

Dynamic simulation of Reversible Solid Oxide Cell (RSOC)

Hanaâ Er-rbib, Nouaamane Kezibri, Chakib Bouallou*

MINES ParisTech, PSL Research University, Centre for Energy Efficiency of Systems, 60 bd Saint Michel, Paris, France
 chakib.bouallou@mines-paristech.frn

A 1D dynamic model was developed in Matlab in order to study the Reversible Solid Oxide Cell (RSOC) behavior in transient state. It is a combination of kinetic, thermal and electrochemical models. The model was validated in steady state using available experimental results and showed a maximum relative error of 4.8 %. Therefore, the developed model can accurately simulate the RSOC performance. A dynamic simulation was performed to illustrate the temperature, the operating voltage and the outlet gas concentrations as a function of time and the fractional cell length for Power-to-Gas process that allows the storage of 10 MW of renewable energy. The co-electrolyser is operated under thermoneutral conditions at 1,073 K and 11,400 A/m². The obtained results showed that the cell has a thermal inertia that causes a temperature peak in dynamic state. This information is important because the temperature must be controlled in transient state to prevent the cell deterioration. It is observed that the operating voltage and outlet gas concentrations reach instantaneously the steady state while the temperature needs about 5 min to reach a constant value.

1. Introduction

Electricity produced globally using renewable sources of energy, reached over 4,699 TWh in 2012. This number exceeds 20 % of the total production of the world electricity (20.8 % in 2012) (Observ'ER, 2013). The EREC (European Renewable Energy Council, 2012) expects 70 % of electricity production to come from renewable sources by 2050 of which 42 % are generated from new technologies (mainly wind and solar). Noting that, the use of renewable sources of energy (RE) must be accompanied by the concept of electricity storage in order to smooth the fluctuation of the RE. A new approach to seasonal storage of renewable energy is based on using excess electricity produced from a renewable source to co-electrolyze at high temperature (1,073 K) steam and CO₂ into syngas via a RSOC (Reversible Solid Oxide Cell) operating in SOEC (Solid Oxide Electrolysis Cell) mode. The produced syngas (H₂ and CO) is fed into a methanation reactor where it is converted into CH₄. This gas is then injected into the natural gas network. When high consumption peaks appear, the RSOC is switched to SOFC (Solid Oxide Fuel Cell) mode which is fed by syngas. This latter is produced by tri-reforming of methane. The global diagram of this process is described in Figure 1 and detailed in Redissi et al. (2013).

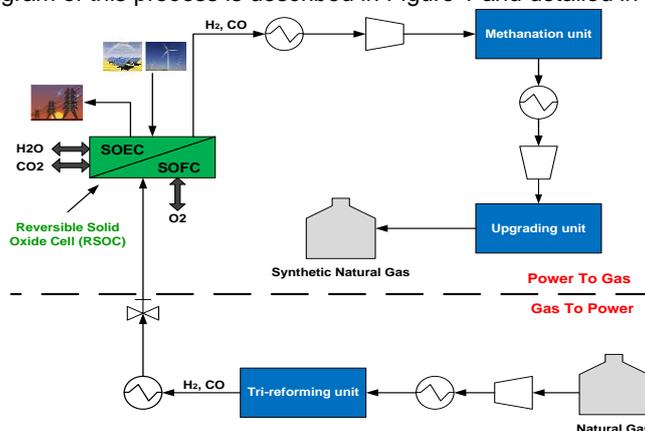


Figure 1: Reversible Power-to-Gas Process

This system undergoes disturbances that are mainly related to the intermittent renewable sources of energy in electricity storage mode and the reversibility of the process. However, there is a lack in studies which evaluate the dynamic operation of such systems mainly due to the lack of experimental data in literature. Each of the process components (in both operating modes) has time-dependant characteristics that affect the behaviour of the whole system. Particularly the electrolyser which should meet the dynamic operating conditions mainly caused by the intermittency of renewable energy. The current experimental tests allow the characterization of the co-electrolyser in steady state operation, but its dynamic behavior is yet to be investigated.

