INTERNATIONAL JOURNAL OF
COASTAL & OFFSHORE ENGINEERING

IJCOE Vol.6/No. 4/Autumn 2021 (19-23)

Available online at http://www.ijcoe.org

The Effect of Silica Nanoparticles'Coating on the Ion Resolution of Anionic Membrane in SGP System

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ARTICLE INFO

Article History:
Received: 24 Aug. 2021
Accepted: 12 Nov. 2021

Keywords:
renewable energy
salinity gradient
reverse electrodialysis membranes
nano silica particles

ABSTRACT

One of the new sources of renewable energy, is salinity gradient power (SGP) being described as; the entropy energy of mixing the two solutions with different salt concentrations. The extraction of this energy is possible through SGP; the function of this system is based on membrane processes. A system of reverse electrodialysis (RED) was used in this study. Power density (W/m^2) and energy efficiency of the system were evaluated due to the impact of nanotechnology on the use of membranes. The analyses showed that when the concentration of silica nanoparticles in the matrix membrane used in the system is 20 percent and when ion concentration in the solution is 0.055*mol/lit*, the selectivity of the membrane for ions will be Na^+, 98.4 percent. However, the selectivity of matrix membrane without the presence of nanoparticles is 82 percent. Also compared to non-nanoscale membranes, the efficiency is increased about 11 percent due to the use of the particles on the anionic membrane as well as their appropriate structure design.

1. Introduction

One of the newest renewable energy issues that have been raised in recent years in the world, is the extraction of energy from salinity gradient in the seas and the ocean. This salinity difference can be found in the residual water of desalination plants, Halocline and estuaries. Reverse electrodialysis (RED) is a promising technology for extracting energy from salinity gradients [1].The concept of energy production through mixing salt and fresh water was introduced by Patel in 1954 [2]. The way to evaluate the extraction and production of salinity gradient energy and electrodialysis methods were studied in IRENA institute in 2014 [3]. May et al. (2018) investigated energy extraction by reverse electrodialysis and found the use of nano membranes effective in increasing energy and flow [4]. Ju et al. conducted a study comparing RED and PRO processes using different solutions with low and high salinity water in terms of power density and deposition potential [5]. SGP system is a system for energy extraction and based on spontaneous processes and membrane techniques. Spontaneous Process refers to a reaction that is performed without receiving energy from an external source. To realize this kind of process, three thermodynamic quantity of entropy, enthalpy and temperatures are examined. Entropy (S) is a thermodynamic state function that shows the distribution of energy and matter in a system. Spontaneity of a process is concerned with the total entropy's changes or in other words; the system's and the environment's total entropy [6].

$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{environment} \qquad (1)$$

However, it is impossible to calculate the entropy changes of the environment. To avoid this problem, we limit ourselves to the processes that occur at fixed temperature and pressure. In practice, this limitation does not cause serious problems. Another important point is that neither entropy nor enthalpy can indicate the spontaneity of a reaction. For this purpose, a new thermodynamic function is introduced. The function is called Gibbs free energy (G)[6].

$$G = H - TS \qquad (2)$$

Equation (2) is a thermodynamic equation of state for each transformation from Mode 1 to Mode 2 at fixed temperature and pressure and it is written as follows:

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1) \qquad (3)$$

Equation (3) can be written as follows;

$$\Delta G_{system} = \Delta H_{system} - T\Delta S_{system} \qquad (4)$$

This equation is called Gibbs – Helmholtz. Spontaneous condition can now be definedexactly for the system that is under constant pressure and temperature. According to the second law of thermodynamics, for a spontaneous process we will have $\Delta S_{Total}>0$ in this case, - $T\Delta S_{Total}<0$ and thus we will have $\Delta G system<0$. In other words, when a spontaneous process occurs in a system being under constant pressure and temperature, the total entropy isincreased and Gibbs' free energy is decreased.

