel cell (URFC) is an electrochemical device which may operate as both fuel cell giving the power supply and electrolyzer generating hydrogen for energy storage. Power generation system based on polymer electrolyte membrane (PEM) URFC is characterized by high power and energy density and low cost in comparison with the system based on separate fuel cell and electrolyzer and could provide the longterm energy storage (in comparison with typical batteries) as well [1,2].

One of the most important part of the URFC is the oxygen electrode (different from PEM fuel cell cathode and electrolyzer anode) on which surface both oxygen reduction (ORR) and the oxygen evolution reaction (OER) take place. Different catalysts and catalytic layers are applied to ORR and OER thus the optimization of the URFC oxygen electrode is of great importance. Great attention has paid to a searching of new mixed electrocatalysts based on Pt, Ru, Os, Ir, Rh etc. For example, in ref. [3] more than 750 mixed catalysts were studied.

From the other hand the model development as an optimization aspect is of great importance as well. The presented research is related to such a theoretical model development.

URFCmodel

Numerical studies of the oxygen electrode (OE) and its catalytic layer (CL) based on the Pt-Ir blacks mixture catalyst (Pt-Ir) were performed using the previously developed models and software [4, 5]. URFC efficiency η_0 was evaluated as the relation of URFC voltage in fuel cell mode U_{FC} to the URFC voltage in the electrolyzer mode U_{EL} .

Pt and Ir based catalysts performance in OER and ORR

The performance of the Pt and Ir catalysts could be evaluated using the data given in Table 1. The Tafel slope and exchange current density at different overvoltages in OER and ORR are presented (Table 1).

Table 1. The performance of the Pt and Ir catalysts in OER and ORR

Catalyst	Reaction	Overvoltage	Tafel slope	Exchange current	Ref.
Pt	ORR	<450mv	46mV	$2.1 \cdot 10^{-3} \text{ A m}^{-2}$	[6]
		>450mV	95mV	0.336 A m^{-2}	[6]
Ir		<650mV	67mV	$1.17 \cdot 10^{-3} \text{ A m}^2$	[6]
		>650mV	90mV	$1.28 \cdot 10^{-2} \text{ A m}^{-2}$	[6]
Pt	ORR	>500mV	66mV	$5.8 \cdot 10^{-2} \text{ A m}^{-2}$	[7]
	OER	>250mV	150mV	$3 \cdot 10^{-4} \text{ A m}^{-2}$	[7]
Pt	ORR	<260mV	35mV	$5.1 \cdot 10^{-5} \text{ A mg}^{-1} \text{Pt}$	[8]
		>260mV	60mV	$4.5 \cdot 10^{-4} \text{ A mg}^{-1} \text{Pt}$	[8]
	OER	<550mV	54mV	$1.9 \cdot 10^{-6} \text{ A mg}^{-1} \text{ Pt}$	[8]
		>550mV	90mV	$1.1 \cdot 10^{-4} \text{ A mg}^{-1} \text{ Pt}$	[8]
Ir	ORR	<400mV	37mV	$2.1 \cdot 10^{-7} \text{ A mg}^{-1} \text{ Pt}$	[8]
		>400mV	70mV	$3.34 \cdot 10^{-5} \text{ A mg}^{-1} \text{ Pt}$	[8]
	OER	<380mV	24mV	$6.8 \cdot 10^{-8} \text{ A mg}^{-1} \text{ Pt}$	[8]
		>380mV	67mV	$4.39 \cdot 10^{-4} \text{ A mg}^{-1} \text{ Pt}$	[8]
Pt	OER	<500mV	54mV	$3.9 \cdot 10^{-2} \text{ A m}^{-2}_{\text{geom}}$	[9]

After the Table 1 data correction (to the same units) the exchange current density varies of ca. 2-3 times at a fixed overvoltage value. According to the literature and experimental data [6 – 9] regarding the electrocatalytic activity of Pt and Ir in OER and ORR the following could be assumed:

1. ORR on Pt and OER on Ir occur according to the mechanism assumed for high overvoltages – >300mV;
2. ORR on Ir and OER on Pt occur according to the mechanism assumed for high overvoltages – >450mV;
3. All electrocatalysts assumed to behave like supported (i.e. TiC) Pt-Ir mixtures with specific surface area of ca. $20 \text{ m}^2 \text{ g}^{-1}$

Mathematical modelling

The following assumptions were made during the mathematical formulation of the mass and charge transfer inside the oxygen electrode CL: the CL is homogeneous and mass transfer is limited by the oxygen diffusion in the fuel cell (FC) mode.

