Electrochemical cell equipment for salinity gradient power generation

Original Research Article

Abstract

Extraction of electricity from the salinity gradient of sea water-river water interface has drawn the key interest of sustainable energy researchers. Different technologies are in the spot light – such as pressure retarded osmosis, reverse electrodialysis, ionic diode membrane, mixing entropy battery, microbial fuel cell, etc. In present research work electrochemical cell equipment is used for this purpose. Two different techniques are described – galvanic cell equipment (GCEQ) and concentration cell equipment (CCEQ). It is observed that extracted energy density is very high (up to $95 Wm^{-2}$) compared to other methods of the same kind reported so far. Implementation of these methods is trivial. Thus, we may conclude that present method will fulfill our requirement of sustainable energy resource.

Keywords: salinity gradient power; sustainable energy; galvanic cell equipment; concentration cell equipment; electrochemical cell

1 Introduction

Salinity gradient power (SGP) is a potentially clean and sustainable form of energy resource that catches the eyes of the researchers in the soaring of energy crisis in the present

decade. [1, 2] Theoretical calculation suggests that we can extract up to 0.8KW energy from one cubic meter sea water mixed with fresh water. [2] Thus, if we consider the flow of all rivers of the world into account, we get an estimated value of the global potential of SGP as 2.6TW, [2] which is nearly 21% of average power consumption (12.3TW) of the world. [3] Currently 800GW power is obtained from the hydroelectric process which is the dominant source of electricity of developing and underdeveloped countries. Thus, the advancement of salinity gradient power generation in an economical way would be a pleasant technique for those countries. But, harness this energy in an efficient manner is a challenge to energy-conversion technologists.

We need interdisciplinary efforts from chemistry, material science, environmental science, geoscience, bio-technology and nanotechnology to invent sophisticated instrumentation for energy conversion from salinity-gradient. [4, 5, 6, 7] Several approaches are in progress to this direction. Among them, the most promising are pressure-retarded osmosis (PRO) [2, 8, 9, 10] and reverse electrodialysis (RED). [6, 11] These two methods use advanced membrane technology. In RED method, numbers of alternately stacked cation exchange membranes (CEM) [12, 13, 14] and anion exchange membranes (AEM) [15, 16, 17, 18] are used. This technique was first proposed by Pattle [19, 20] in 1954. But, it is gaining interest in the first decade of the twenty first century when search for sustainable energy resource takes place at the top of the global research interests. [21] In PRO method, semipermeable membranes [22, 23, 24, 25] are used to allow the transport of water from a low-concentration solution (such as river or waste water) into the high-concentration solution (such as sea water). [21, 26, 27, 28, 29]

Though, energy conversion efficiency of PRO and RED are very good, 50% and 30% respectively, commercialization of these methods are restricted by cost and fouling of membranes which suffer from deteriorated ion selectivity and inadequate mass transportation. Elongation of life time of membranes is the most challenging task for these two methods to be implemented successfully in making of SGP station. Over past two decades, fabrication methods are advanced exceptionally, also the membrane technology. Thus, we may expect reduction of installation and maintenance cost of RED and PRO based electric power generation in near future.

Closed loop PRO and RED methods are developing which would be capable of extracting much higher power density from salinity gradient. Not only that, closed loop systems would reduce bad environmental impact of PRO and RED. A closed-loop system, which is termed as a heat engine, [28, 30] converts thermal energy to mechanical work or electricity. In this method PRO or RED method is used to generate electricity from mixing of sea water and river water and then the resultant mixture is separated by thermal energy to high-concentration and low-concentration solution to recycle back. To make this process economically viable, in general, waste heat, like geothermal energy from shallow wells [31] and low-grade heat of power plants, is used for thermal separation. Advantage of this process is that we may use any concentrated electrolyte instead of sea water and river water as recycling is possible. It is obvious that the use of high concentrated solution would produce higher energy density extraction. For example, an ammonia-carbon-dioxide solution of 5M concentrations is capable of generating power densities of $250Wm^{-2}$. [2, 31] Thus, closed loop heat engine is also promising, but also have the same limitations as PRO and RED.

Parallel to this, mixing entropy battery [32] and ionic diode membrane (IDM) [33] are two alternative devices which are also capable of extracting electricity from water salinity

difference. Mixing entropy battery may be useful for small scale use, like in a car, in house hold etc., as it is similar to a nano battery which is made of $Na_{2-x}Mn_5O_{10}$. This is recharged in sea water and discharged in river water. Energy efficiency is very high (74%) for this method. On the other hand, IDM is an alternate to ion exchange membrane used in RED. IDM is fabricated using mesoporous carbon having pore size nearly 7nm over microporous alumina having pore size nearly 80nm. Using IDM, we may extract energy from salinity gradient with energy density up to $3.46Wm^{-2}$ which is very high compare to organic membrane based RED (energy density is $0.35 - 0.93Wm^{-2}$). In addition to this, IDM shows better ion selectivity which doesn't deteriorate with time. It is cost effective also.

