

Study of Methanol Concentration Effect in Direct Methanol Fuel Cells by Electrochemical Impedance Spectroscopy

Original

Study of Methanol Concentration Effect in Direct Methanol Fuel Cells by Electrochemical Impedance Spectroscopy / Giordano, Elena; Zaffora, Andrea; Iannucci, Leonardo; Santamaria, Monica; Grassini, Sabrina. - ELETTRONICO. - (2023), pp. 1-5. (Intervento presentato al convegno 2023 IEEE International Instrumentation and Measurement Technology Conference (I2MTC) tenutosi a Kuala Lumpur (Malaysia) nel 22-25 May 2023) [10.1109/I2MTC53148.2023.10176090].

Availability:

This version is available at: 11583/2981182 since: 2023-08-22T12:13:36Z

Publisher:

IEEE

Published

DOI:10.1109/I2MTC53148.2023.10176090

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

IEEE postprint/Author's Accepted Manuscript

©2023 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collecting works, for resale or lists, or reuse of any copyrighted component of this work in other works.

(Article begins on next page)

Study of Methanol Concentration Effect in Direct Methanol Fuel Cells by Electrochemical Impedance Spectroscopy

Elena Giordano
Dipartimento di
Scienza Applicata e Tecnologia
Politecnico di Torino
Torino, Italy
elena_giordano@polito.it

Andrea Zaffora
Dipartimento di
Ingegneria
Università degli Studi di Palermo
Palermo, Italy
andrea.zaffora@unipa.it

Leonardo Iannucci
Dipartimento di
Scienza Applicata e Tecnologia
Politecnico di Torino
Torino, Italy
leonardo.iannucci@polito.it

Monica Santamaria
Dipartimento di
Ingegneria
Università degli Studi di Palermo
Palermo, Italy
monica.santamaria@unipa.it

Sabrina Grassini
Dipartimento di
Scienza Applicata e Tecnologia
Politecnico di Torino
Torino, Italy
sabrina.grassini@polito.it

Abstract— This paper analyzes and discusses the performance of a DMFC as a function of methanol aqueous solution concentration fed at the anode, using the Electrochemical Impedance Spectroscopy (EIS). Impedance data obtained were analyzed through the development of an equivalent circuit model. Electrochemical impedance spectroscopy was used to estimate the membrane conductivity and to model the electrochemical behavior of electrodic reactions inside the fuel cell, revealing a worse overall performance by increasing methanol concentration at the anode.

Keywords—Fuel Cells, Electrochemical Impedance Spectroscopy, Impedance Measurements, Direct Methanol Fuel Cells

I. INTRODUCTION

Direct methanol fuel cells (DMFCs) are considered a very promising energy source for portable devices because they have high energy efficiency, low emissions, compact cell design, fast refueling, low temperature and pressure operation, low methanol cost and no liquid electrolyte [1]. However, the main disadvantages that prevent their use are low power density caused by the permeation of methanol through the polymer membrane and the slow electrochemical oxidation of methanol. Therefore, a better and more thorough understanding of the chemical and electrical processes that define FC behavior and reliability is needed to overcome these limitations. Fuel cells are complex systems, and their behavior depends on many variables such as current, operating temperature, pressure, methanol concentration, catalyst loading, and electrolyte characteristics [1]–[3].

Methanol concentration is a critical parameter to be optimized to improve the performance of DMFCs, as it is necessary to eliminate or, at least, reduce methanol crossover. As methanol reaches the membrane, it diffuses from the anode to the cathode, carried by hydrated protons under the influence of the electric current flowing through the cell. The concentration difference between anode and cathode can also

result in methanol transfer from one compartment to another [4]. Methanol crossover during DMFC operation causes a lowering of power due to chemical oxidation of methanol at the cathode, this causes depolarization of electrode with lowering of open circuit voltage (OCV). In addition, there is not only O₂ consumption but there can be also catalyst poisoning at the cathode. The overall fuel utilization efficiency decreases due to methanol crossover [5].