The development of the modified oxygen electrode CL transport model was based on the results described in ref. [10]. Equations which describe the charge transfer in the CL in the electrolyzer (EL) mode and the boundary conditions are given below (Eq. 1):

$$\begin{aligned}
 \sigma_e \frac{d\varphi_e}{dx} &= -i_e & 0 \leq x \leq h_c \\
 \sigma_p \frac{d\varphi_p}{dx} &= i_p & i_e & i_0 \\
 \frac{di_p}{dx} &= i_{aPt} \exp\left(\alpha_{aPt} \frac{\varphi_e - \varphi_p}{\varphi_t}\right) - i_{aIr} \exp\left(\alpha_{aIr} \frac{\varphi_e - \varphi_p}{\varphi_t}\right) & i_p & h_c & i_0 \\
 i_e &= i_p = i_0 & \varphi_p & h_c & i_0 R_{mem}
 \end{aligned} \tag{1}$$

The equations which describe the charge transfer in the CL in the FC mode and the boundary conditions are given below (Eq. 2):

$$\begin{aligned}
 \sigma_e \frac{d\varphi_e}{dx} &= -i_e & \leq & \leq & c \\
 \sigma_p \frac{d\varphi_p}{dx} &= i_p & e & & 0 \\
 \frac{di_p}{dx} &= c_{Pt} \frac{C_O}{C_{Oref}} \left[\left(\alpha_{cPt} \frac{\varphi_p - \varphi_e}{\varphi_t} \right) - c_{Ir} \left(\alpha_{cIr} \frac{\varphi_p - \varphi_e}{\varphi_t} \right) \right] \varphi_e & p & c & 0 \\
 & & \varphi_p & c & 0 \text{ mem} \\
 \frac{dC_O}{dx} &= -\frac{i_p}{4FD_{OCL}} & C_O & & 00
 \end{aligned} \quad (2)$$

The coordinate of the CL outer surface is $x=0$ and the one of the CL with membrane boundary is $x=h_c$.

In equations (1) – (2):

φ_e, φ_p – the electron potential in the electron-conducting subsystem and the proton potential in the proton-conducting subsystem of the CL;

i_e, i_p – the electron current density in the electron-conducting subsystem and the proton current density in the proton-conducting subsystem of the CL;

σ_e, σ_p – the specific conductivity of the electron-conducting subsystem and the proton-conducting subsystem of the CL;

$\varphi_a, \frac{RT}{2F\alpha_a}, \varphi_c, \frac{RT}{2F\alpha_c}$ – Tafel slopes for anodic and cathodic reactions, respectively;

α_a, α_c – transfer numbers of anodic and cathodic reactions, respectively.

C_{O0}, C_{Oc} – oxygen concentration at the outer boundary and the inside one of the CL, respectively;

D_{OCL} – the efficient oxygen diffusion coefficient of the oxygen in the CL porous media; C_{Oref} – the value of the comparative oxygen concentration ($C_{Oref}=8.2 \text{ mol/m}^3$).

“aPt”, cPt”, “aIr” and cIr” indexes refer to Pt and Ir catalysts, respectively.

The equation systems (1– 2) were solved numerically using the Runge-Kutta method (4th order).

$\sigma_e [\text{S}\cdot\text{m}^{-1}]$ – conductivity of the electronic-conductive subsystem of the CL;

$$\sigma_e = \sigma_{e0} (1 - \varepsilon_0)^{1.5} \quad (3)$$

where σ_{e0} – effective conductivity of the electronic-conductive subsystem of the CL at zero porosity;

$\sigma_p [\text{S}\cdot\text{m}^{-1}]$ – conductivity of the proton-conductive subsystem of the CL;

$$\sigma_p = \sigma_{p0} (1 - \varepsilon_p)^{1.5} \quad (4)$$

where σ_{p0} – effective conductivity of the polymer electrolyte membrane.

ε_{gc} – porosity of the CL taking into consideration the proton-conductive subsystem.

$$1 - \varepsilon_{ga} = 1 - \varepsilon_0 - \varepsilon_p \quad (5)$$

Therefore, the CL effective diffusion coefficient D_{OCL} could be calculated as follows:

$$D_{OCL} = D_{O0} \cdot (1 - \varepsilon_p - \varepsilon_0)^{1.5} \quad (6)$$

Results and discussions

The main purpose of calculations is the optimization of Pt and Ir mass loading with respect to the CL geometric surface area in order to maximize the $\eta_0 = \frac{U_{FC}}{U_{EL}} \text{ max}$ criterion.

The analysis of the equations given above shows (Fig. 1) that the addition of less active component has a significant effect on the OE CL performance in both FC and EL modes. Whereby the addition of Pt to the CL leads to the cell voltage decreasing in the EL mode (Fig.

1A). From the other hand the addition of Ir leads to the sharp decreasing of the cell voltage in the FC mode (Fig. 1A). These trends are associated with two main reasons:

1. The URFC performance is less influenced by mass transfer in the EL mode. When the CL thickness and the Pt loading increasing the water, which is necessary for OER is still effectively supplied to the CL due to the capillary forces. In the FC mode the oxygen diffusion to the CL is slow and sharply decreases when the Pt and/or Ir loading increased.
2. The essential fact is that that the CL ionic resistance growth when the mass loading of Pt and Ir (CL thickness) increases. The CL resistance significantly affected by the layer ionomer (solid polymer electrolyte – Nafion) humidity. The CL water content in the FC mode depends on the air humidity. In the EL mode the ionomer is in contact with liquid water which resulted in 2-3 lower CL resistance value.

