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Basic mathematical modeling and experimental validation of electrochemical hydrogen compressor

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A mathematical modeling of electrochemical hydrogen compression process is presented. The model is based on theoretical thermodynamic functions and kinetic equations. The calculations are performed using free Scilab 6.0 software at varying input parameters such as current density, temperature and pressure. The developed model allows determination of polarization U/j characteristics, ohmic drop and energy efficiency of the compressor. It is validated using real experimental data from a laboratory prototype of electrochemical compressor in a single mode operation. The prototype system works with a membrane electrode assembly containing magnetron sputtered Pt catalysts on both electrodes (0.25 $mg_{Pt}.cm^{-2}$ loading) and Nafion 117 polymer electrolyte membrane. The model is further developed to predict the behavior of the compressor at high differential pressure and elevated temperature.

Keywords: Electrochemical hydrogen compressor, differential pressure, energy efficiency, temperature dependency, mathematical modeling

INTRODUCTION

Hydrogen economy is a rapidly growing industry, which is expected to contribute essentially in reducing the energy consumption and harmful air pollutions, as well as in stimulating the global economic growth. Hydrogen is a flexible energy carrier, capable to address the grid balancing issues and energy delivery in remote places. It is a sustainable alternative to fossil fuels, however, it suffers from a low volumetric energy density [1-3]. The most technically challenging barrier in regard to hydrogen economy is the development of safe, compact, and cost-effective hydrogen storage technology [4]. Hydrogen can be stored in a gaseous or liquid form, in metals, glass micro spheres, carbon nanotubes, etc. For efficient storage, each of the listed approaches requires medium to high pressure [5]. The electrochemical hydrogen compression (EHC) is highly efficient, low-maintenance and silent technology, considered as a potentially viable and cost-competitive alternative to the mechanical piston compression [6-8]. Over the time the EHC systems have been significantly improved in regard to energy efficiency, size, weight, level of compression, etc. The key element in these systems is the membrane electrode assembly where, in similarity to the PEM FC, the electrochemical conversion takes place [9-11]. The working principle of the EHC is presented schematically in Fig. 1.

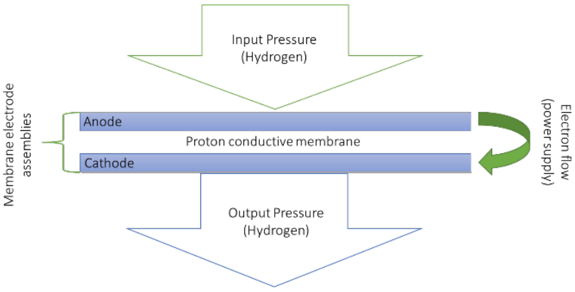

Fig. 1. Principle scheme of electrochemical hydrogen compressor in a single-mode operation.

The electrochemical hydrogen compression cell, in similarity to the fuel and electrolysis cell, consists of two chambers, one for each partial reaction. The hydrogen gas is delivered in the anode chamber of the system where the hydrogen molecules are split to protons and electrons (eq. 1). The protons move through the proton-conductive membrane to the cathode side where the reverse hydrogen evolution reaction takes place (eq. 2) and the obtained H_2 is accumulated and pressurized.

Anode reaction: $H_2 \rightarrow 2H^+ + 2\bar{e}$ (1)
Cathode reaction: $2H^+ + 2\bar{e} \rightarrow H_2$ (2)
Overall: $H_2 \rightarrow H_2$ (3)

