

doi:10.15199/48.2024.01.09

The analysis of electrode material efficiency in hydrogen production through electrolysis from seawater solution

Abstract. Where there is a shortage of fresh water but abundant solar and wind power is available during the day, seawater electrolysis to produce hydrogen used as fuel for fuel cells to generate electricity at night is an attractive alternative. The electrode is one of the key parts of the seawater electrolysis process. Moreover, this study focused on the commercial electrodes as a preliminary study to see if it was possible to use the low-cost and easy-to-access materials. Four electrodes, including graphite, brass, stainless steel, and steel, were used to study the effects of electrode materials on hydrogen production via seawater electrolysis. In addition, the effects of reaction times on operating parameters such as voltage, current, and pH were reported. Hydrogen production using graphite electrodes showed higher hydrogen production than that using metal electrodes. For 360-min reaction times, the hydrogen production using graphite, stainless steel 316, steel, and brass electrodes decreased from 1.46 to 0.7, 0.74 to 0.62, 0.62 to 0.52, and 0.24 to 0.01 ml min⁻¹ cm⁻² at the current density of about 150, 4 - 24, 110, and 110 mA/cm², respectively. However, when the power input to the electrolysis process was considered to compare the efficiency of hydrogen production per power input, it was found that graphite produced more hydrogen than other materials, but after 60 min, stainless steel gave the highest hydrogen production. At pH > 7.5, the OCl⁻ is the main cause of electrode corrosion, resulting in decreasing hydrogen production.

Streszczenie. Tam, gdzie brakuje słodkiej wody, ale w ciągu dnia dostępna jest duża ilość energii słonecznej i wiatrowej, atrakcyjną alternatywą jest elektroliza wody morskiej w celu wytworzenia wodoru wykorzystywanego jako paliwo do ogniw paliwowych wytwarzających energię elektryczną w nocy. Elektroda jest jedną z kluczowych części procesu elektrolizy wody morskiej. Co więcej, w ramach tego badania skupiono się na elektrodach dostępnych na rynku, aby sprawdzić, czy możliwe jest zastosowanie tanich i łatwo dostępnych materiałów. Do zbadania wpływu materiałów elektrod na produkcję wodoru w procesie elektrolizy wody morskiej wykorzystano cztery elektrody, w tym grafit, miedź, stal nierdzewna i stal. Ponadto opisano wpływ czasów reakcji na parametry operacyjne, takie jak napięcie, prąd i pH. Produkcja wodoru przy użyciu elektrod grafitowych wykazała wyższą produkcję wodoru niż przy użyciu elektrod metalowych. Dla czasów reakcji 360 min produkcja wodoru przy użyciu elektrod grafitowych, Stal nierdzewna 316, stalowych i mosiężnych spada z 1,46 do 0,7, 0,74 do 0,62, 0,62 do 0,52 i 0,24 do 0,01 ml min⁻¹ cm⁻² przy gęstości prądu odpowiednio około 150, 4 - 24, 110 i 110 mA/cm². Jednakże, gdy wzięto pod uwagę moc wejściową procesu elektrolizy w celu porównania wydajności produkcji wodoru na pobór mocy, stwierdzono, że grafit wytwarza więcej wodoru niż inne materiały, ale po 60 minutach stal nierdzewna dała największą produkcję wodoru. Przy pH > 7,5 OCl⁻ jest główną przyczyną korozji elektrod, powodując zmniejszenie wytwarzania wodoru. (Analiza efektywności materiału elektrodowego w produkcji wodoru metodą elektrolizy z roztworu wody morskiej)

Keywords: Electrode corrosion, electrode materials, graphite, hydrogen production, seawater electrolysis

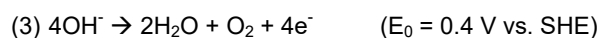
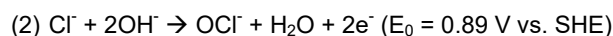
Słowa kluczowe: Korozja elektrod, materiały elektrod, grafit, produkcja wodoru, elektroliza wody morskiej