There are hybrid technologies which use two or more methods to overcome limitations of single methods. Forward-osmosis membranes may be used in bioreactors to increase the salinity of waste water. Placing the cathode in the draw solution of microbial fuel cell (MFC) [34, 35, 36] eliminates solution resistance in the cathode chamber and enhances the efficiency. But, hybrid systems require co-localization of different sources, like waste water, sea water and waste heat. This condition imposes another restriction on the implementation.

A contrast to the above mentioned technologies, concentration cell equipment (CEQ) for generation of electricity from salinity gradient which is described in the present article, has no such burden. So far, no attempt has been made or reported to produce electricity from sea water and river water in this fashion. Semipermeable membrane is also required in this method, but we need membrane with larger pore size. We may replace polymer membrane by inorganic membrane also.

2 Theoretical back ground

We can extract electricity from sea water in two different ways -

- I) using galvanic cell equipment (GCEQ)
- II) using concentration cell equipment (CCEQ)



Figure 1: Galvanic cell equipment (CEQ) for salinity gradient power generation

Experimental setup for GCEQ is presented in Figure 1. In GCEQ, two different electrodes

UNDER PEER REVIEW

are immersed in the same sea water container which is similar to normal galvanic cell used for generation of electric potential from chemical reaction. But, the generation of electrode potential in GCEQ is not similar to that of a galvanic cell. In galvanic cell, positive potential arises due to neutralization of cation near cathode and negative potential arises due to the oxidation of anode material. On the other hand, in GCEQ used for generation of electric potential using sea water, a potential arises due to accumulation of charge on the electrodes. We get high and low potentials due to the different charge accumulation capacity of different electrodes. Metal ions present in sea water are highly electro positive than used electrodes (zinc, aluminum, iron and carbon). Thus, normal redox reactions are not possible. Neufeld et. al. [37] reported that electrode potential developed on Zn metal when it is immersed in chloride solution due to charge accumulation through a series of complex reactions. As sea water is highly concentrated solution of chloride, it is expected that if we immerse Zn electrode in sea water we shall get electrode potential. Similar is true for other electrodes also. But, all electrodes get negative potential as only anions are accumulated on electrode. We get potential differences as charge accumulation capacity is different for different electrodes.

Theoretically, using GCEQ we get electricity from sea water without loosing the electrode. But, in practice, metal electrodes are destroyed with time due to corrosion. Use of proper nonmetal electrodes would be very handy for extraction of electricity from sea water using GCEQ. This method would be easier to implement in a large scale also. Carbon rod electrode is a very good choice for this purpose. We may use graphite electrode, fabricated graphene electrodes also. But, generated electrode potentials for all these carbon based electrodes would be nearly same. Thus, we shall get very small potential difference if we use any of these electrode pair. To have high potential difference, we should use one carbon electrode (carbon rod or graphite or graphene) and another nonmetal electrode different carbon electrode. We may use IDM for this purpose. Few more are described in proposal section. If we get proper pair of nonmetal electrodes which are sustainable in sea water, GCEQ would be the best way to generate electricity from sea water.



Figure 2: Concentration cell equipment (CEQ) for salinity gradient power generation

Use of CCEQ is an alternate way to get electricity from sea water using two carbon electrodes. Experimental setup for CCEQ is presented in Figure 2. But,we have to use

salinity gradient for this purpose. River water or rain water may be used as low concentration solution. Though we use same electrodes, different electrode potentials are generated due to different concentrations of the solutions. There are two major difficulties for implementation of CCEQ. We need porous barrier to separate two solutions from one another. Co-existence of sea water and river water or rain water is another burden. Few proposals are presented in proposal section to avoid these limitations.

3 Experimental details

Electrode potential(V) and electric current(I) are measured for sea water using GCEQ. Sea water sample is taken from Bay of Bengal at 21.65N longitude and 88.41E latitude. Electrode potential(V) and electric current(I) are also measured for sea water and pond water using CCEQ. Pond water sample is taken from locality near to 21.65N longitude and 88.41E latitude. All these samples are taken on 7^{th} October, 2005. DT830D digital multimeter of HAOYUE company is used for potential and current measurements. Carbon rod electrode is taken from old dry cell battery. Zinc, aluminum and iron electrode are made from unbranded sheet available in local market. Normal filter paper is used as porous barrier. Immersed surface area of carbon electrode is $3.77cm^2$ and that of each metal electrode is $3.76cm^2$.

4 Results and discussion

4.1 GCEQ results

Measured current and voltage of sea water using GCEQ are presented in Table- 1. Three different pairs of electrodes, Zn-C, Al-C and Fe-C are used. It is observed that, highest voltage (1.2V) and current (55mA) obtained for Zn-C electrode pair. Obviously, this pair of electrodes yields highest power density (87.65 Wm^{-2}). Generated power density is lowest for Fe-C pair (22.31 Wm^{-2}), but it is still higher than other reported methods like PRO (7.7 Wm^{-2}), RED (0.9 Wm^{-2}), IDM (3.5 Wm^{-2}) etc. Thus, with respect to power density, GCEQ method is the best among all reported methods of this class.