The dependence of the URFC efficiency have a maximum value of *ca.* 0.45 which corresponds to the following noble metal loadings: $m_{Pt} = 1 \text{ mg cm}^{-2}$ and $m_{Ir} = 0.75 \text{ mg cm}^{-2}$ (Fig. 1B). But the FC mode is crucial for the URFC efficiency.

Fig. 2 shows the proton current density distribution in the CL, potentials of proton- and electron-conducting subsystems (Fig. 2A), the relative oxygen concentration in the FC mode (Fig. 2B), current density, potentials of proton- and electron-conducting subsystems in EL mode (Fig. 2C) at the optimal η_0 value. From the other hand the ionomer volume fraction ($X_{pV} = 0.24$) was chosen in order to induce the significant gradient of the oxygen concentration in CL. In this case the reaction overvoltage suggested to be constant and the reaction rate suggested to be independent from the CL thickness.

Fig. 3 shows the dependence of the URFC performance from the catalysts loading. The URFC current density increasing leads to the shift of URFC efficiency maximum value towards the lower Pt and Ir loading values: $m_{Pt} = 0.8 \text{ mg cm}^{-2}$ and $m_{Ir} = 0.25 \text{ mg cm}^{-2}$. At the increased current density in the FC mode becomes more important for the URFC efficiency.

The volume fraction of ionomer in the CL significantly affect the URFC performance in both FC and EL modes (Fig. 4B). This influence is mainly come from the change in the CL proton-conducting subsystem ohmic resistance. A noticeable effect of the oxygen diffusion rate on the URFC performance begins only at high volume fraction of the ionomer i.e. low free volume (porosity) fraction in the CL. The position and the value of the maximum η_0 (Fig. 4B) depends on the ORR overvoltage and the ohmic resistance of the CL. Maximum URFC efficiency is *ca.* 0.47 at $m_{Pt} + m_{Ir} = 1.3 \text{ mg cm}^{-2}$ and $X_{pV} = 0.21$). All characteristics and dependencies have the optimal values (minimal voltage in EL mode and the maximum efficiency and voltage in FC mode). When the current density increased the optimal value of the ionomer volume fraction increases because to obtain higher efficiency the higher proton conductivity is required.

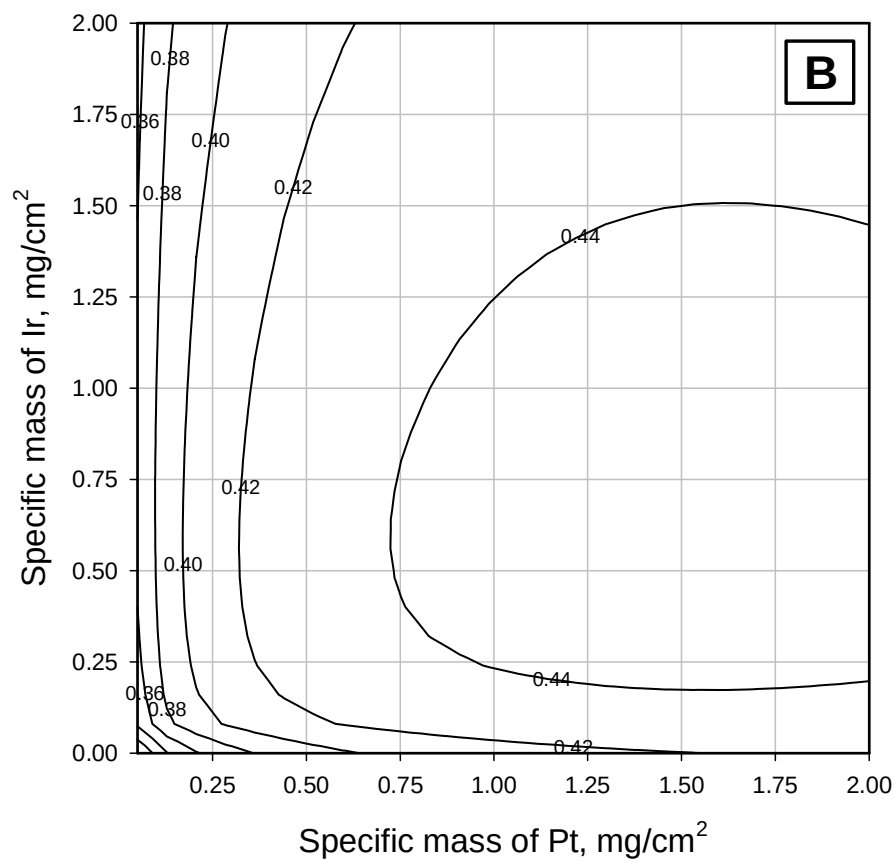
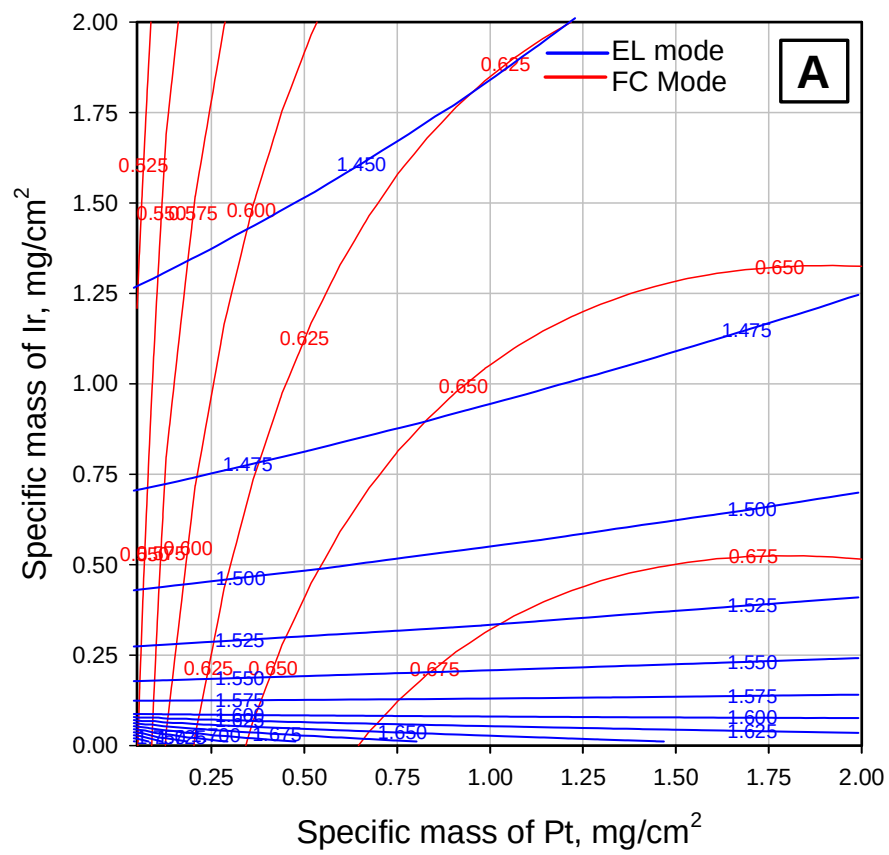


