Thesis of doctoral dissertation

Study of the transient behaviour of proton exchange membrane fuel cells by using multi-scale models

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Introduction

Fuel cells are among the most promising candidates, which can substitute heat engines in the production of electricity. Although the first H₂ – O₂ fuel cell (“gas cell”) was invented in 1839, the industrial utilization of fuel cells has not become widespread. Consequently, the study and research of fuel cells and fuel cell systems not only have scientific interest, but a better and more efficiently functioning fuel cell is of great business importance, as well. The static behaviour of fuel cells has been elucidated in details; however the transient behaviour, i.e. the time-dependent variation of the characteristic properties of fuel cells during the frequent load change, is seldom found in the literature. These phenomena happen very frequently during the operation of a vehicle, which was studied by a self-made city car. It was called HY-GO, which was the first hydrogen-air operated fuel cell vehicle in Hungary. It was built by a group of a very committed researchers and engineers of the Laboratory of Electrochemistry and Electroanalytical Chemistry at Eötvös Loránd University, Institute of Chemistry.

Aims and methodology

The purpose of my doctoral research was the development, optimization and electrochemical modeling of hydrogen-air proton exchange membrane fuel cells (PEMFC). In the course of the work I performed electrochemical experiments with the platinum catalyst, membrane electrode assemblies, fuel cell stacks and fuel cell systems. The complex model of the fuel cell system has been developed by using multi-scale modeling approach. The first level, the molecular level was the model of the electrochemical behaviour of oxygen reduction reaction and the behaviour of the Pt surface. The second level was the time dependent model of the active layer taking into account the macro-structure of the membrane electrode assembly. The third was the global level of the business ecosystem modeling the effect of the previous level’s technical properties (i.e. PEMFC size, rated power, efficiency, etc) on the economic sustainability of the hydrogen economy.

Achievements and conclusions

Molecular level: Smooth and platinized platinum electrodes in contact with sulfuric acid solutions were studied using electrochemical quartz crystal nanobalance (EQCN) technique at different temperatures. The reduction of platinum oxide, the extent of which depends on the positive potential limit and the scan rate, i.e., the duration of time that the system spends at the potential region of oxide formation allowing the formation of the oxide and the platinum–oxygen surface exchange process. The effect of temperature is practically insignificant in this respect. The results of the chronoamperometric experiments supplied evidence that the dissolution of platinum atoms (clusters) or ions occurs after the completion of the reduction of oxide. This phenomenon has to be considered when the proton exchange membrane fuel cell is used under frequently changing load, e.g., in a vehicle, when the potential decreases from a high positive value to a potential of ca. 0.3–0.4 V. Furthermore, at elevated temperatures (above ca. 50 °C) an anodic dissolution of the platinum takes place, i.e., a dissolution of the platinum catalyst can be expected at the working temperature (60–80 °C) of a PEMFC. The mass changes in the oxide layer region is in accordance with the formation of PtO on the electrode surface. However, the electroreduction of the PtO layer may lead to a Pt loss which effect strongly depends on the
positive potential limit and the scan rate. It is most likely that the place exchange process involving Pt and O atoms is responsible for this phenomena. The reduction of oxide results in a partial dissolution of platinum and the formation of Pt$^{2+}$ ions, which can be detected in the solution phase.

An unusual change of the surface mass with time has been observed during the oxygen reduction reaction on Pt by using chronopotentiometry and simultaneous electrochemical quartz crystal nanobalance (EQCN) measurements. A simplified kinetic model of Damjanovic and Brusic, which involves two electrochemical and a chemical step, was analyzed by using phase plane analysis. The theoretical analysis predicted that bistability might occur in this system at a certain set of parameter values. The mathematical simulation of the different trajectories explained well the strong influence of the starting potential and the current density on the change of the surface mass observed. Evidence was found that the surface coverage can increase at lower potentials which can lead to the formation of hydrogen peroxide even if it is energetically unfavorable.