Table 1. Gibbs free energy and the type of transformation

the type of transformation	**$\Delta Gsystem$In constant T and P**
Spontaneous	$\Delta Gsystem<0$
Balance	$\Delta Gsystem=0$
Non-Spontaneous	$\Delta Gsystem>0$

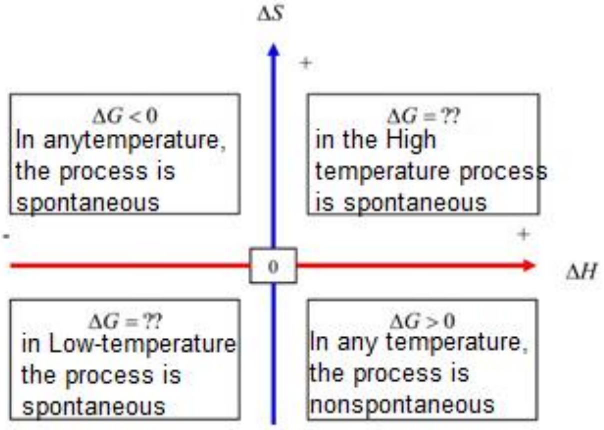

Figure 1. Gibbs free energy and the process

Membrane techniques used in this study, is the Reverse Electro Dialysis (RED) in which the anionic and cationic membranes are used. Electrodialysis techniques (ED) was invented by Maigrot and Sabates(1982). One application of this technique is its use in seawater desalination systems [7].

Manecke(1852) proposed to save energy by using reverse electrodialysis process[8]. He proved that the reuse of consumed electrical energy is possible by the reverse membrane process (Fig 2).

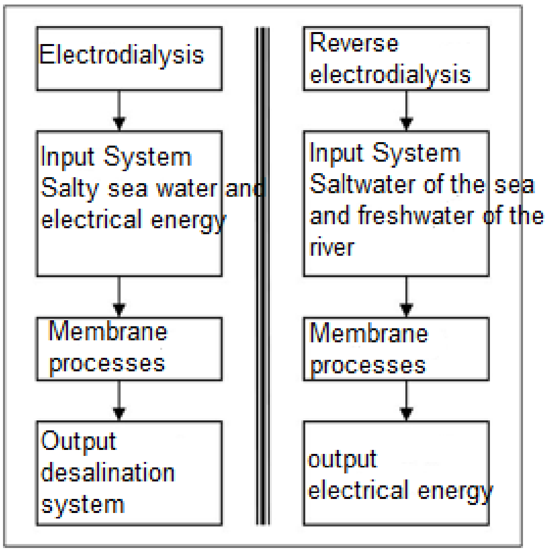

Fig. 2. Different stages of electro dialysis and reverse electro dialysis

In contrast to the electro dialysis method, in reverse electrodialysis, the concentration difference between consecutive cells is used instead of the power supply to excite the ions to cross the anionic and cationic membranes. The ions are then separated by membranes, and entered electrodes chamber on both sides, through where redox reactions, an ionic current is turned into an electron current. This phenomenon creates a potential difference between the electrodes, resulting in a battery charging. Figure (3) shows the performance of anionic and cationic membranes in the separation of sodium and chloride ions [9].