Fig. 1. The dependency of the URFC voltage in both FC and EL modes (A) and the URFC efficiency (B) from the Pt and Ir loadings in the OE CL. The ionomer volume fraction in the OE CL is $X_{pV}=0.15$. Current density is $i=0.5 \text{ A cm}^{-2}$.

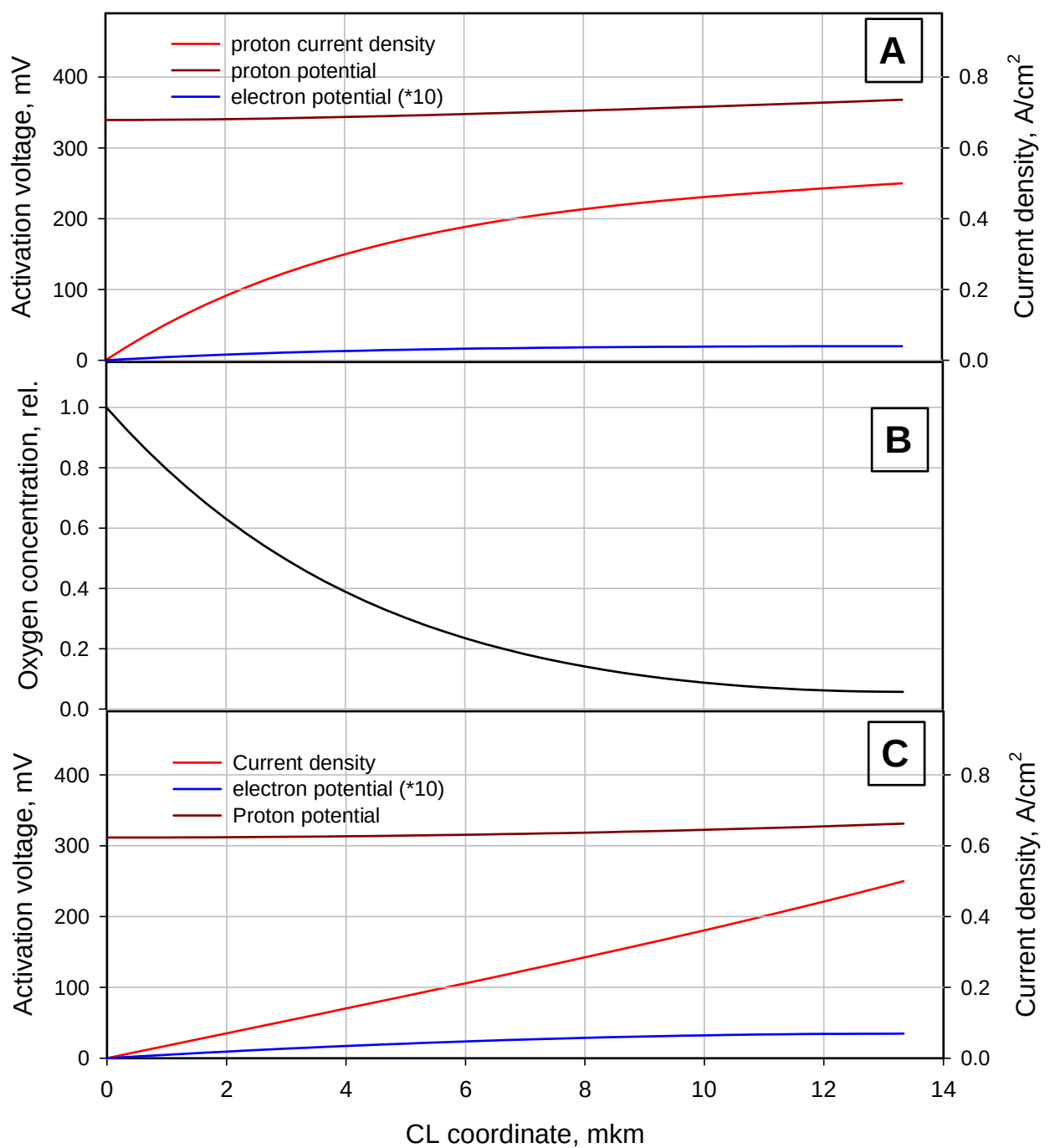


Fig. 2. The numerical simulation of the OE CL in both FC and EC modes: proton current density distribution in the CL, the potentials of proton- and electron-conducting subsystems (A), the relative oxygen concentration in the FC mode (B), current density, the potential of proton- and electron-conducting subsystems in EL mode (C) in the CL of OE at $X_{pV}=0.24$, $m_{Pt}=1 \text{ mg cm}^{-2}$ and $m_{Ir}=0.75 \text{ mg cm}^{-2}$.