The total cell voltage U_{EHC} required for the overall process (eq. 3) is a sum of the Nernst potential, E_{Nernst}, the activation energy, E_{act}, and the ohmic losses, E_{ohmic} (eq. 4):

$$U_{EHC} = E_{Nernst} + E_{ohmic} + E_{act} \quad (4)$$

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Due to the low activation energy of the process the assumption in eq. 5 is accepted:

$$U_{EHC} = E_{Nernst} + E_{ohmic} \tag{5}$$

The Nernst potential, E_{Nernst}, is determined by eq. 6:

$$E_{Nernst} = E^0 + \frac{RT}{nF}\ln\left(\frac{a_{oxid}}{a_{red}}\right) \tag{6}$$

where R is the universal gas constant, T is the temperature, n - the number of electrons, F – the Faraday constant. In case of electrochemical hydrogen compression, the electrolyte is a solid proton conductive membrane and using eq. 7, eq. 6 is transformed in eq. 8:

$$\ln\left(\frac{a_{oxid}}{a_{red}}\right) = \ln\left(\frac{P_{an}}{P_{cath}}\right) \tag{7}$$

$$E_{Nernst} = E^0 + \frac{RT}{nF}\ln\left(\frac{P_{an}}{P_{cath}}\right) \tag{8}$$

where, P_{cath} is the output pressure of the compressor (at the cathode side) and P_{an} is the input pressure (at the anode side). The ohmic potential of a reversible electrochemical process with fast kinetics such as the one in (eq. 3) can be determined/modeled by eq. 9:

$$E_{ohmic} = \left(\frac{\delta}{\varrho}\right) i \tag{9}$$

where, δ is the membrane thickness (cm), ρ is the cell conductivity (S.cm^{-1}), and i is the operating current density. The membrane conductivity is a function of the temperature and it is estimated using eq. 10:

$$\rho = 0.0007t + 0.0574 \tag{10}$$

where, t is temperature in °C. The differential pressure between both cell chambers is given by eq. 11:

$$P_{diff} = P_{cath} - P_{anode} \tag{11}$$

The most important operating parameter of the electrochemical hydrogen compression is the energy efficiency, also called voltage efficiency (eq. 12). It expresses the hydrogen conversion efficiency from which the electrical losses are subtracted.

$$E_{ef} = \frac{E_{Nernst}}{U_{EHC}}\,100 \tag{12}$$

The operation at open-circuit voltage would yield 100% voltage efficiency. However, at open-circuit voltage no compression would be accomplished.

In this paper a simple modeling of an electrochemical hydrogen compressor is presented based on its working principle (Fig. 1), the corresponding electrochemical reactions (eqs. 1-3), the thermodynamic formulas (eqs. 4-8), and the assumptions (eqs. 9-12). The goal was to calculate the energy requirements of the electrochemical hydrogen conversion at different input operating parameters. The results were validated using the experimental data from real tests performed in a laboratory prototype of electrochemical compressor in a single-mode of operation.

Mathematical model

The basic mathematical modeling was carried out using free Scilab 6.0 software. The eqs. 4-12 were applied as a programmable code directly in the Scinote part of the software. After validation, the obtained data were used to predict the behavior of the EHC at 2 operational regimes: *i)* regime "filter" (differential pressure 0 bar) which can be used to separate hydrogen from gaseous mixtures and obtain highly clean hydrogen; and *ii)* regime "hydrogen pump" (at 10 bars differential pressure) used for compression. The variables used in the developed model are summarized in Table 1:

Table 1. Nomenclature of variables

Symbol	Parameter	Dimension	Value
U_{EHC}	Cell voltage	[V]	-
E_{Nernst}	Nernst potential	[V]	-
E_{ohmic}	Ohmic potential	[V]	-
i	Current density	[A.cm^{-2}]	0-0.14
n	Number of electrons	-	2
F	Faraday constant	[C/mol]	96.485
R	Universal gas constant	[J K^{-1} mol^{-1}]	8.314
T	Temperature	[K]	293 - 353
P_{anod}	Pressure in the anode chamber (input)	[Bar]	1
P_{cathod}	Pressure in the cathode chamber (output)	[Bar]	1-11
P_{diff}	Differential pressure	[Bar]	10
E_f	Voltage efficiency	%	-

EXPERIMENTAL

The developed mathematical model was validated using a laboratory developed electrochemical hydrogen compressor with a single membrane electrode assembly (MEA) capable to operate in the temperature range up to 120°C and pressure up to 160 bar. A picture of the device is presented in Fig. 2.