Moreover, this study is conducted using a chitosan membrane, a low-cost and environmentally friendly biopolymer as a membrane alternative to commercial perfluorosulfonic Nafion [6].

Research activity focuses on optimizing performance through the characterization of assembly materials. Component characterization has been extensively studied using DC bias techniques to evaluate the cell voltage versus current density and thus also the resulting power providing useful information on voltage drops and thus cell efficiency [6]–[11]. Because the cell operates in direct current, it provides only the entire equivalent resistance of the cell, without distinguishing between the different contributions and without providing information on the kinetics of the electrochemical phenomena occurring within the cell. A strong method of analysis for evaluating the kinetic contribution of components is Electrochemical Impedance Spectroscopy (EIS) in alternating current [12].

EIS is widely employed in the literature for the characterisation, diagnosis and modelling of batteries and fuel cells. EIS provides, in a non-destructive way, the most complete information about the physical processes occurring within the fuel cell allowing, therefore, the possibility to develop control and diagnostic tools to ensure proper operating conditions.

Till now, impedance measurements have been successfully employed to characterize PEM fuel cells in order to evaluate the current ripple effect [13] or to develop drying and flooding diagnosis [14]. Moreover, different methods have been developed for the EIS analysis, i.e. the time-domain least

squares approach [15], and to perform accurate measurement uncertainty evaluation by ensuring an accurate determination of equivalent circuit parameters [16]. This paper aims to study the behavior of a DMFC as the concentration of methanol changes, through EIS studies and the development of an equivalent circuit model. In particular, tests were performed at different voltage values to predict the transient behavior of fuel cells and their performance.

II. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY MEASUREMENTS

The EIS technique is widely used because it provides insight into the electrochemical mechanisms occurring at the interfaces of an electrochemical system, such as DMFCs [17].

EIS is a type of measurement that allows the analysis of linear time-invariant systems by transfer functions. Therefore, for electrochemical systems EIS uses a small amplitude potential or current perturbation to excite the electrochemical system at different frequencies. Measuring the system's response to the perturbation, a transfer function is calculated, which in the case of electrochemical systems is referred to as electrochemical impedance, expressed as:

$$Z(\omega) = \frac{\Delta \bar{V}}{\Delta \bar{I}} = Z_{re} + jZ_{im} \quad (1)$$

where ω is the angular frequency, related to the frequency f (Hz) by $\omega=2\pi f$. When the input and output are in phase, the imaginary part has value zero and the impedance will have only a real contribution, Z_{re} . If the input and output are out of phase, the real part has value zero and the impedance has only an imaginary contribution, Z_{im} . The variation of impedance with frequency can be visualized in several ways. In the Bode diagram, $\log |Z|$ and ϕ are plotted as a function of $\log \omega$, whereas when the imaginary component Z_{im} is plotted as a function of the real component Z_{re} , an alternative representation of impedance, the Nyquist diagram, is obtained [17], [18].

The critical issues remain to be the interpretation of the EIS data through the determination of an equivalent circuit best suited to model the impedance results and in the physical meaning of the passive elements used for the equivalent circuit. The most frequently used passive components are the resistor, inductor and capacitor. In particular, the impedance of a resistor consists only of the real part, equal to the resistance of the resistor itself. The current flowing through it will be in phase with the applied voltage. Capacitors are used to store electrical energy in the form of an electric field thus they are elements that introduce capacitance into a circuit. The impedance of a capacitor is characterized by only the imaginary part and is inversely proportional to the voltage and frequency of the applied signal. The current will be shifted by -90 degrees with respect to the applied voltage. An inductor is used in the circuit to represent energy storage in the form of a magnetic field. The impedance of an inductor increases as the frequency of the applied voltage signal increases, and the current through it will be shifted by 90 degrees relative to the applied voltage. If an electrode is nonuniform, the reactivity can vary along the surface and, therefore, there can be a distribution of time constants

(defined as RC). This variation can be modeled by a constant phase element (CPE), Q [18].