Introduction

Due to the continuous increase in energy demand and the rapid growth in the use of fossil fuels, which comes with environmental problems, green energy as an alternative to fossil fuels becomes an essential part of building a roadmap towards a sustainable energy future [1]. Among green energy resources, hydrogen is considered a clean energy resource with high abundance and energy density because it can be produced from water without emitting carbon dioxide or other toxic products in the process of converting to other forms of energy [1]. There are several approaches to producing hydrogen, and pure water electrolysis is one of the most basic methods that only requires water and electricity as inputs [2]. At present, fresh water is used for the hydrogen production in commercial water electrolysis processes, but fresh water is a finite resource in many areas, and more than 80% of the world's population faces high-risk water security [3]. Compared with fresh water, sea water and oceans represent 96.5% of the world's total water reserves, which is why sea water is an almost limitless resource [4]. For coastal areas with concentrated solar and wind power, especially in coastal areas where there is a shortage of pure water, they could become preferred potential areas for hydrogen production by seawater electrolysis powered by photovoltaic and wind turbines. Previous work presented the possibility of using seawater electrolysis for a hybrid photovoltaic/fuel cell system for coastal areas in Thailand [5]. There are many studies assessing sustainable hydrogen production via seawater electrolysis using renewable energy resources [2, 4, 6-8].

Under normal conditions, using seawater as a feedstock to produce hydrogen, mass transfer limitations and reaction

kinetics combine to make the cell products H₂/Cl₂ rather than H₂/O₂ [9]. Large volumes of chlorine and hypochlorite are generally evolved at the anode by the oxidation of Cl⁻ under acidic (pH < 3) and alkaline (pH > 7.5) conditions as Eqs. (1) and (2), respectively, instead of O₂ evolution by the oxidation of water in Eq. (3), causing a major environmental problem [10-12].



The corrosion and degradation of metal components are mainly induced by Cl⁻ or OCl⁻ species at both electrodes [13]. Metal active sites may be corroded or blocked at the electrochemical reaction because of complex ions in seawater. Hence, on the basis of traditional electrodes, seawater-based electrodes require high stability and corrosion resistance [14]. In recent years, seawater electrolysis electrodes have continuously developed [1, 10-16].

Koster et al. [17] proposed the use of consumable electrodes (shaped as rods) of graphite, the material ranked as the most noble within the Galvanic Series (i.e., graphite has the best survivability in the extremely corrosive local environment at the anode). Good electrodes for use in seawater electrolysis are of course good conductive electrodes, economical price, and also resistant to seawater corrosion [18]. Consequently, this research focused on the use of commercial metal materials such as brass, steel, and

stainless steel rods compared with the use of commercial non-metal electrodes such as graphite rods. The effects of electrode materials on hydrogen production by direct seawater electrolysis are investigated. The effects of time on the changes of voltage, current density, pH and hydrogen production are reported.

Experimental Work

In this experiment, graphite, brass, stainless steel 316 (SS 316), and steel materials were used as cathodes and anodes. The metal electrode rods were prepared with dimensions of 19 mm diameter by 70 mm length, and the commercial graphite electrode rods were used with dimensions of 10 mm diameter by 100 mm length. They were kept under dry conditions.

For the electrolysis from seawater solution, as seawater contains a variety of salts with an average salinity of 3.5%, predominantly sodium chloride [18-19], the 3.5% NaCl (0.598 M) solution was prepared as the synthetic seawater for the experiment.