The Idaho National Laboratory (INL) in US has carried out research studies on the possibilities of producing synthesis gas by co-electrolysing CO₂ and H₂O (O'Brien et al., 2009). The models presented are 0D and steady state macro level based on the material and energy balances as well as the WGS (Water Gas Shift) reaction equilibrium constant (Stoots et al., 2009). The Polytechnic University of Hong Kong has proposed a 1D and 2D stationary model of a cathode supported planar SOEC operating at 1,073 K. The 1D model allows the prediction of WGS contribution in the production of CO and defining the limiting operating conditions (Ni M., 2012a). The 2D model is more accurate and studies each contribution of the involved chemical reactions (i.e WGS and methanation). The study concluded that the influence of methanation reaction can be neglected while WGS reaction has a significant impact on CO production (Ni M., 2012b).

There are only few works have dealt with dynamic behavior of SOEC. The models aimed to define control strategies and study the effects of operating conditions on transient performance. Udugawa et al. (2008a) developed a SOEC stack dynamic model operating at 1,073 K based on their previous model of the SOFC. Although the equations used were time dependent, only a steady state analysis was presented.

In second paper, Udugawa et al. (2008b) presented additional results on the air flow introduction at the anode side of the cell. They concluded that decreasing the concentration of oxygen on the air electrode lowers the Nernst potential required to start the cell operation. Cai et al. (2010), focused on simulating the behavior of the stack at various temperatures, and for different inlet gas compositions. They found that temperature and current density are the main parameters affecting the stack performance. In this work, they proposed to operate at a temperature of 1,073 K and a current density of 10,000 A/m². Under these conditions, the dynamic response of the cell temperature was stable.

In all of the above mentioned work, no model results have been compared to experimental data. Petipas et al. (2013) developed a 0D model for a system approach. It was based on physical equations (Nernst, current density and energy and mass balances) and experimental value of Area Specific Resistance (ASR). The model is composed of two sub-models describing the electrolysis module and the system balance. The results showed that the efficiency of the system can reach 91 % (HHV based) which is higher than that of low temperature and pressurized electrolysers (Bailera et al., 2017). However, since the thermal stress of the ceramic material, the maximum tolerable temperature gradient across the cells is ± 100 K, which reduces the average operating temperature to the range $1,073 \pm 50$ K to prevent mechanical failure. As the temperature is a function of the system power load, this latter is limited to a range of 60-100 %.

Kasempoor et al. (2014) developed a unit cell and then a stack model of the regenerative high temperature co-electrolyser (RSOC). This 1D model on a planar cell allows a static-dynamic simulation. Although, the authors presented equations of dynamic model, no transient simulation was performed. This work proposes an improvement of existing models to allow investigation into the effect of cell geometry, operating conditions and the inlet gas composition.

Despite all the current research, there is still a lack of understanding of the fundamental reaction and degradation mechanism of the high temperature co-electrolysis process. There are only few experimental studies on long-term degradation of a SOEC and no model takes into account this parameter. Moreover, few models have been validated with experimental results at steady state. In most cases, validation has been limited to a single V-J curve or was even absent. Furthermore, dynamic simulation results of the electrolyser and co-electrolyser have not been reported yet. Therefore, the present work addresses this issue through a dynamic simulation of the co-electrolyser.

2. Model description and steady state validation

2.1 Model description

The SOEC models are based on SOFC models and includes the following processes: porous gas diffusion, adsorption/desorption, reaction kinetics, electrolyte transport and charge transfer. The most common method to model the SOEC is to describe the limiting process mentioned previously by introducing the overpotential contribution: anode and cathode concentration $\eta_{\text{conc,an}}$ and $\eta_{\text{conc,ca}}$, activation η_{act} and ohmic overvoltages η_{ohm} (i.e. Eq(1)). Where V_{op} is the cell operating voltage and V_{Nernst} is the Nernst potential.

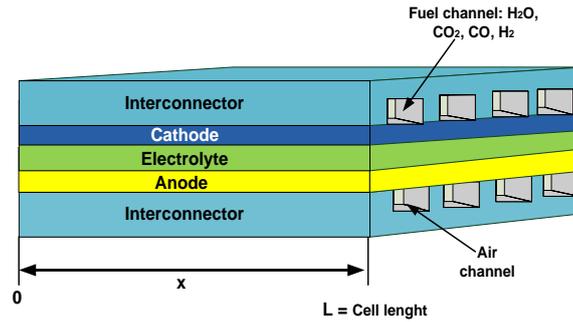


Figure 2: Representation of the RSOC unit cell

A 1D dynamic model on a planar RSOC cell is developed in Matlab (see Figure 2). It is a combination of kinetic, electrochemical and thermal models. It takes into account the electrochemical reaction of steam as well as the thermo-fluid phenomena inside the cell.