For a fuel cell, the associated equivalent circuit model consists of a parallel between a constant-phase element (Q_A and Q_C), which is necessary to model the nonideal double layer capacitance of the electrode, and a Charge Transfer Resistance ($R_{ct,A}$ and $R_{ct,C}$) related to the reaction kinetics for each electrode, either the anode or the cathode. The electrolyte, on the other hand, can be simply modeled with a resistance (R_Ω) that is the intercept of the real axis at high frequencies. This results in series with the two parallels relative to the electrode reaction interfaces. This model is generally accepted for H_2/O_2 fuel cell systems at low and moderate current densities [19], [20].

In addition to the two time constant (R_{ct} - Q), related to methanol oxidation and oxygen reduction respectively, in series with the ohmic resistance of the cell (R_Ω) that is mainly due to the electrolyte resistance, there can be the onset of an inductive loop at low frequencies due to the kinetics of the electrochemical reaction at the anode, modeled by an inductance, as displayed in the Nyquist representation for a DMFC. The reaction mechanism is quite complex and involves several electrochemical steps, specifically the oxidation of methanol to a reaction intermediate, CO_{ads} , and then the oxidation of these adsorbed species to CO_2 , implying the crucial role of adsorbent species at the electrode [21], [22].

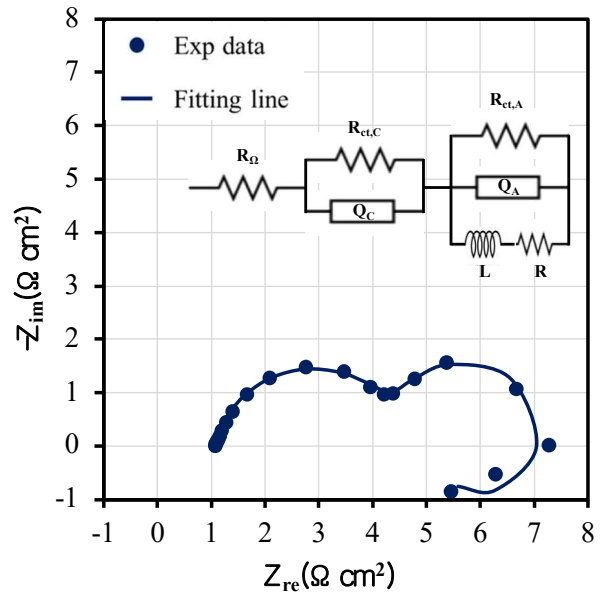


Fig. 1. A typical experimental and fitted EIS spectrum of a DMFC in Nyquist representation. The equivalent circuit for data fitting is also shown.

III. EXPERIMENTAL SETUP

Electrochemical impedance spectroscopy measurements were obtained for an Electrochem Inc. fuel cell using a Parstat 2273 (Princeton Applied Research), and the results of the EIS spectra were modeled through an equivalent circuit with ZSimpWin software.

EIS measurements were carried out at different cell voltages for each methanol concentration (500 mV, 400 mV, 300 mV, 250 mV, 200 mV), specifically by superimposing a 10 mV

amplitude sinusoidal signal in the frequency range of 100 kHz to 10 MHz on the constant DC cell voltage.

The study was conducted using electrodes prepared by spraying a catalytic ink on a commercial Sigracet-24 BC gas diffusion layer (from the SGL group)[23]. Anode side used a catalyst with a Pt/Ru end-loading of $3.45 \text{ mg}\cdot\text{cm}^{-2}$; Cathode side used a catalyst with a Pt loading of $0.5 \text{ mg}\cdot\text{cm}^{-2}$.

A chitosan (CS)/phosphotungstic acid (PTA) based polyelectrolyte membrane, prepared through an ionotropic gelation process performed at room temperature, described in previous work, was used. It has been shown that it can be successfully employed as a proton exchange membrane in a low-temperature fuel cell [22], [24].