Fig. 1 shows a seawater electrolysis equipment. The dimensions of the electrolysis reaction vessel are 16 cm x 30 cm x 20 cm, with a thickness of 7 mm. In the vessel, there were two 50-ml gas collection tubes for the storage of the produced gas. The electrode rods were inserted inside tubes. Using the "water displacement" method [20], the produced hydrogen volume can be measured by determining the amount of water existing in the gas collection tubes before and after the electrolysis process occurs within a certain measurable time used to calculate the rate of hydrogen gas production. The electrolysis process was powered by a DC power supply (30 volts, 5 A). In the preliminary study of hydrogen production using tap water to investigate the effects of voltage on the amount of hydrogen produced, it was found that all electrode materials at the highest voltage, which is limited to 30 volts, gave the highest production of hydrogen. Therefore, at the start of the test for seawater electrolysis, the highest voltage of this power supply of 30 volts was adjusted to be used in the electrolysis process for all electrode tests. In the experiment, the flowrates of hydrogen in the cathode side were measured, and the voltage, electrical current density, pH of solution in chamber were measured with reaction times for 360 minutes. It is noted that the hydrogen production was presented in terms of volumetric flow rate per surface area of the cathode for easy calculation when the electrodes are scaled up.



Fig. 1. Seawater electrolysis equipment

Results and Discussion

As mentioned in the experiments, a DC power supply of 30 volts was set for the seawater electrolysis to test all electrodes; however, after starting the electrolysis process, the set 30 volts were dropped, as shown in Fig. 2. The voltages for graphite gradually decreased from 13.4 to 11.6 volts. The voltages of SS 316 increased from 9.9 to 13.8 volts since 150 min, and the voltages of steel electrodes

increased from 9.7 to 11.1 volts since 120 min, while the voltages of brass constantly ranged between 29.8 and 30 volts as of the beginning setup. The electrical current density and power density of all electrodes are shown in Figs. 3 and 4, respectively. Because of the limitation of the voltage setting device, the decreases in voltage of graphite, SS 316, and steel were not adjusted to 30 volts as they were initially. The electrolysis tests of graphite, SS 316, and steel were performed with the current density at approximately 150 mA/cm², 110 mA/cm², and 110 mA/cm², respectively.

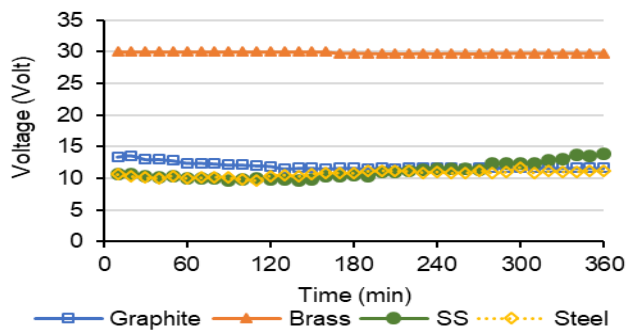


Fig. 2. Relation between voltage and time for seawater electrolysis using various electrodes

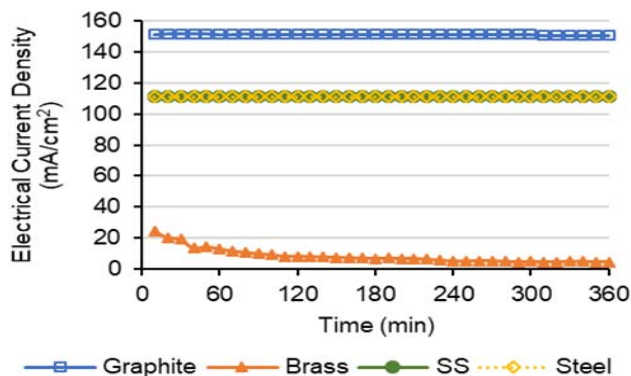


Fig. 3. Relation between current density and time for seawater electrolysis using various electrodes.