$$V_{op} = V_{nernst} - (\eta_{ohm} + \eta_{act} + \eta_{conc,an} + \eta_{conc,ca}) \quad (1)$$

The model allows the study of the effect of cell geometry, operation conditions and the inlet gas composition. It can easily predict the performance of SOEC/SOFC for different current density (J) and under various operating conditions. The operating mode (SOFC or SOEC) is defined by changing the sign of current density. When it is negative, the model is operating at SOEC mode and when it is positive, the model is in SOFC mode. The cells are electrically in series.

2.2 Model validation

The steady state model validation is based on the prediction of V-J performance characteristic curve and the reactant utilization. The model developed in this work has been validated by comparing numerical results against experimental data in steady state carried out by and Zhan et al. (2009) and later Graves (2010) for different cases. The operating conditions used for this experimental work are presented in Table 1.

The predicted model results are in excellent agreement with the experimental data even at different operating conditions and inlet compositions. The maximal relative error between experimental and numerical results is around 4.8 %. Figures 3(a) and 3(b) show the experimental data points vs the numerical model behavior for all considered cases. The final adjusted values of the model parameters (The fitted values are confidential) are then used to assess the dynamic behavior of the RSOC unit within the reversible Power-to-Gas process shown earlier in Figure 1.

Table 1: Operating conditions for the available experimental data

Experimental data	Graves (2010)			Zhan et al. (2009)
Temperature (K)	1,123			1,073
Pressure (MPa)	0.1			0.1
Total molar flow in fuel side (mol/s)	2.84×10 ⁻⁴			1.74×10 ⁻⁴
Composition in fuel side (%)	Composition 1	Composition 2	Composition 3	
H ₂ O	45	50	25	50
CO ₂	45	50	25	25
H ₂	10	0	25	25
CO	0	0	25	0
Total molar flow in air side (mol/s)	5.68 ×10 ⁻⁴			5×10 ⁻¹⁰
Composition in air side (%)	Composition 1	Composition 2	Composition 3	
O ₂	1	1	1	1
N ₂	0	0	0	0

3. RSOC unit dynamic simulation

The dynamic simulation was performed for the considered composition in the Power-to-Gas process: 68.7 % H₂O, 6.3 % H₂, 23 % CO₂ and 2 % CO. The reversible co-electrolyser has been sized for storing 10 MW of renewable electricity. In order to scale up the unit cell to a stack, the value of ASR was set to 1.7×10⁻⁵ Ω.m².

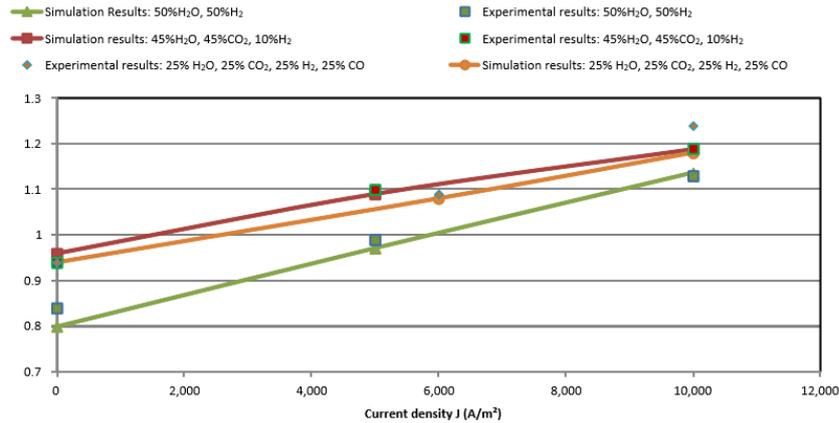


Figure 3(a): Steady state model validation with Graves (2010) experimental data

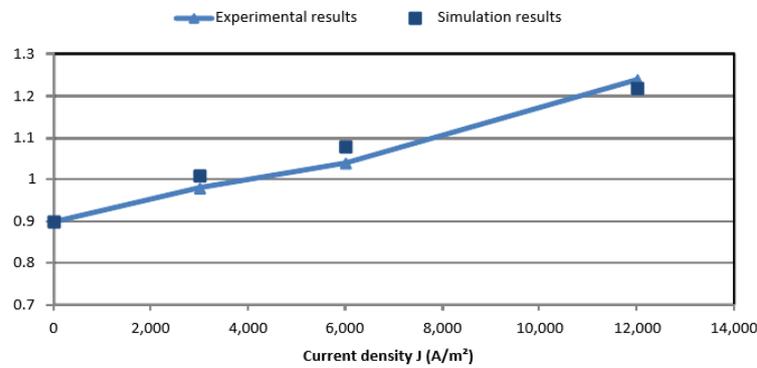


Figure 3(b): Steady state model validation with Zhan et al. (2009) experimental data