Chitosan powder, acetic acid, and $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$, required for membrane synthesis, were provided by Sigma Aldrich. CS powder (2% w/v), acetic acid (2% w/v) and distilled water were mixed to achieve protonation and solubilization of CS. By using a porous medium previously impregnated with an aqueous solution of PTA (0.38 M), cross-linking of the CS solution was induced. The cross-linking time chosen for this work, necessary for the thickness of the membrane, was 60 min. Prior to assembly in the cell, the membrane was functionalized for 24 h to increase its proton conductivity by soaking the membrane in PTA aqueous solution at room temperature.

The Membrane Electrode Assembly (MEA) was assembled by placing the CS/PTA membrane between the two electrodes in the single-cell module with an applied torque of 4 Nm. To evaluate the performance and characterize the DMFC, different concentrations of methanol (1 M, 2 M, 5 M) were used on the anode side at a flow rate of $3 \text{ mL}\cdot\text{min}^{-1}$, while on the cathode side humidified oxygen (99.5% purity) was fed at $50 \text{ mL}\cdot\text{min}^{-1}$ at 1 bar. The supply was provided by high-purity graphite plates with high electrical and thermal conductivity. These were combined with gold-plated plates required for heating the cell and as current collectors. In addition, 0.01" thick silicon gaskets were inserted between the MEA and the graphite plates.

All tests refer to an active area of 1 cm^2 and a temperature of 50°C .

IV. RESULTS AND DISCUSSION

As remarked in the introduction, DC measurements are usually not sufficient to understand the kinetics of the system, but they are needed to choose the right cell voltage range to perform AC measurements by Electrochemical Impedance Spectroscopy. To do so, polarization and power density curves were measured for different methanol concentrations.

As shown in Figure 2, as the methanol concentration increased from 1 M to 5 M, the current density and OCV decreased dramatically, because of a significant methanol crossover resulting in catalyst poisoning. The power decreased rapidly as the methanol concentration increased. Therefore, it is possible to infer that the methanol concentration of 1 M is best suited to operate a single DMFC with the highest power density

and efficiency. This result is consistent with those reported in the literature[6], [7], [25].

It is possible to identify two areas of interest to be studied by EIS: the activation region (between OCV and $\sim 400 \text{ mV}$), where the kinetic losses are due to the electrochemical reaction, and the ohmic region where the potential drop is mainly due to membrane resistance.

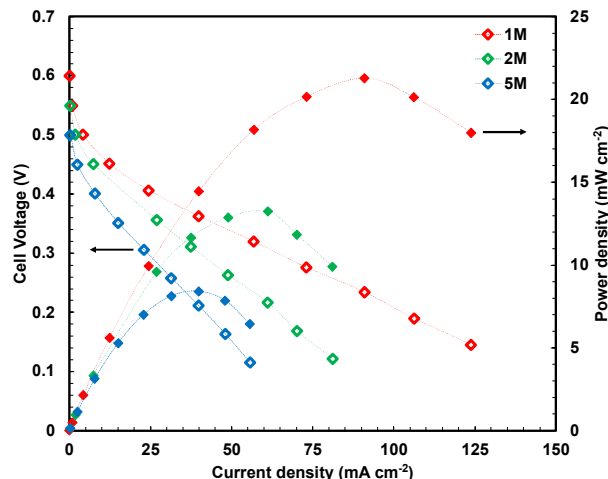


Fig. 2. Polarization (\diamond) and power density (\blacklozenge) curves related to CS/PTA membranes for different methanol concentrations.

It was decided to study in AC how the kinetic parameters vary as the potential changes for each analyzed methanol concentration. A high potential drop is found in the activation region due to the electrooxidation of methanol. With EIS spectra recorded at constant potential in the activation region (from 500 mV to 400 mV), its parameters can be studied.