The membrane electrode assembly (MEA) is the active element of the device where the electrochemical reactions proceed (HOR at the anode and HER on the cathode). It also separates both chambers of the compressor. The geometric area of the MEA under study was 7 cm^2. The polymer membrane used was a proton-conductive Nafion 117.

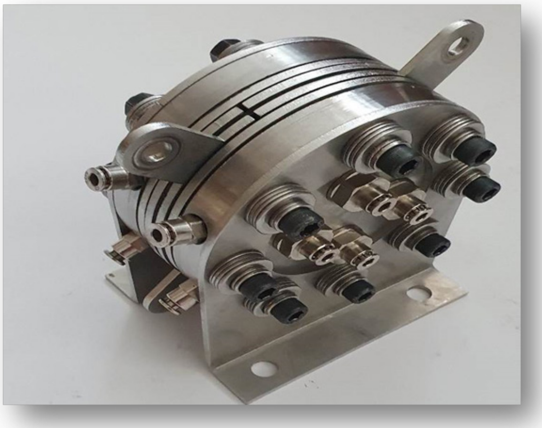

Fig. 2. Picture of the self-developed electrochemical hydrogen compressor.

Both electrodes had identical structure. The gas diffusion layer was a commercially available Freudenberg H2315 C2 covered by sputtered Pt catalytic film with loading of 0.25 $mg_{Pt}.cm^{-2}$. The MEA preparation procedure was described in details elsewhere [12]. The input hydrogen was supplied from a bottle with precisely controlled output pressure in the range from 1 to 5 bars. The electrochemical performance was investigated using Potentiostat / galvanostat Gamry model 1010E.

RESULTS AND DISCUSSION

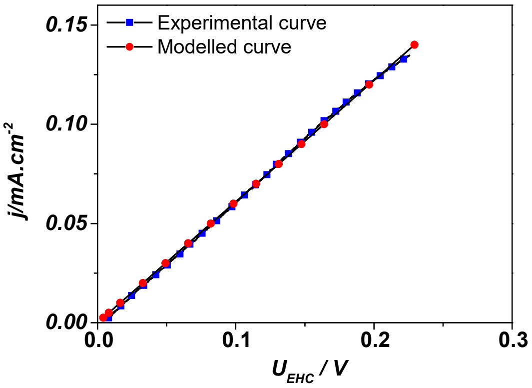

Fig. 3. Model and experimental voltampere characteristics of EHC at operating temperature 20°C and 0 bar differential pressure (regime “filter”); potential scan rate 1mV.s^{-1}.

The electrochemical performance of EHC is characterized by its voltampere characteristics (also called polarization curves and voltammograms) illustrating the dependency between the cell voltage and the density of the passing current at different operating conditions such as pressure, temperature, etc. Voltammograms gained from the mathematical model and those obtained experimentally are compared in Fig. 3.

Both polarization curves show a linear increase of current density with the increasing cell voltage and identical slopes which evidences the feasibility of the developed model.

To predict the behavior of the EHC at higher temperatures and differential pressures, the model was further developed. In Fig. 4 are shown the obtained results at a differential pressure varying in the range 0 – 10 bar and temperature 20°C.

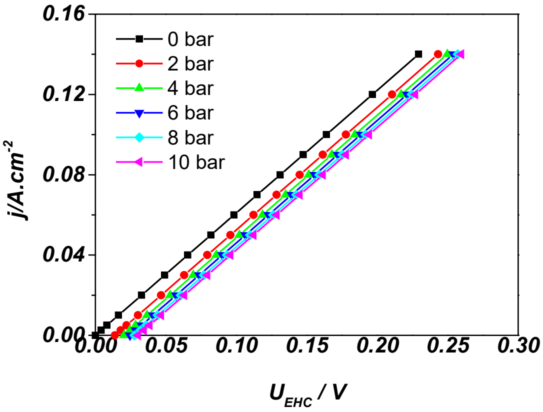

Fig. 4. Model voltampere characteristics of EHC at temperature 20°C and varying differential pressure in the range of 0 - 10 bars; potential scan rate 1mV.s^{-1}.