The RSOC is then modeled as a parallel set of stacks of equal number of cells which are fed by the same flow of fuel and sweep air. Consequently a total of 49,190 cells are used in the 10 MW RSOC unit and fueled by around 56 mol/s of gas with the specified composition and 10 mol/s of sweep air. The co-electrolyser operates at 1,073 K and 0.3 MPa. A current density of 11,400 A/m² is applied for thermoneutral operation.

3.1 Thermal behavior

Figure 4(a) shows temperatures profile as a function of time. As shown in this figure the steady state is reached in about 5 min. First, a short temperature decrease is observed which is mainly caused by the endothermic nature of the involved reactions (i.e. WGS and methanation). The time to reach equilibrium is almost instantaneous (half a second). Then, the stack temperature reaches its maximum before finding its steady state later on. When the enthalpy of the involved endothermic reactions is minimal and the applied power becomes maximal, the temperature increases because the gap between these two physical parameters is enough to change the temperature. Then, when this latter reaches its peak, the gap between the applied power and the electrochemical reaction enthalpy becomes minimal and therefore the temperature decreases.

Therefore, it is safe to conclude that the dynamic response of stack temperature is mainly dictated by thermal inertia. Indeed, the stack remains in steady state until the thermal disturbance is sufficient to change it. The mentioned thermal inertia is nothing but the resistance of stack materials to temperature change. It is as a function of thermal diffusivity of the used materials - i.e. Eq(2).

This physical parameter (i.e. D_{th}) which characterizes the ability of a material to transmit a temperature signal from one point to another and is related to the material's ability to transport heat (λ thermal conductivity) and its ability to store heat (C_p thermal capacity) and its density ρ .

$$D_{th} = \frac{\lambda}{C_p \rho} \quad (2)$$

As shown in Figure 4(b), the thermal gradient across the cell length is 297.15 K. According to Nakajo et al. (2009), the probability of cell failure increases significantly above 10 K/cm. For the cell length used in this study (120 mm), the maximum tolerable temperature gradient across the cell is thus 393.15 K.