Figure 3 shows all EIS spectra recorded at varying potential and methanol concentration. The charge transfer resistance of both half-cell reactions, methanol oxidation and oxygen reduction, are suggested by the two depressed semicircles. These experimental results suggest that the performance of DMFC is strongly influenced by the concentration of the methanol aqueous solution fed at the anode, as is evident in Figure 3.

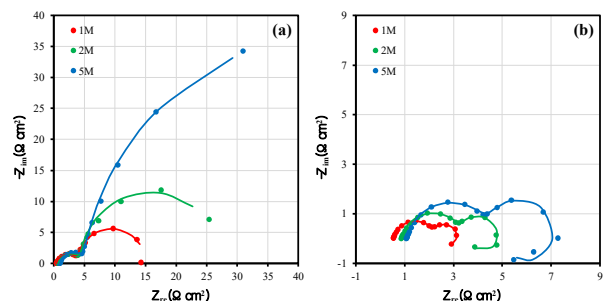


Fig. 3. Experimental and fitted EIS spectra in Nyquist representation recorded at (a) 500 mV and (b) 250 mV, for methanol solution at different concentrations (1M, 2M, 5M). Nyquist diagrams are interpreted according to the equivalent circuit shown in Figure 1.

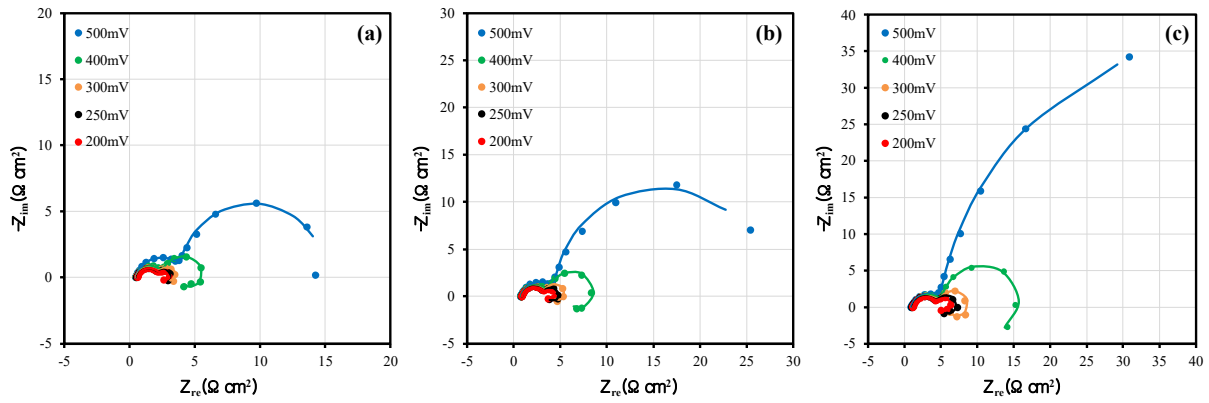


Fig. 4. Experimental and fitted EIS spectra in Nyquist representation recorded at 500 mV, 400 mV, 300 mV, 250 mV and 200 mV, for different methanol solution at concentrations: (a) 1M, (b) 2M and (c) 5M. Nyquist diagrams are interpreted according to the equivalent circuit shown in Figure 1.

Furthermore, as the potential decreases, an inductive loop, characteristic of the low-frequency domain, begins to be more evident. This impedance response implies that the surface coverage of the anode has a significant impact on the kinetics of the electrochemical reaction, highlighting the importance of species adsorption at the electrode.

Nyquist diagrams are interpreted according to the equivalent circuit shown previously (Figure 1), where R_{Ω} represents the ionic resistance of the membrane, the parallel between $R_{ct,C}$ and Q_C is representative of the charge transfer and double-layer capacitance at the cathode, and finally the electrochemical behavior at the anode is modeled with a parallel between $R_{ct,A}$ and Q_A with the parallel contribution, visible at low frequencies, of the inductive loop due to the adsorption of species at the electrode.