Macro-level (MEA model): The performance of a proton exchange fuel cell (PEMFC) is substantially influenced by the properties of the membrane electrode assembly (MEA). A knowledge of the effects of the composition of MEA and the operation conditions is crucial regarding the fabrication of an efficient fuel cell. It is a rather difficult task to separate the combined effects of different processes occurring and affected by the working parameters applied in an assembled fuel cell. In this work the effects of the Nafion content of the MEA, the temperature and gas pressure on the performance of a H$_2$-Air PEM fuel cell at 100 % RH were studied experimentally. A numerical model and a parameter estimation technique have been developed in order to extract the quantities characteristic to the microstructure of the MEA such as porosity, Pt utilization, and active surface area. In the model the several processes, structural parameters and their variation upon the operation conditions have been included. The whole cell has been investigated, however, the anodic process has been considered as a very fast one, i.e., the anode is practically a hydrogen electrode at equilibrium. Therefore, the oxygen reduction at the cathode, proton transport, gas diffusion within pores and in the agglomerates, dissolution of oxygen in the ionomer have been taken into account as the rate determining processes at different operating conditions. The respective electrochemical, distribution, and transport equations used contain the quantities
such as exchange current density, proton conductivity, oxygen permeability, real surface area of Pt catalyst etc. and their temperature and pressure dependences. The results obtained by simulation have been compared with the sets of data measured during functioning of the cell.

The model has been validated by the effects of temperature and pressure on the different characteristic parameters rather than the match of the fitting to a single potential – current curve. The parameters like average radius of the agglomerates, Pt utilization, and the gas-phase porosity in principle should not change with temperature and pressure, however, those are sensitive to the Nafion content. The variation of the exchange current density with temperature has been taken into account but the effects of pressure and Nafion content were neglected.

The porosity and the radius of the agglomerates were proven to be independent from the variation of temperature and pressure. It was found that the porosity was increased with increasing Nafion content. It may be related to the surfactant properties of the Nafion in as much as at higher Nafion contents the surface of the agglomerates was covered with Nafion more extensively, which prevented the agglomerates to stick together. At higher Nafion content the porosity decreased (the layer was more dense), which might be related to the formation of the inverse micelles of the Nafion. The radius of agglomerates calculated was in agreement with the porosity, because the smallest size was found near the optimal Nafion content.

**Characterization of the transients:** Periodical modulation technique has been developed and applied for estimation of the most important electrochemical parameters characterizing the proper functioning of PEMFC. The effectiveness and the reliability of this approach have been tested by using a factor analysis method (ANOVA). It was found that the quantities derived, such as Tafel-slope, double-layer capacitance, the exchange current density and the cell resistance, can be determined with a very good statistics. Therefore, the method and the algorithm elaborated for this purpose is suitable for real-time monitoring and the regulation of the functioning fuel cell.

The correlations found so far, e.g., between the double layer capacitance and the duty ratio, or between the exchange current density and the duty ratio, can be diminished by using higher frequency data acquisition, however, it makes the measurement somewhat more
expensive. Since the parameters are independent from the interaction effects of the applied parameters (current, frequency, duty ratio), i.e., from the combined influence of current and frequency, current and duty ratio etc., the higher frequency data acquisition is not really necessary. The influence of the relaxation time on Tafel slope cannot be interpreted by the previously mentioned reasons, because the duty ratio and the current have no effects on it. The values of the Tafel slope calculated from the current interruption curves are substantially smaller than those calculated from the performance curves. Therefore this effect might be in connection with the changes of the surface coverage related to the adsorbed species and the double layer composition which are periodically varied during the potential excursion between ca. 0.45 V and 0.75 V with the frequencies from 1 Hz to 5 Hz.