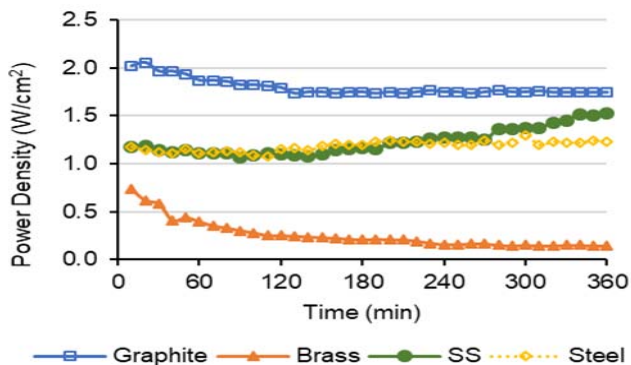


Fig. 4. Relation between power density and time for seawater electrolysis using various electrodes

Rustana et al. [20] presented the decreasing of electric current through the equipment of electrolysis process because of corrosion process of electrodes, especially for copper electrode that it was different with graphite which showed that the current was decreased after the first 10 min. Since the main component of brass is copper, it has a noticeable current reduction effect.

In order to compare the hydrogen production of each electrode, the results of hydrogen production/power input were introduced to describe the effects of different electrode

types on the hydrogen produced. Fig. 5 illustrates the results of the highest hydrogen production/power input of graphite between 43 - 40 ml/Wh during the first 60 min, followed by SS 316, steel, and brass, but after 60 minutes, SS 316 can produce more hydrogen than graphite. However, the increase in time decreases hydrogen production. As mentioned in the operation conditions of each electrode, the hydrogen production per cathode surface area is shown in Fig. 6. For 360 min reaction times, the hydrogen production of graphite, SS 316, steel, and brass ranged between 1.46 - 0.7, 0.74 - 0.62, 0.62 - 0.52, and 0.24 - 0.01 ml min⁻¹ cm⁻², respectively. Abdel-Aal et al. [9] used a platinum electrode, and the quantity of hydrogen produced on an area of 1.5835 cm² was 85 ml h⁻¹ (representing 0.89 ml min⁻¹ cm⁻²) for a 120 mA cm⁻² current density. The results showed that graphite and SS 316 can compete with platinum electrodes in terms of operating duration. However, the corrosion and degradation of electrodes, especially SS 316 and steel, was the main problem of continuously decreasing hydrogen with operating time.

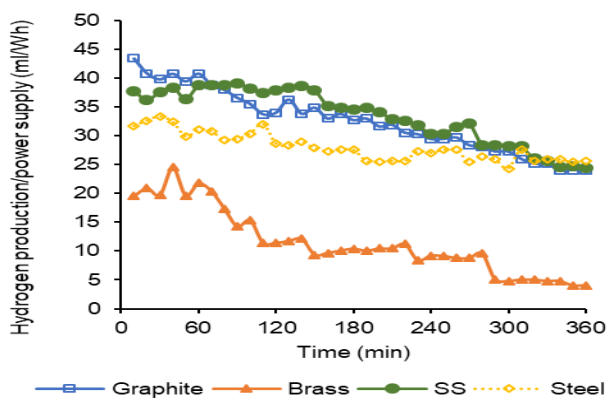


Fig.5. Relation between hydrogen production/power input and time for seawater electrolysis using various electrodes

The reduced current occurs because the longer the electrode is used. There will be an oxidation reaction due to the corrosion of chlorine in sea water. Therefore, the efficiency of the electrode can be reduced. The corrosion process on the electrodes of voltaic cells reduces the electrode life. This, of course, has implications for the reduction of hydrogen gas produced in the electrolysis of seawater [20].