As already discussed, the differential pressure is the difference between the pressure in the cathode and anode chambers of the cell (eq. 11). According to the model, the varying differential pressure has several distinct effects on the EHC operating characteristics. First of all, as it is seen from the curves in Fig. 4, the increase of P_{diff} leads to a shift of the open circuit potential (U at $j = 0$) in positive direction. Secondly, with the increasing differential pressure all curves demonstrate linearity but the slope for each curve is slightly different and decreases with the increase of the pressure. Finally, the cell voltage at a given current density increases with the increasing P_{diff}. The higher differential pressure means higher concentration of hydrogen in the cathodic chamber of EHC which in turn, leads to transport limitations since the removal of hydrogen molecules produced on the cathode slows down. As a result, the HER overpotential and the cell voltage increase as well, meaning that more energy is required to convert hydrogen and thus, the efficiency of the EHC decreases.

Further simulations were performed to investigate the behavior of the system under varying operating temperature (up to 80°C) in both “filter” and “pump” regimes. The obtained results are presented in Figs. 5 and 6, respectively.

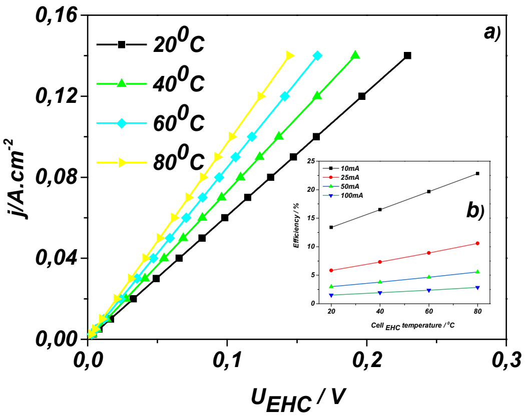

Fig. 5. Model voltampere characteristics in “filter” regime of EHC at varying temperature (a) and voltage efficiency at different current densities (b).

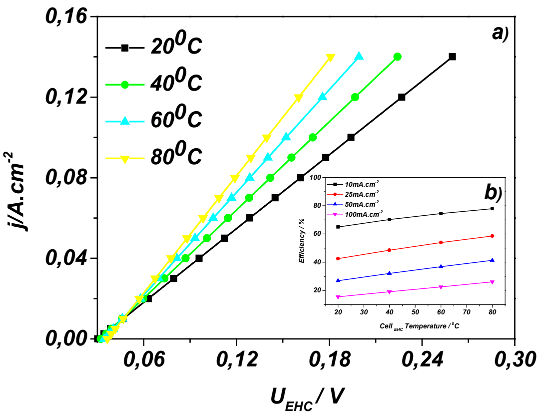

Fig. 6. Model voltampere characteristics in “hydrogen pump” regime of EHC at varying temperature (a) and voltage efficiency at different current densities (b).

At zero differential pressure (regime “filter”) the open circuit potential does not change with the increase of temperature, while the cell voltage essentially decreases. At a fixed current density of 140 mA.cm^{-2} the decrease is with 40 mV per each 20ºC. The voltage efficiency of EHC is also strongly temperature-dependent. The inset in Figure 5 shows the values of the efficiency calculated by eq. 12 at different current densities. It is seen that with the increasing temperature the EHC voltage efficiency increases, while the increase in the current density has an opposite effect. The highest efficiency value of 22% was calculated at 10 mA.cm^{-2} and 80ºC.

The calculations performed at differential pressure of up to 10 bar (regime “hydrogen pump”) demonstrate a similar behavior of the compressor. The cell voltage at 140 mA.cm^{-2} drops with the increasing temperature with approximate 50-60 mV per each 20ºC, the current density has the opposite effect, while the energy efficiency increases reaching a maximum value of nearly 80% at 10 mA.cm^{-2} and 80ºC.

CONCLUSIONS

The developed mathematical model based on fundamental thermodynamics and electrochemical relationships describes the influence of different operating parameters of the electrochemical hydrogen compressor on its U/j characteristics and energy efficiency. The model was validated by real experimental data and applied to predict the working characteristics of the compressor in “filter” and “pump” regime at varying operative temperatures.

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