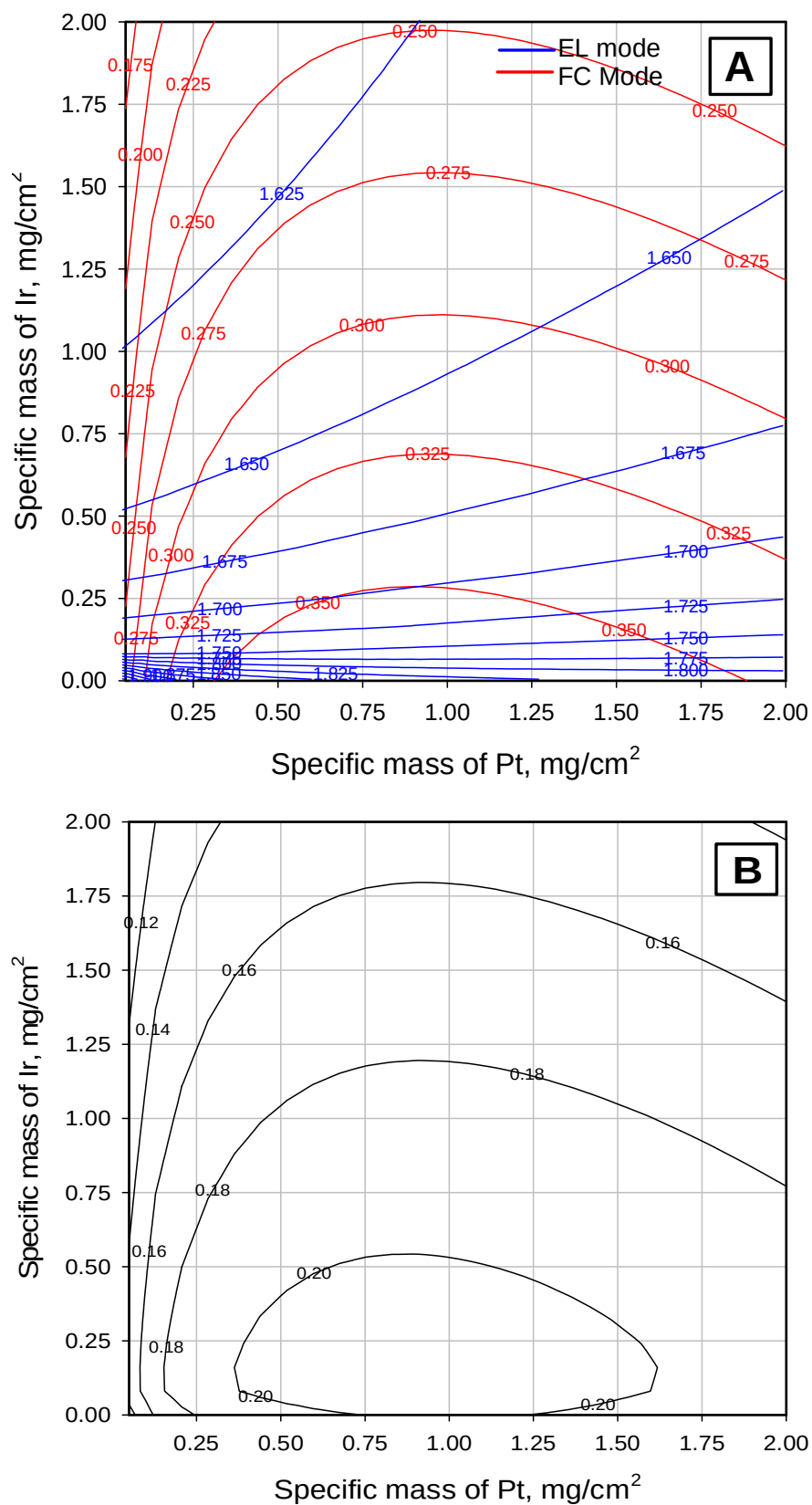


Fig. 3. The dependence of the URFC voltage (V) in both FC and EL modes (A) and its efficiency (B) from the Pt and Ir loadings in CL of OE. The ionomer volume fraction in CL is $X_{pV}=0.15$ and the current density is $i = 1.0 \text{ A cm}^{-2}$.