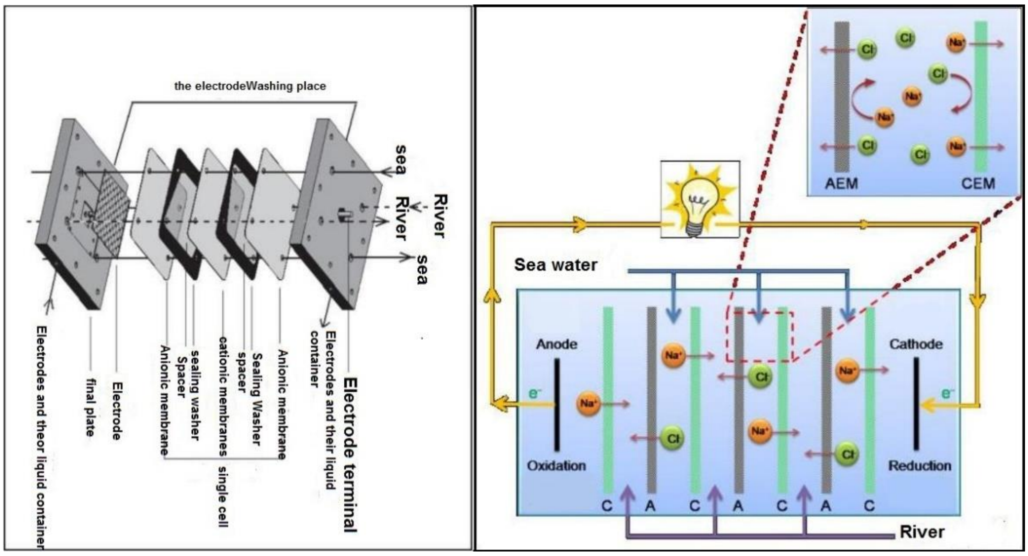

Figure 3. a view of the SGP system based on reverse electro dialysis membrane process RED

In the figure (3) AEM represents the anion exchanger membrane and CEM represents the cation exchange membrane. The use of this process in the physical model design is an important part of this research.

2. Calculation of entropy energy of mixing the two solutions with different concentrations

As shown in Figure 3, containers of reverse electrodialysis system are filled with a volume of seawater (V_S) and river (V_R) with different salt concentrations of C_S and C_R. In this system, an ionic current is produced and turned into electron current by redox reactions in the electrodes. This process continues until the concentration of the solution is the same on both sides of each chamber. The concentration is shown by C_M and calculated as follows [10,11].

$$C_M = \frac{C_S V_S + C_R V_R}{V_S + V_R} \tag{5}$$

To calculate the recoverable energy from mixing the two solutions of different concentrations, we need to calculate the entropy of mixing between the two solutions. To calculate this quantity we can use the following equation;

$$\Delta S = \int \frac{dQ}{T} \tag{6}$$

The first law of thermodynamics states that any thermodynamic system in equilibrium has a variable called internal energy (U) whose changes is obtained through the equation (7);

$$dU = dQ - dW \tag{7}$$

In the above equation, *dQ* and *dW* are a small fraction of the heat exchanged and the amount of work performed by system. For processes that occur at fixed temperature and pressure, internal energy change of the system is zero ($dU = 0$) and consequently $dQ = dW$. However, it can be noted that in reverse electro dialysis system with the movement of ions, concentration of solutions has changed and then the system will be faced with volume changes, though slightly. In this case, the amount of work done can be calculated from equation (8);

$$W = \int dQ = \int \Pi dV \tag{8}$$

In relation (8), Πosmotic pressure is based on pa that can be calculated through (9) classical state equation.

$$\Pi V = nRT \tag{9}$$

In this regard, volume (v) is calculated based on m^3 and n represents the number of moles which is defined as $n = 2CV$. Factor 2 is Van 't Hofffactor that is caused by the decomposition of a one-mole *NaCl*, to two-mole ions and C is the concentration of the solution. Given the approximate isothermal process, Gibbs free energy is obtained through (10) relationship.

$$\Delta G = -T\Delta S_{Total} = -\left[\int \Pi_S dV + \int \Pi_R dV\right] = -\left[-n_S RT \int_{C_S}^{C_M} \frac{dC}{C} - n_R RT \int_{C_R}^{C_M} \frac{dC}{C}\right] \tag{10}$$

Equation (3) can be written as follows;

$$\Delta G = -2RT\left[C_S V_S \ln \frac{C_S}{C_M} + C_R V_R \ln \frac{C_R}{C_M}\right] \tag{11}$$

3. SGP System

SGP system used in this study is based on the performance of reverse electrodialysis membrane; it is an electrochemical cell being based on the concentration gradient. The system is a single-cell system that uses two anionic membrane and a cationic membrane. In addition, the membranes are another important part of this system includes spacer, electrode compartment electrode, electrolyte and sealing washers. Figure 4 video system shows the SGP made in this project [12]. In addition to the membranes, the system has other important: spacer, electrodes, electrode compartment, electrolyte and sealing washers. Figure 4 shows a picture of the SGP made in this project.