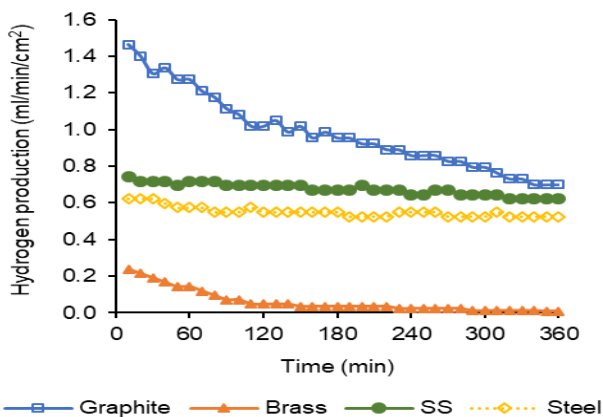


Fig.6. Relation between hydrogen production and time for seawater electrolysis using various electrodes

The pH values in the electrolyte medium affect both the cathode and anode, and a large amount of chlorine and hypochlorite is usually evolved at the anode by the

oxidation of Cl⁻ in acidic medium (pH < 3) and alkaline medium (pH > 7.5), respectively. In addition, it can be found from Eqs. (1) and (2) that the pH of electrolytes can affect the reduction of chloride ions, which can be adjusted to control the anodic reactions in seawater electrolysis. The oxygen evolution reaction OER is considered to be more favorable at pH > 7.5 according to the Pourbaix plot with an overpotential below 480 mV [21]. As shown in Fig. 7, the pH values of the solution medium in the seawater electrolysis process were above 7.5, which means the medium contains more volume of OCl⁻ than Cl₂.

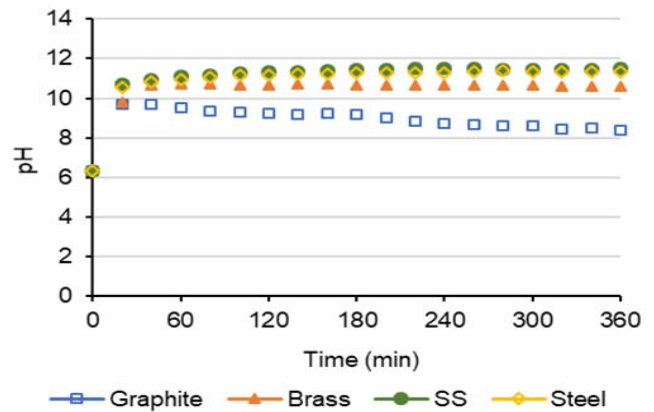


Fig.7. Relation between pH and time for seawater electrolysis using various electrodes

The use of graphite as cathode and anode shows the small amount of corroded graphite in the electrolyte medium, as shown in Fig. 8. The corrosion of metal electrodes can be obviously found in the seawater electrolyte solution, which contained a large amount of corroded metal, as demonstrated in Figs. 9, 10, and 11 for brass, SS 316, and steel, respectively.

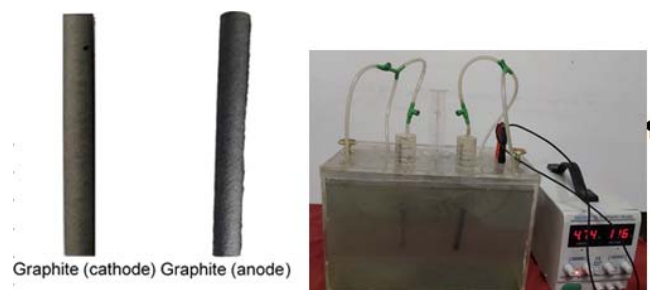


Fig.8. The used graphite cathode and anode after 360 min testing, and the electrolyte medium during the operating time of about 150 min.

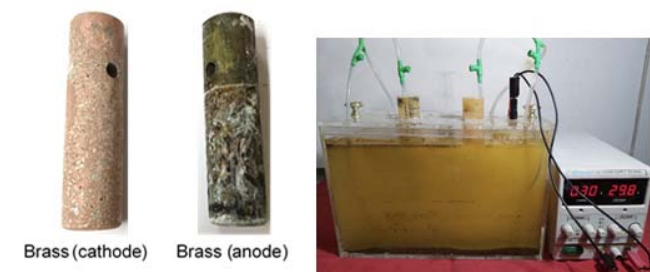


Fig.9. The used brass cathode and anode after 360 min testing, and the electrolyte medium during the operating time of about 150 min