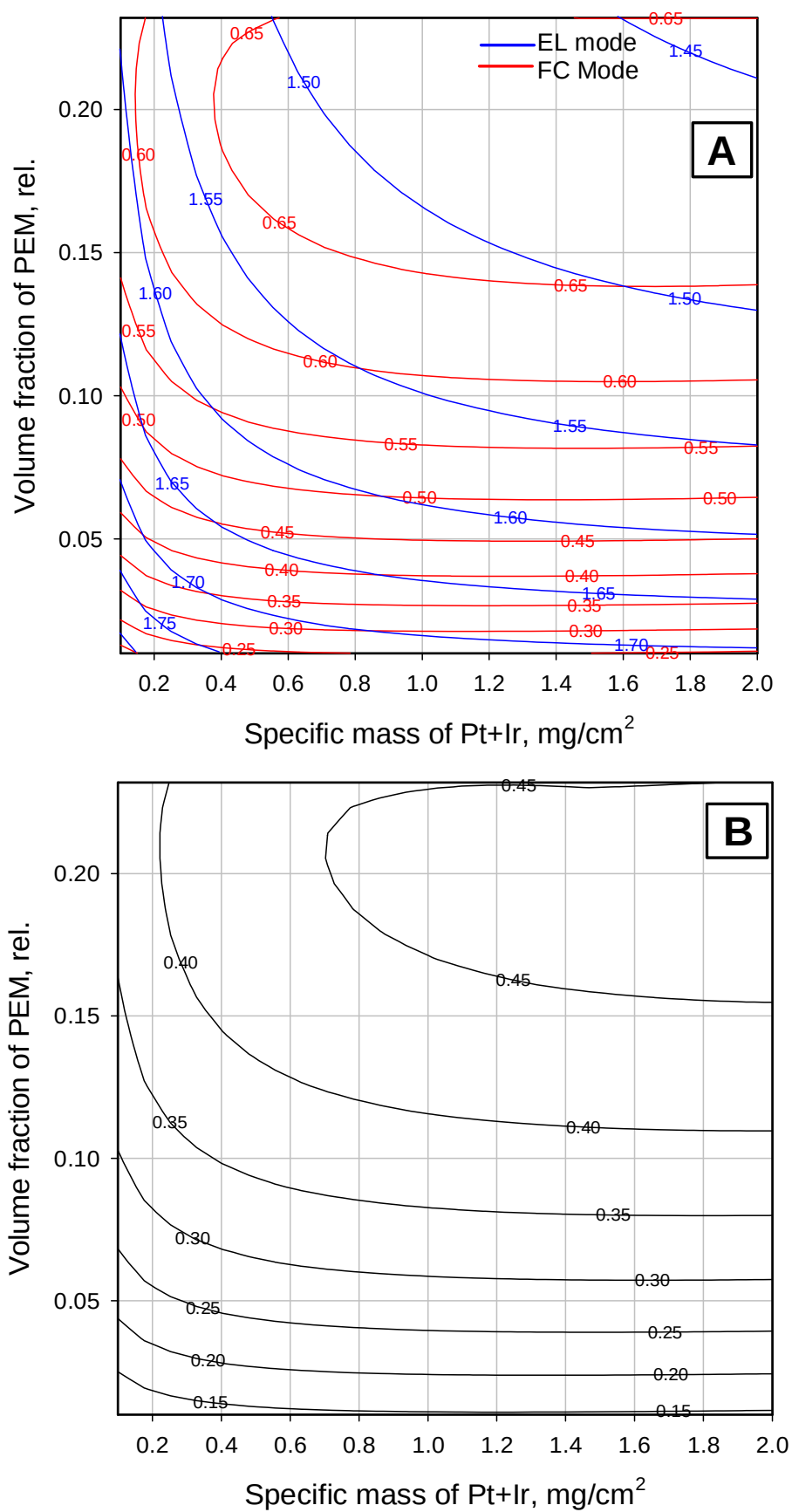


Fig. 4. The dependence of the URFC voltage (V) in both FC and EL modes (A) and its efficiency (B) from the Pt+Ir loading and the ionomer volume fraction in the CL of OE. The Pt/Ir ratio is $m_{Pt}/m_{Ir}=1.5$. Current density is $i = 0.5 \text{ A cm}^{-2}$.

Experimental model verification

Experimental validation of the proposed model was carried out using the URFC testing cell with the 7 cm^2 working area described in ref. [11]. Porous titanium plates and carbon paper Sigraset 10bb with microporous sublayer were used as the current collectors (gas diffusion electrodes) on the oxygen and hydrogen side, respectively. Nafion 115 membrane was used as the polymer electrolyte membrane. Hydrogen electrode CL consists of $\text{Pt}^{40}/\text{Vulcan XC-72}$ catalyst, PTFE (10 wt.%) and Nafion ionomer (20 wt.%) with Pt loading of 0.35 mg cm^{-2} . OE CL consists of TiC supported Pt-Ir catalyst and Nafion ionomer (10 wt.%) with Pt+Ir loading of ca. 1.5 mg cm^{-2} . The Pt weight content in OE CL varies in the range of 10 – 100 wt.%.

Fig. 5 shows that the calculated polarization curves of MEAs with different Pt weight content in OE are in a good agreement with those obtained by URFC cell testing.