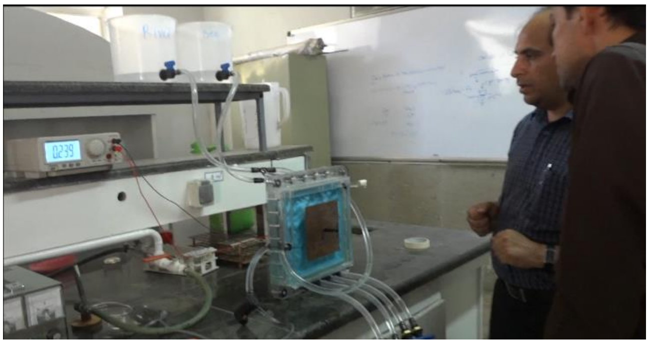

Figure 4. SGP system with nano-structured membranes used in this study

4. Cationic and anionic heterogeneous membranes coated with nano

As it was stated the construction of the battery involves heterogeneous membrane ion exchanger (Figure 5)

Figure 5. Heterogeneous anionic and cationic membranes of nanostructures on preservatives frames

Table 2, represents physical and chemical characteristics of the membranes before the placement of nano particles on them.

Table 2. Physical and chemical properties of heterogeneous ion exchanger membranes

Items tested	**Unit**	**Membrane type**	
		cationic membranes (CEM)	**Anionic membranes (AEM)**
Exchange capacity ≥	*mol/kg*	2.0	1.8
Resistance of membranes	Ω.cm^2	2	2
The degree of dimensional change ≤	%	3	3
Bearable pressure due to membrane's strength against tearing ≥	*MPa*	0.6	0.6
Chemical stability	*PH*	1 ~10	1 ~10
Selectivity of the membrane ≥	*%*	90	89
Penetrability and water permeability ≤	*Ml/h.cm^2*	0.1	0.1
Thermal or heat stability ≤	∘*C*	40	40
Dimensional properties of membranes			
Thickness	Error thickness in the dry state		
0.42 mm	±0.04mm		

In the desalination systems of seawater whose activity is based on electrodialysis, heterogeneous membranes have shown a unique technical performance. These membranes are widely used in other industries such as the semiconductor industries, input water heaters, boilers, machinery, electronics, pharmaceutical industries, biological experiments and researches related to water use. The use of these nano-structured membranes for reverse electrodialysis systems paves the way for the arrival of the product to renewable energy industries.

In this project the performance of the uncoated membranes with nanoparticles, were studied in their structure. The function of the membranes in reverse electro dialysis battery was studied and compared with the results of research conducted by Veerman [13,14]. It was found that in all studies, membranes' performances were faced with considerable problems:

- High deposition rate on the surface of the membrane and disruption in reverse electrodialysis process.
- Low speed and volume of ion transfer in membrane, followed by the reduction of energy extraction process

Nanotechnology was used to overcome the problems. In this regard, the idea of using nanoparticles in the membrane structure of the ion exchanger was formed. The investigation showed that the nanoparticles enhance thermal and mechanical stability due to their unique properties of the membranes. Also according to the type of nanoparticles, we can increase the selectivity of the membrane. Therefore, desirable properties of the membrane can be improved by adding suitable nanoparticles to the matrix of a polymer membrane. For this purpose, after careful study of the performance of nano-particles on the membrane ion exchanger, we decided to use silica nanoparticles in the structure of cation exchanger heterogeneous membrane. Silica or silica dioxide is the most abundant material on earth's crust. The compound with the chemical formula of SiO_2 has a structure similar to diamond being a white crystalline substance. It has a relatively high melting and boiling temperature and exists in the nature as crystal and amorphous. Nanoparticles of silicon dioxide are spherical with a diameter of less than 100nm. These particles are in the form of dry powder or solution. In this study, the coating of silica nanoparticles is used with an average diameter of 40nm. After the coating of membrane with silica nanoparticles, its features were evaluated through the produced images by a scanning electron microscope (SEM) (Figure 6).