The real-time simulation of fuel cells has become an important task regarding the control and automation of functioning applications. The operator splitting methods provides an opportunity to monitor the actual state of fuel cells in real time, because it splits the complex system to different subsystems, and the most effective numerical methods can be applied for every subsystem. The complex limiting current kinetics was compared with the measurements. The parameters of the fuel cell were calculated by the composition of the catalyst layer and no further parameter optimization was done. A good fit was found for the simulation of V-I curves, but the simulated and the measured relaxation states showed a substantial difference in the case of the examination of current steps. These results indicate that the effect of variation of the surface coverage (e.g., oxides, chemisorbed species) during fast changes of potential or current, which occur many times in real applications, can also be treated, which is in correlation with the results obtained by the current interruption technique.

A novel and simple optimization tool has been introduced, which can help to develop better short-circuit protection for fuel cell systems. The potential difference between the steady state and the short time transients has been calculated analytically taking into account the non-linear reaction kinetics and the double layer charging. The asymptotic solutions of the performance curve were used and some simple relationship has been derived for the maximum potential increase, and the maximum short-circuit current. The maximum short-circuit current was found to be inversely proportional with time, which seems to be
reasonable at high currents and short load time. This relationship may be very useful for the design of a DC-DC converter, a control device and not only for the sizing of circuit breakers.

**Global-level:** During the simulation a hydrogen fuel cell based urban mini-car fleet has been analyzed for urban car-sharing application by different parameters like the fleet size, the rating power of the fuel cell, the cost of the vehicle the cost of the energy and the hydrogen. Two different operating strategies have been taken into account: hydrogen comes from regular supply at public hydrogen stations, or hydrogen is generated by electrolysis and all of the by-products are utilized (sold) like oxygen and heat.

The final price of 1 hour usage of the vehicles was set to $8.75, which is only a bit higher than a normal car sharing service fee. The sensitivity analysis showed that the key performance indicators were the utilization of the fleet, namely the sold hours/24 hours and the price of the by-products like oxygen and heat. As it was expected, the increase of the utilization of the fleet decreases the day of return (DoR), i.e., shows better financial conditions. The variation of oxygen price was more interesting. Below 2.5 USD/m$^3$ a smaller rated power fuel cell size showed shorter DoR, while if oxygen could be sold at higher price the application of a bigger fuel cell was preferable. The effect of the fuel cell size was different in the two operating conditions. If the hydrogen is bought from regular supply, the increase of the cell size increases the DoR linearly, however in the case of the on-site electrolysis the DoR leveled off by the increasing cell size. It was also clear from the figures that the effect of the cost of the energy or the hydrogen is insignificant in the case where a smaller fuel cell was applied. The price of the vehicle (without the powertrain) became insignificant if the utilization exceeded 50%. The economies of scale were reached at 50 cars fleet. The application of different hydrogen storage technologies, i.e. metal hydrate and high pressure canister, which requires low and high pressure refueling station, respectively, did not showed big differences. However, the specific investment cost of refueling station was substantially lower in the case of low pressure technology, but the longer refueling time required more station and the lower maximal utilization reduced the utilization.

It can be concluded that at the beginning the application of smaller fuel cells is more favourable, but if the utilization exceeds a critical value (30% in our case) bigger cars with bigger fuel cells might be also profitable.
Publications

Publications connected with dissertation:
1. Á. Kriston, G. Inzelt:
   Estimation of the characteristic parameters of PEMFCs Proton Exchange Membrane Fuel
   Cells under operating condition

2. Á. Kriston, G. Inzelt, I. Faragó, T. Szabó:
   Simulation of the transient behaviour of fuel cells by using operator splitting techniques
   for real-time applications

3. Ákos Kriston, Tamás Szabó, György Inzelt:
   The marriage of car sharing and hydrogen economy: A possible solution to the main
   problems of urban living

4. G. Inzelt, B.B. Berkes and Á. Kriston:
   Temperature dependence of two types of dissolution of platinum in acid media. An
   electrochemical nanogravimetric study

Publications linked to dissertation:
5. G. Inzelt, B.B. Berkes and Á. Kriston:
   Two Types Dissolution of Platinum in Acid Media. An Electrochemical Nanogravimetric
   Study