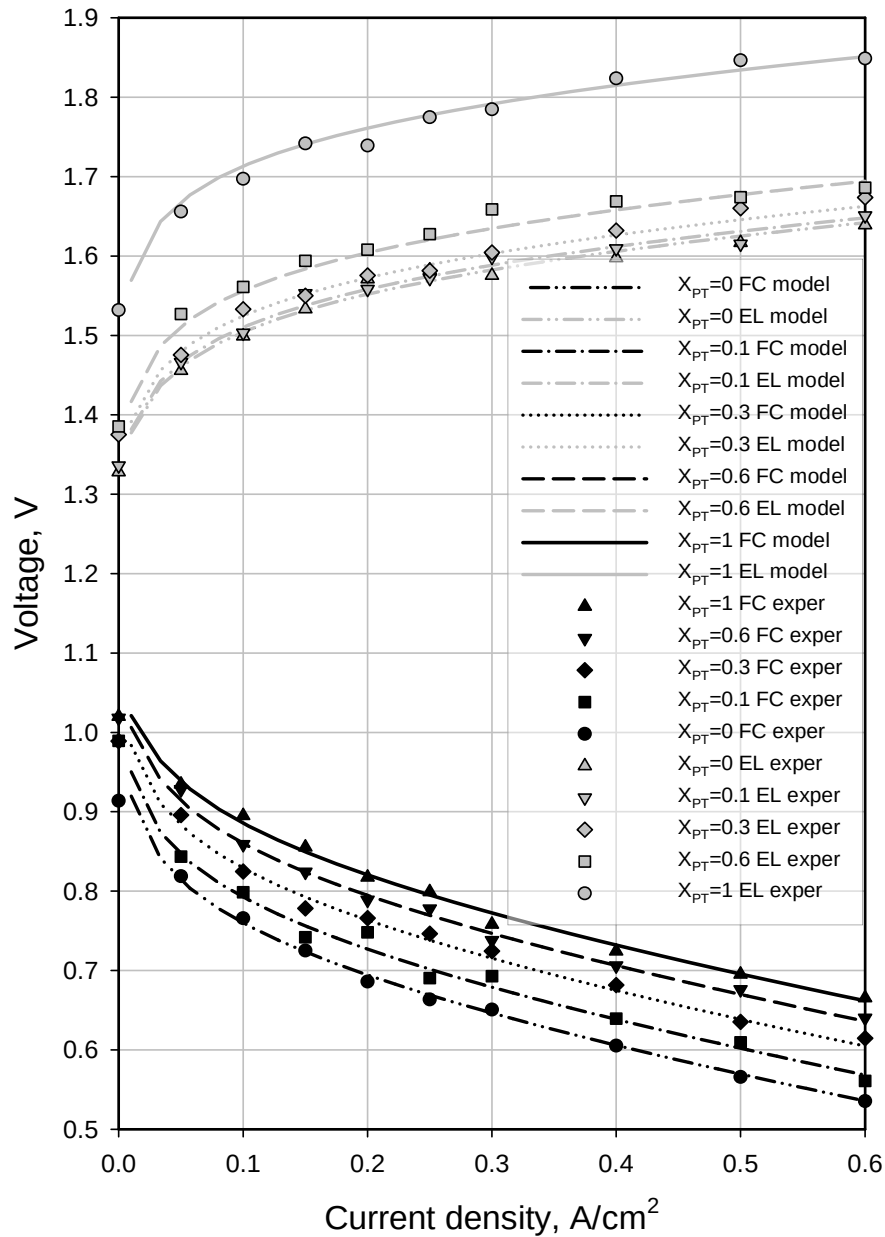


Fig. 5. Polarization curves of the URFC testing cell (dots) and the results of their numerical modelling (lines). The CL of the OE contains Pt+Ir catalysts with different $m_{\text{Pt}}/m_{\text{Ir}}$ ratio (X_{Pt}) varied from 0 to 1). Cell temperature is $50 \text{ }^{\circ}\text{C}$. Hydrogen and oxygen pressure is 1 bar. The temperature of gas humidification (in FC mode) is $40 \text{ }^{\circ}\text{C}$.

Conclusions

The mathematical model of the URFC oxygen electrode catalytic layer was developed. The calculations made using the developed model allows to postulate the following:

1. The ORR exchange currents on Pt is *ca.* 20 times higher than those on Ir. The OER exchange currents on Ir is *ca.* 10-40 times higher than those on Pt depending on the overvoltage. The OER Tafel slope in Pt is 1.5 times larger than those on Ir at overvoltages > 450 mV. These catalysts concentration must be optimized for concrete cell operating modes.

2. The maximum URFC efficiency (η_0) of *ca.* 0.45 at the selected current density of 0.5 A cm⁻² is obtained at the following catalysts loadings in CL: $m_{Pt}=1\text{ mg cm}^{-2}$ and $m_{Ir}=0.75\text{ mg cm}^{-2}$. The FC mode is the most crucial to obtain a maximum URFC efficiency.

3. The dependence of the OE CL structure (ionomer volume fraction) on the URFC maximum efficiency and conditions was studied. The value of ionomer volume fraction in the OE CL significantly affects the URFC performance in both FC and EL modes. This effect is due to the ohmic resistance of the proton-conductive subsystem and is limited by the oxygen diffusion rate only at very low value of the free volume fraction (porosity) in the CL. The relation of the ORR overvoltage and CL ohmic losses determine the obtained maximum URFC efficiency of *ca.* 0.47 at $m_{Pt}+m_{Ir}=1.3\text{ mg cm}^{-2}$ and $X_{pV}=0.21$.

4. When current density increased from 0.1 to 1 A cm⁻² the optimal value of the ionomer volume fraction increases from 0.15 to 0.22 vol.% due to the stronger effect of CL proton conductivity.