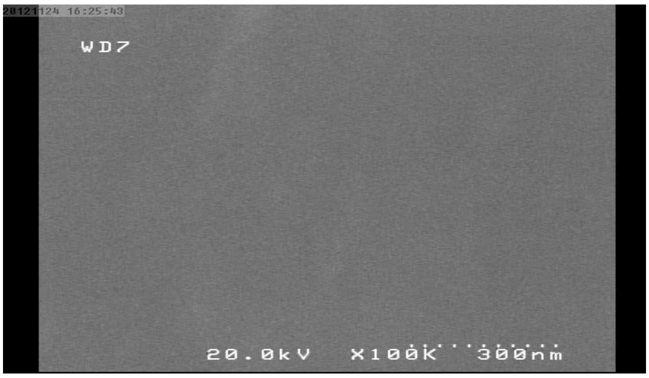

Fig. 6 Obtained images of the cation exchanger membrane coated with nanoparticles produced by SEM

The analyses showed that when the concentration of silica nanoparticles in the matrix membrane used in the system is 20 percent and when ion concentration in the solution is 0.055 *mol/lit*; the selectivity of the membrane for ions will be Na^+, 98.4 percent. However, the selectivity of matrix membrane without the presence of nanoparticles is 90 percent. If the concentration of silica nanoparticles in the matrix membrane is 0.28 percent, ion diffusion coefficient of Na^+ will be obtained through$11.16\times12^{-12}m^2$/s. While the diffusion coefficient for the ion in the cation exchanger membrane and without the presence of silica nanoparticles is$3.71\times12^{-12}m^2$/s.Comparing these two features shows the importance of the presence of silica nanoparticles in the membrane structure. The cationic membranes with nano-coating have other features that some of them are mentioned below.

- Silica nanoparticles reduce water's alkalinity through chemical reactions with calcium hydroxide $(Ca\ (OH)_2)$ and prevent its deposition on the membrane. So the particles increase the membrane antifouling properties and cause long persistence of ions’ flux (to overcome the first problem)

- Silica nanoparticles lead to high thermal and mechanical stability of the membrane.
- Silica nanoparticles do not have any environmental emission
- For membranes containing silica nanoparticles, surface morphology of the membrane, the water capacity, selectivity (ions selection) (water absorption) hydrophilicity and capacity of ion exchange of membranes were measured and evaluated. For example, the selectivity of the membrane with silica nanoparticles *(SiO_2)* increases but its increase is related to the concentration of the nanoparticles in the membrane matrix.

5. Discussion and Conclusion

So far, a few research centers and businesses have manufactured reverse electrodialysis batteries. Some of these centers work on membranes with high efficiency and low cost activities and others on the design of the battery its cells. Table 3, indicates several types of batteries that are designed from 1854 up until now; they are compared with each other in terms of output power density. As you can see with the passage of time and improvements in the designing membrane batteries’ structure, their output power density has increased significantly.

Table 3. Membrane’s thickness and power density *P(W/m^2)* inRED System

Power density *W/m^2*		**Membrane thickness**	**year**	**Researcher**	**No**
0.05		0.7	1955	Pattel	1
0.17		1	1976	Weinstein and Litz	2
0.40		3	1983	Adynus	3
0.41		0.55	1986	GroZynsky et al.	4
0.46		0.19	2007	Turkish	5
0.26		1	2007	Sevda	6
0.95		0.2	2008	Veerman et al	7
1.18		0. 2	2009	Veerman et al	9
0.52	Non nano-coating	0.42	2014	SabetAhd et al	8
0.58	nano-coating				

Another feature of the RED system is the application of silica nanoparticles on the membrane surface. This led to the 11 percent increase of the extraction of membrane surface unit provided in the physical model. Therefore, the coating of silica nanoparticles’ membrane has had an effective role in improving system performance. Of course, this laboratory process was limited due to high costs and lack of financial resources. Therefore, more research is needed to assess the exact impact of nano-coatings.

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