6. G. Inzelt, B.B. Berkes, Á. Kriston and A. Székely:
   Electrochemical nanogravimetric studies of platinum in acid media

7. G. Inzelt, B.B. Berkes, Á. Kriston:
   Electrochemical nanogravimetric studies of adsorption, deposition, and dissolution
   processes occurring at platinum electrodes in acid media

   Unusual surface mass changes in the course of the oxygen reduction reaction on platinum
   and their explanation by using a kinetic model
**Book chapter:**

1. Faragó István, Inzelt György, Kornyik Miklós, Kriston Ákos, Szabó Tamás:
   Stabilization of a numerical model through the boundary conditions for the real-time simulation of fuel cells.

**Other publications:**

1. Faragó István, Inzelt György, Kriston Ákos, Kornyik Miklós, Szabó Tamás:
   Tüzelőanyag-cellafajlesztés mágny szemmel

3. Kriston Ákos, Molnár Norbert, Orosz Mihály, Miklósi József, Vaspál Gábor:
   Patent application: Process and device for producing Ice of gel consistency, WO 2007/054752 A1

3. Á. Kriston, M. Lakatos-Varsánya:
   Testing and Analyzing Metastable Pitting Corrosion

4. www.fuelcell.hu

5. www.hy-go.com

**Conferences:**

1. Kriston Ákos:
   Relation between the Hydrogen and the Knowledge Base Economy
   First Budapest International Hydrogen Energy Forum, 9-10 October, 2006

2. Kriston, Á., Szabó, T., Faragó, I., Inzelt, G., Kornyik, M.:
   Transient behaviour of fuel cells and its control strategy for electric vehicles. (lecture)

3. Szabó, T., Kriston Á.:
   Reliability of the numerical simulation of fuel cells using operator splitting method. (lecture)
   European Seminar on Coupled Problems Jetrichovice, Czech Republic

4. Faragó I., Inzelt G., Kriston, Á., Szabó T.:
   Investigation of fuel cell’s transients for real time parameter estimation and control algorithms. (poster)
   59th ISE Meeting, Seville, Spain

5. Kriston Á., Szabó T., Faragó I., Inzelt Gy.,
Development of novel characterization tool for studying fuel cell’s pulsed power performance. (poster)
NHA Conference and Hydrogen Expo, Columbia, SC, USA

6. Á. Kriston, T. Szabó, G. Inzelt, I. Faragó:
Detailed Analysis of Fuel Cell’s Peak Power Performance: Simulation and Measurement (oral)
216th ECS Meeting in Vienna, Austria

7. G. Inzelt, B. Berkes, A. Kriston:
Two Types of Platinum Dissolution in Acid Media: An Electrochemical Nanogravimetric Study (oral)
216th ECS Meeting in Vienna, Austria

8. Ákos Nemes, Ákos Kriston, György Inzelt, Tamás Szabó:
Analysis of the effects of variation of the MEA microstructure at different Pt/Nafion ratios, pressures and temperatures (poster)
61st Annual Meeting of the International Society of Electrochemistry, September 26th - October 1st, 2010, Nice, France

9. Ákos Kriston, Tamás Szabó, Ákos Nemes, Soma Vesztergom, Balázs B. Berkes, Horváth Tamás, Norbert Molnár, Dr. Karl Dobos:
The application of multi-level simulation during the development of a hydrogen fuel cell vehicle (poster)
61st Annual Meeting of the International Society of Electrochemistry, September 26th - October 1st, 2010, Nice, France

10. Kriston A, B. B. Berkes, P. Simon, G. Inzelt:
Investigation of oxygen reduction reaction on Pt by using electrochemical quartz crystal nanobalance and numerical simulation (poster)
61st Annual Meeting of the International Society of Electrochemistry, September 26th - October 1st, 2010, Nice, France

11. Kriston Ákos: The crucial step in the road towards efficient fuel cells: the reduction of oxygen (Invited lecturer)

12. Organizing workshops about renewable energy and electromobility, Budapest: www.meet-up.com/electromobility