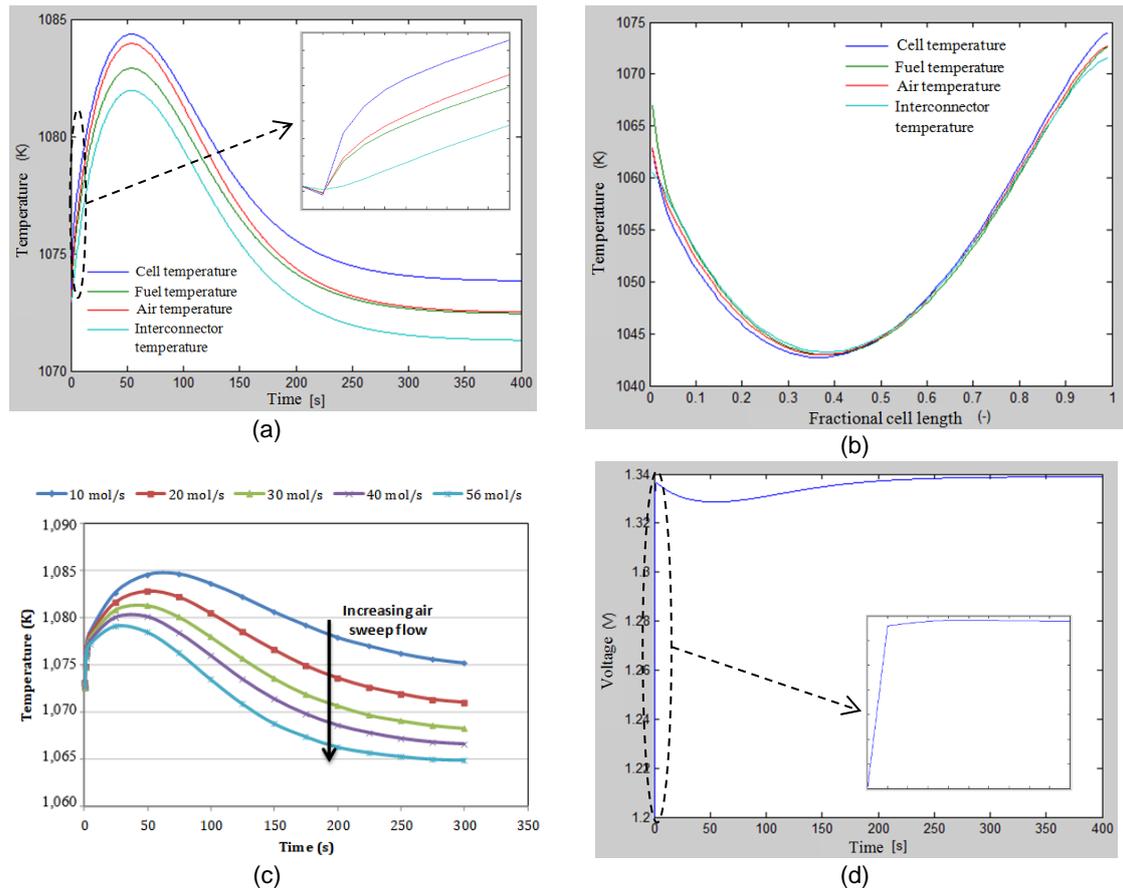


Figure 4: RSOC unit dynamic state results: (a) Cell, fuel, sweep air and interconnector temperatures; (b) Temperatures across cell length; (c) Air sweep flow effect on cell temperature; (d) Operating cell voltage.

The air sweep effect has been also studied in order to define the suitable air flow for the thermoneutral operation. As shown in Figure 4(c), by increasing the sweep air, the cell temperature decreases. Indeed, the velocity in air side increases, therefore, the air channel temperature decreases due to heat advection increase. Thus, the cell temperature decreases by convection. Based on this result and for thermoneutral operation, the air sweep flow has been set at a value of 10 mol/s.

3.2 Electrochemical behavior

Figure 4(d) illustrates the voltage evolution as a function of time. The operating voltage increases instantaneously (0.5 s) and significantly due to ohmic and activation overvoltages (Eq(1)) and particularly the Nernst voltage which increases when the temperature decreases. Indeed, as shown in Figure 4(a), in about half a second, the temperature decreases because of the endothermic reactions. Then, the operating voltage slightly decreases before reaching steady state after 4.2 min.

4. Conclusions

In order to study the dynamic behavior of the RSOC in the 10 MW Power-to-Gas storage unit, a 1D static-dynamic model was developed using Matlab. Firstly, the cell model was validated with available experimental data in steady state. It was demonstrated that the model can predict the RSOC performance under different operating conditions. Then, it was scaled up to a stack by considering a repetition of unit cell and adding the ASR for precise operating voltage calculation. The studied system is fed by a composition of 68.7 % H₂O, 6.3 % H₂, 23 % CO₂ and 2 % CO in order to produce a syngas with H₂:CO ratio of 3 which is suitable for CO methanation reaction (De Saint Jean et al., 2015). The dynamic results showed that the cell has a low thermal diffusivity which requires a significant gap between the endothermic reaction enthalpy and the applied power to change the temperature. Because of its thermal inertia, the cell absorbs heat and leads to a temperature peak in transient state. This information is crucial to prevent cell deterioration and a steady state model would not be enough to demonstrate this behavior.

The operating voltage and concentrations reach the steady state instantaneously (0.5 s) while the cell temperature requires more time (around 5 min). In order to avoid the cell deterioration caused by the temperature gradient across the cell length, the evolution of the temperature as function of the fractional cell length has been studied. It was shown that the difference between inlet and outlet temperature should be below 393.15 K for the chosen length. In this work, the air sweep flow effect on the cell temperature analysis was also presented to define the suitable sweep air flow for a thermoneutral operation. Indeed, due to the thermal advection in the air channel, the cell temperature decreases by increasing the air sweep flow.