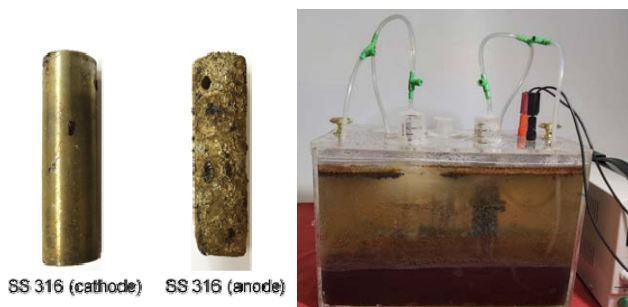


Fig.10. The used stainless steel cathode and anode after 360 min testing, and the electrolyte medium during the operating time of about 150 min

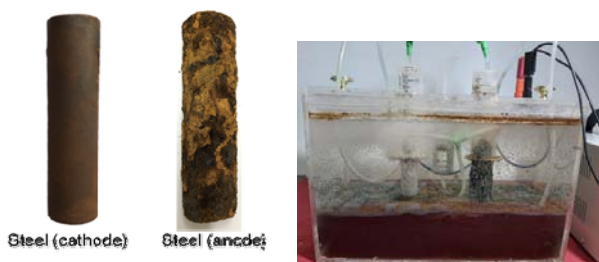


Fig.11. The used steel cathode and anode after 360 min testing, and the electrolyte medium during the operating time of about 150 min

The local pH value of the electrode surface will vary significantly at high current densities. In the process of electrocatalysis, the surface is acidic at the anode side and alkaline at the cathode; when $\text{pH} > 9$, precipitates will be formed on the cathode side to block the active site of the cathode and reduce catalytic activity [14].

Conclusion

Seawater electrolysis using commercial metal and non-metal electrodes was performed to study the effects of electrode materials on hydrogen production. Graphite, brass, stainless steel, and steel were used as electrodes. As the anode reaction in the seawater electrolyte solution presented the chloride ions, causing the corrosion and degradation of electrodes, especially the metal materials. In all electrode testing, the pH values are above 7.5; therefore, in the alkaline medium, OCl^- occurs at the anode side. The results of corrosion on the used cathodes and anodes confirmed the decrease in hydrogen production with the reaction times. In the seawater electrolysis testing for 360 min, the hydrogen production per surface electrode area decreased with time; by using brass, the highest reduction was 95.8%, followed by graphite, steel, and stainless steel 316, representing a reduction of 52.1%, 19.2%, and 16.2%, respectively. Moreover, stainless steel 316 provided more hydrogen production per power input than graphite, after 60 min. However, when the used electrodes were considered, it was found that the use of graphite showed the potential to develop for seawater electrolysis because of the lowest corrosion.

In future work, an extension of the testing time and the corrosion rate will be considered. Moreover, the effects of adjusting pH values and voltages on hydrogen production will be studied.

Authors: Assoc. Prof. Dr. Anuchart Srisiriwat, Pathumwan Institute of Technology, Bangkok, Thailand, E-mail: anuchart@pit.ac.th; Assoc. Prof. Dr. Nawadee Srisiriwat, Pathumwan Institute of Technology, Bangkok, Thailand, E-mail: nawadee@pit.ac.th; Rungchai Kaensakol, doctoral student, Department of Electrical Engineering, Faculty of Engineering, Pathumwan Institute of Technology, Bangkok, Thailand, E-mail: rungchai_22@hotmail.com