The parameters derived from the best-fitting procedure using the equivalent circuit are shown in Table 1. First, R_{Ω} increased slightly with increasing methanol concentration, probably due to the lower level of hydration of the solid electrolyte during the EIS measurement and, therefore, lower proton conductivity that

is strongly dependent on the level of membrane hydration. The contribution to the overall impedance of the cell from the oxygen reduction reaction, given by $R_{ct,C}$, was slightly higher with increasing concentration. An increase in methanol concentration in fact implies the associated increase in methanol crossover, resulting in more oxygen consumption for methanol oxidation at the cathode electrode and reduced oxygen concentration. $R_{ct,A}$, on the other hand, is strongly influenced by methanol concentration. The diameter of the anodic capacitive semicircle increases contrary to what might be expected for methanol oxidation, i.e., the greater the amount of methanol the greater its oxidation at the electrode. What occurs is that with increasing methanol concentration there is an increase in coverage by adsorbed CO, and this is consistent with the literature [26].

TABLE I. EQUIVALENT CIRCUIT PARAMETER VALUES

	1M					2M					5M				
	500mV	400mV	300mV	250mV	200mV	500mV	400mV	300mV	250mV	200mV	500mV	400mV	300mV	250mV	200mV
R_{Ω} [$\Omega \cdot \text{cm}^2$]	0.48	0.50	0.49	0.54	0.60	0.77	0.82	0.87	0.88	0.89	0.99	1.07	1.09	1.09	1.21
$R_{ct,C}$ [$\Omega \cdot \text{cm}^2$]	3.55	2	1.77	1.71	1.67	3.77	2.75	2.51	2.46	2.44	3.87	4.06	3.78	3.39	3.22
Q_C [$\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$]	0.022	0.019	0.019	0.019	0.019	0.021	0.017	0.017	0.016	0.017	0.017	0.016	0.017	0.017	0.016
n_C	0.84	0.87	0.86	0.85	0.85	0.82	0.86	0.86	0.86	0.85	0.85	0.84	0.83	0.87	0.88
$R_{ct,A}$ [$\Omega \cdot \text{cm}^2$]	11	3.59	1.35	0.96	0.83	22.79	6.50	2.44	1.57	1.50	84.51	11.50	4.22	2.82	2.27
Q_A [$\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$]	0.45	0.52	0.59	0.66	0.78	0.35	0.47	0.60	0.63	0.81	0.25	0.37	0.50	0.54	0.49
n_A	1	0.93	1	1	0.95	1	0.89	1	1	0.89	0.92	0.99	1	1	0.97
L [$\text{H} \cdot \text{cm}^2$]	-	31.16	9.63	4.44	3.11	-	54.50	11.21	7.13	2.68	-	251.10	30.49	15.16	8.84
R [$\Omega \cdot \text{cm}^2$]	-	2.35	1.29	0.58	0.35	-	3.26	1.71	0.47	0.39	-	4.73	1.46	0.82	1.13
χ	4.41E-03	7.17E-04	6.07E-04	4.28E-04	4.04E-04	2.09E-03	8.39E-04	7.15E-04	6.45E-04	4.47E-04	5.57E-04	4.73E-04	9.03E-04	7.88E-04	1.20E-03

V. CONCLUSION

DMFC performance analysis was carried out using Electrochemical Impedance Spectroscopy (EIS), recording impedance spectra in several operating conditions, i.e. changing cell voltage and methanol aqueous solution concentration at the anode.

Based on the polarization curve measurement and fitting of impedance data, methanol concentration of 1 M is the optimal concentration to achieve maximum power density and efficiency. The performance of the DMFC is strongly influenced by the concentration of the aqueous methanol solution fed to the anode. Indeed, an increase in methanol concentration implies an increase in methanol crossover, resulting in higher oxygen consumption for methanol oxidation at the cathode electrode and a reduction in oxygen concentration. EIS data helped in understanding methanol electrooxidation process, i.e. the higher the amount of methanol, the higher is the coverage by the adsorbed CO on the PtRu electrocatalyst, with a worsening of overall cell performance.