Acknowledgments

This work was partially supported by the French National Research Agency (ANR) through "Systèmes Energétiques Efficaces et Décarbonés (SEED)" Program (project DEMETER) ref. ANR-11-SEED-0005-02.

References

- Bailera M., Kezibri N., Romeo L. M., Espatolero S., Lisbona P., Bouallou C., 2017. Future applications of hydrogen production and CO₂ utilization for energy storage: Hybrid Power to Gas-Oxycombustion power plants. *International Journal of Hydrogen Energy*, In press, Corrected Proof, Available online 11-03-2017, doi: 10.1016/j.ijhydene.2017.02.123.
- Cai Q., Luna-Ortiz E., Adjiman C.S., Brandon N.P., 2010. The Effects of Operating Conditions on the Performance of a Solid Oxide Steam Electrolyser: A Model-Based Stud. *Fuel Cell*, 10, 1114–1128.
- De Saint Jean M., Baurens P., Bouallou C., Couturier K., 2015. Economic assessment of a power-to-substitute-natural-gas process including high-temperature steam electrolysis. *International Journal of Hydrogen Energy*, 40, 6487–500.
- EREC, 2007. Energy revolution towards a clean and sustainable energy future <greenpeace.org/Luxembourg/Global/luxembourg/report/2007/1/r-evolution-energetique-vers.pdf>accessed 25.02.2016 (in French).
- Graves C.R., 2010. Recycling CO₂ into Sustainable Hydrocarbon Fuels: Electrolysis of CO₂ and H₂O. Thesis in Colombia University. New York, USA.
- Kazempoor P., Braun R., 2014. Model validation and performance analysis of regenerative solid oxide cells: Electrolytic operation. *International Journal of Hydrogen Energy*, 39, 2669–2684.
- Nakajo A., Wullemmin Z., Van Herle J., Favrat D., 2009. Simulation of thermal stresses in anode-supported solid oxide fuel cell stacks. Part I: Probability of failure of the cells. *Journal of Power Sources*, 193, 203-215.
- Ni M., 2012a. An electrochemical model for syngas production by co-electrolysis of H₂O and CO₂. *Journal of Power Sources*, 202, 209–216.
- Ni M., 2012b. 2D thermal modeling of a solid oxide electrolyzer cell (SOEC) for syngas production by H₂O/CO₂ co-electrolysis. *International Journal of Hydrogen Energy*, 37, 6389–6399.
- O'Brien J.E., Mc Kellar M.G., Stoots C.M., Herring J.S., Hawkes G.L., 2009. Parametric study of large-scale production. *International Journal of Hydrogen Energy*, 34, 4216–4226.
- Observ'ER, 2013. Worldwide electricity production from renewable energy sources. Stats and figures series. <www.energies-renouvelables.org/observ-er/html/inventaire/pdf/15e-inventaire-Chap03-3.1-Intro.pdf> accessed 08.06.2017.
- Petipas F., Brisse A., Bouallou C., 2013. Model-based behaviour of a high temperature electrolyser system operated at various loads. *Journal of Power Sources* 2013, 239, 584–595.
- Redissi Y., Er-rbib H., Bouallou C., 2013, Storage and restoring the electricity of renewable energies by coupling with natural gas grid. *International Renewable and Sustainable Energy Conference (IRSEC'13)*, Ouarzazate, Morocco, 430-435, doi:10.1109/IRSEC.2013.6529646.
- Stoots C.M., O'Brien J.E., Herring J.S., Hartvigsen J.J., 2009. Syngas production via high-temperature coelectrolysis of steam and carbon dioxide. *Journal of Fuel Cell Science and Technology*, 6(1), 1-12.
- Udagawa J., Aguiar P., Brandon N., 2008a. Hydrogen production through steam electrolysis: Control strategies for a cathode-supported intermediate temperature solid oxide electrolysis cell. *Journal of Power Sources*, 180, 354–364.
- Udagawa J., Aguiar P., Brandon N., 2008b. Hydrogen production through steam electrolysis: Model-based dynamic behaviour of a cathode-supported intermediate temperature solid oxide electrolysis cell. *Journal of Power Sources*, 180, 46–55.
- Zhan H., Kobsiriphat W., Wilson J.R., Pillai M., Kim I., Barnett S. A., 2009. Syngas Production By Co-electrolysis of CO₂/H₂O: The Basis for a Renewable Energy Cycle. *Energy Fuels*, 23, 3089–3096.