REFERENCES

- [1] Jiang S., et al., Recent Advances in Seawater Electrolysis. Catalysts, 12 (2022), 123
- [2] Meier K., Hydrogen production with sea water electrolysis using Norwegian offshore wind energy potentials. Int. J. Energy Environ. Eng., 5 (2014), 104-106
- [3] Gao F.Y., Yu P.-C. and Gao M.-R., Seawater electrolysis technologies for green hydrogen production: challenges and opportunities, Current Opinion in Chemical Engineering, 36 (2022), 100827
- [4] Dresp S., et al., Direct Electrolytic Splitting of Seawater: Opportunities and Challenges, ACS Energy Letters, 4 (2019), No. 4, 933-942
- [5] Srisiriwat A. and Pirom W., Feasibility Study of Seawater Electrolysis for Photovoltaic/Fuel Cell Hybrid Power System for the Coastal Areas in Thailand, IOP Conf. Ser.: Mater. Sci. Eng., 241 (2017), 012041
- [6] Rezaei M., et al., Hydrogen production using wind energy from sea water: A case study on Southern and Northern coasts of Iran, Energy & Environment, 29 (2018), 0958305X1775005
- [7] Dokhani S., Assadi M. and Pollet B.G., Techno-economic assessment of hydrogen production from seawater, Int. J. Hydrogen Energy, 48 (2023), No. 26, 9592-9608
- [8] d'Amore-Domenech R. and Leo T.J., Sustainable hydrogen production from offshore marine renewable farms: Techno-energetic insight on seawater electrolysis technologies, ACS Sustainable Chemistry & Engineering, 7 (2019), No. 9, 8006-8022
- [9] Abdel-Aal H.K., Zohdy K.M. and Kareem M.A., Hydrogen Production Using Sea Water Electrolysis, The Open Fuel Cells Journal, 3 (2010), 1-7
- [10] Fukuzumi S., Lee Y.-M. and Nam W., Fuel Production from Seawater and Fuel Cells Using Seawater, ChemSusChem, 10.1002/cssc.201701381
- [11] ul Haq, T. and Haik Y., Strategies of Anode Design for Seawater Electrolysis: Recent Development and Future Perspective, Small Science, 2 (2022), No. 9, 2200030
- [12] Liu G., et al., Recent advances in electrocatalysts for seawater splitting, Nano Mater. Sci., 5 (2020), No. 1, 101-116
- [13] Frisch M. L., et al., Seawater Electrolysis Using All-PGM-Free Catalysts and Cell Components in an Asymmetric Feed, ACS Energy Lett., 8 (2023), 2387-2394
- [14] Zhao L., et al., Design Strategy of Corrosion-Resistant Electrodes for Seawater Electrolysis. Materials, 16 (2023), 2709
- [15] Tong W., et al., Electrolysis of low-grade and saline surface water, Nat. Energy, 5 (2020), 367-377
- [16] Kuang Y., Kenney M.J. and Meng Y., Solar-driven, highly sustained splitting of seawater into hydrogen and oxygen fuels, PNAS, 116 (2019), No. 14, 6624-6629
- [17] Koster J.W., et al., Explicitly controlling electrical current density overpowers the kinetics of the chlorine evolution reaction and increases the hydrogen production during seawater electrolysis, Int. J. Hydrogen Energy, 48 (2023), No. 13, 4994-5000
- [18] Rustana C.E., et al., The Effect of Voltage and Electrode Types on Hydrogen Production from The Seawater Electrolysis Process, J. Phys.: Conf. Ser., 2019 (2021), 012096
- [19] Mu L., Wang Y. and Tarpeh W.A., Validation and Mechanism of a Low-Cost Graphite Carbon Electrode for Electrochemical Brine Valorization, ACS Sustainable Chem. Eng., 8 (2020), No. 23, 8648-8654
- [20] Rustana C.E., et al., Preliminary Study on The Effect of Time on Hydrogen Production from Electrolysis of The Seawater, J. Phys.: Conf. Ser., 2019 (2021), 012095
- [21] Dionigi F., et al., Design criteria, operating conditions, and nickel-iron hydroxide catalyst materials for selective seawater electrolysis, ChemSusChem, 9 (2016), 962-972