REFERENCES

- [1] C. K. Dyer, 'Fuel cells for portable applications', *J Power Sources*, vol. 106, no. 1–2, pp. 31–34, 2002, doi: 10.1016/S0378-7753(01)01069-2.
- [2] B. C. Ong, S. K. Kamarudin, and S. Basri, 'Direct liquid fuel cells: A review', *Int J Hydrogen Energy*, vol. 42, no. 15, pp. 10142–10157, Apr. 2017, doi: 10.1016/j.ijhydene.2017.01.117.
- [3] S. Surampudi *et al.*, 'Advances in direct oxidation methanol fuel cells', *J Power Sources*, vol. 47, no. 3, pp. 377–385, 1994, doi: 10.1016/0378-7753(94)87016-0.
- [4] A. Heinzl and V. M. Barragan, 'A review of the state-of-the-art of the methanol crossover in direct methanol fuel cells', *J Power Sources*, vol. 84, no. 1, pp. 70–74, 1999, doi: 10.1016/S0378-7753(99)00302-X.
- [5] M. Ahmed and I. Dincer, 'A review on methanol crossover in direct methanol fuel cells: Challenges and achievements', *Int J Energy Res*, vol. 35, no. 14, pp. 1213–1228, Nov. 2011, doi: 10.1002/er.1889.
- [6] S. H. Seo and C. S. Lee, 'A study on the overall efficiency of direct methanol fuel cell by methanol crossover current', *Appl Energy*, vol. 87, no. 8, pp. 2597–2604, 2010, doi: 10.1016/j.apenergy.2010.01.018.
- [7] J. Ge and H. Liu, 'Experimental studies of a direct methanol fuel cell', *J Power Sources*, vol. 142, no. 1–2, pp. 56–69, Mar. 2005, doi: 10.1016/j.jpowsour.2004.11.022.
- [8] Jianguo Liu, Tian-Shou Zhao, Rong Chen, and Chung Wai Wong, 'Effect of methanol concentration on passive DMFC performance', *Fuel Cells Bulletin*, vol. 2005, no. 2, pp. 12–17, 2005.
- [9] O. Popovici, 'The Study of the Efficiency of a Direct Methanol Fuel Cell', *Journal of Electrical and Electronics Engineering*, vol. 7, no. 2, pp. 31–34, 2014.
- [10] A. Oedegaard and C. Hentschel, 'Characterisation of a portable DMFC stack and a methanol-feeding concept', *J Power Sources*, vol. 158, no. 1, pp. 177–187, Jul. 2006, doi: 10.1016/j.jpowsour.2005.06.044.
- [11] S. Uhm, S. T. Chung, and J. Lee, 'Activity of Pt anode catalyst modified by underpotential deposited Pb in a direct formic acid fuel cell', *Electrochem Commun*, vol. 9, no. 8, pp. 2027–2031, Aug. 2007, doi: 10.1016/j.elecom.2007.05.029.
- [12] A. M. Dhirde, N. v. Dale, H. Salehfar, M. D. Mann, and T. H. Han, 'Equivalent electric circuit modeling and performance analysis of a PEM fuel cell stack using impedance spectroscopy', *IEEE Transactions on Energy Conversion*, vol. 25, no. 3, pp. 778–786, Sep. 2010, doi: 10.1109/TEC.2010.2049267.
- [13] Ferrero R, Marracci M, and Tellini B, 'Impedance Spectroscopy on a Single PEM Fuel Cell for the Evaluation of Current Ripple Effects', in *IEEE International Instrumentation and Measurement Technology Conference Proceedings*, 2012, pp. 52–56. doi: 10.1109/I2MTC.2012.6229480.
- [14] G. Dotelli, R. Ferrero, P. G. Stampino, S. Latorrata, and S. Toscani, 'Diagnosis of PEM fuel cell drying and flooding based on power converter ripple', *IEEE Trans Instrum Meas*, vol. 63, no. 10, pp. 2341–2348, Oct. 2014, doi: 10.1109/TIM.2014.2318371.