5. Experimental validation of the proposed model of the URFC OE CL charge transfer was carried out using the URFC testing cell with the 7 cm² working area. The results of calculations are in a good agreement with the experimental data.

The calculated values of URFC efficiency and optimal OE CL composition may be a little bit different for catalysts with another chemical composition and structure. However, the proposed model and performed studies are an example of the URFC OE optimization which is based on the selected catalysts.

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ОПТИМИЗАЦИЯ СОСТАВА И СТРУКТУРЫ КАТАЛИТИЧЕСКОГО СЛОЯ КИСЛОРОДНОГО ЭЛЕКТРОДА ОБРАТИМОГО ТОПЛИВНОГО ЭЛЕМЕНТА

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В данной работе рассмотрен вопрос оптимизации структуры и состава каталитического слоя кислородного электрода обратимого топливного элемента на основе твердого полимерного электролита. Разработана модификация теоретической модели транспорта в каталитическом слое кислородного электрода. Результаты расчетов на основе модели позволили установить влияние содержания Pt и Ir на эффективность работы каталитического слоя при различных режимах работы топливного элемента. Проведена экспериментальная верификация модели с использованием лабораторной ячейки топливного элемента, подтверждающая адекватность разработанной модели.

Ключевые слова: обратимый топливный элемент, твердый полимерный электролит, каталитический слой, кислородный электрод

DÖNƏR YANACAQ ELEMENTLƏRİN OKSİGEN ELEKTRODUNUN KATALİTİK TƏBƏQƏSİNİN STRUKTUR VƏ TƏRKİBİNİN OPTİMALLAŞDIRILMASI

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Məqalədə bərk polimer elektrolit əsasında dönər yanacaq elementinin oksigen elektrodunun katalitik təbəqəsinin struktur və tərkibinin optimallaşdırılması məsələsinə baxılıb. Oksigen elektrodunun katalitik təbəqəsində transportun nəzəri modelinin modifikasiyası işlənib hazırlanıb. Yanacaq elementinin müxtəlif iş rejimində model əsasında aparılmış hesablamalar Pt və Ir miqdarının katalitik təbəqənin effektiv işləməsinə təsirini müəyyən etməyə imkan verir.

Açar sözlər: yanacaq elementi, bərk polimer elektroliti, oksigen elektrodu