- [15] P. A. Lindahl, M. A. Cornachione, and S. R. Shaw, 'A time-domain least squares approach to electrochemical impedance spectroscopy', *IEEE Trans Instrum Meas*, vol. 61, no. 12, pp. 3303–3311, 2012, doi: 10.1109/TIM.2012.2210457.
- [16] G. Dotelli, R. Ferrero, P. G. Stampino, and S. Latorrata, 'Analysis and Compensation of PEM Fuel Cell Instabilities in Low-Frequency EIS Measurements', *IEEE Trans. Instrum. Meas.*, vol. 63, no. 7, pp. 1693–1700, 2014.
- [17] X. Z. Yuan, C. Song, H. Wang, and J. Zhang, *Electrochemical impedance spectroscopy in PEM fuel cells: Fundamentals and applications*. Springer London, 2010. doi: 10.1007/978-1-84882-846-9.
- [18] Orazem Mark E. and Tribollet Bernard, *Electrochemical Impedance Spectroscopy*. NJ, 2008. doi: 10.1002/9780470381588.
- [19] N. Wagner, 'Characterization of membrane electrode assemblies in polymer electrolyte fuel cells using a.c. impedance spectroscopy', *J Appl Electrochem*, vol. 32, no. 8, pp. 859–863, 2002, doi: 10.1023/A:1020551609230.
- [20] R. Makharia, M. F. Mathias, and D. R. Baker, 'Measurement of Catalyst Layer Electrolyte Resistance in PEFCs Using Electrochemical Impedance Spectroscopy', *J Electrochem Soc*, vol. 152, no. 5, p. A970, 2005, doi: 10.1149/1.1888367.
- [21] G. Wu, L. Li, and B. Q. Xu, 'Effect of electrochemical polarization of PtRu/C catalysts on methanol electrooxidation', *Electrochim Acta*, vol. 50, no. 1, pp. 1–10, Nov. 2004, doi: 10.1016/j.electacta.2004.07.006.
- [22] A. Zaffora, F. di Franco, E. Gradino, and M. Santamaria, 'Methanol and proton transport through chitosan-phosphotungstic acid membranes for direct methanol fuel cell', *Int J Energy Res*, vol. 44, no. 14, pp. 11550–11563, Nov. 2020, doi: 10.1002/er.5777.
- [23] I. Gatto, A. Saccà, A. Carbone, R. Pedicini, F. Urbani, and E. Passalacqua, 'CO-tolerant electrodes developed with PhosphoMolybdic Acid for Polymer Electrolyte Fuel Cell (PEFCs) application', *J Power Sources*, vol. 171, no. 2, pp. 540–545, Sep. 2007, doi: 10.1016/j.jpowsour.2007.06.003.
- [24] M. Santamaria, C. M. Pecoraro, F. di Franco, F. di Quarto, I. Gatto, and A. Saccà, 'Improvement in the performance of low temperature H₂-O₂ fuel cell with chitosan-phosphotungstic acid composite membranes', *Int J Hydrogen Energy*, vol. 41, no. 11, pp. 5389–5395, Mar. 2016, doi: 10.1016/j.ijhydene.2016.01.133.
- [25] A. Oedegaard and C. Hentschel, 'Characterisation of a portable DMFC stack and a methanol-feeding concept', *J Power Sources*, vol. 158, no. 1, pp. 177–187, Jul. 2006, doi: 10.1016/j.jpowsour.2005.06.044.
- [26] P. Piel, R. Fields, and P. Zelenay, 'Electrochemical Impedance Spectroscopy for Direct Methanol Fuel Cell Diagnostics', *J Electrochem Soc*, vol. 153, no. 10, p. A1902, 2006, doi: 10.1149/1.2266623.