4.2 CCEQ results for same electrodes

Electrode potentials and current of an unit cell of CCEQ measured for sea water of Bay of Bengal and pond water are presented in Table 2. For this measurement same electrode pairs like, Zn - Zn, Al - Al, Fe - Fe and C - C, are used. It was previously stated that there is no point to use metal electrode. But, for an academic purpose metal electrodes are used for this study. We observe that power density of C - C electrode is $0.40 Wm^{-2}$ which is very promising for this method. Though power density of C - C electrode is less than that of IDM ($3.46 Wm^{-2}$), yet we should prefer C - C electrode as it is very much cheaper than IDM. Metal electrodes have very good power density in CCEQ setup. Zn - Zn electrode is the best among them with $3.62 Wm^{-2}$ power density.

for different electrode pairs immersed in sea water taken from Bay of Bengal						
Electrode	Potential	Currant	Power density			
pair	(V)	(mA)	(Wm^{-2})			
Zn-C	1.2	55	87.65			
Al - C	0.9	34	40.64			
Fe-C	0.8	21	22.31			

Table 1: Electric current, voltage and power density of one unit cell of GCEQ

Table 2: Electric current, voltage and power density of one unit cell of CCEQ using same electrodes. Sea water taken from Bay of Bengal and pond water are used for salinity gradient.

Electrode	Potential	Currant	Power density
pair	(V)	(mA)	(Wm^{-2})
C - C	0.05	6	0.40
Al - Al	0.16	9	1.91
Zn - Zn	0.21	13	3.62
Fe - Fe	0.13	8	1.38

CCEQ setup using different electrodes 4.3

Electric current, voltage and power density of one unit cell of CCEQ using different electrodes are also studied. Measured values are presented in Table 3. It is observed that with different electrodes in CCEQ setup both potential and current increase. We get $94.62 Wm^{-2}$ power density for Zn - C electrode pairs. For different electrode pair, CCEQ setup yield 8 - 12%increase of power density from GCEQ setup. Thus, for generating high power density we should use different electrode pair in CCEQ setup. But, we should keep in mind that for this process we need porous barrier and co-localization of sea water and river water or pond water. At the same time we have a loss of metal electrode.

water are used for salinity gradient.								
Electrode	Potential	Currant	Power density	% increase of				
pair	(V)	(<i>mA</i>)	(Wm^{-2})	power density				
Zn - C	1.25	57	94.62	7.95				
Al - C	0.95	36	45.42	11.8				
Fe-C	0.85	22	24.83	11.3				

Table 3: Electric current, voltage and power density of one unit cell of CCEQ using different electrodes. Sea water taken from Bay of Bengal and pond water are used for salinity gradient.

5 Proposal

From above studies, we may come to the conclusion that for generation of electricity from sea water or from salinity gradient with very good power density, we have to find out nonmetal electrodes which would be able to generate very high potential and at the same time would have long life in saline environment. As in GCEQ or CCEQ setup, potential is developed due to the charge accumulation on electrode surface, it is expected that surface polarity of the electrode is the key factor for the generated potential. Thus, we may expect mesoporous carbon electrode may be a very good nonmetal electrode we are searching for. This is used in IDM which supports this proposal. In Figure 3 few such modeled electrodes are presented which use mesoporous carbon. Type-1 is a metal electrode which is covered by mesoporous carbon. Type-2 is nonmetal electrode in real sense. Here metal electrode is replaced by macroporous alumina. Alumina is needed for support of mesoporous carbon. We may use both alumina and metal as shown in Type-3 electrode.



Figure 3: Modeled electrodes

For CCEQ setup, we need co-coexistence of sea water and river water or pond water. The natural source is of course where a river mixes with the sea. But, we can't only depend on natural sources as it is limited and in some cases may not be suitable for contraction of

UNDER PEER REVIEW

a power station. Thus, we may make water reservoir near the sea which would be filled by rain water. A porous barrier should be placed between sea water and rain water. Such a model is shown in Figure 4.



Figure 4: Proposed setup of CCEQ for SGP station

On the other hand setup of GCEQ power station is very trivial. A model is shown in Figure 5. We may use carbon electrode with metal electrode or fabricated electrode. We have to properly placed our electrodes and connect them. But, if there is a flow of water it would be better for power generation.



Figure 5: Proposed setup of GCEQ for SGP station

6 Conclusion

Electrochemical cell equipment for power generation from saline water (GCEQ) and from salinity gradient (CCEQ) is a very promising method to fulfill our energy requirements. It is easy to implement, yields high energy density (up to $95 Wm^{-2}$, environment friendly

and endless source. Present study just opened up the journey towards a green energy world. Future research, particularly development of new electrodes would enrich this method. Proposed electrodes and implementation techniques may help others to invent more advanced and sophisticated equipments for extraction of electricity from salinity gradient.

References

- S Pacala and R Socolow. Stabilization wedges: solving the climate problem for the next 50 years with current technologies. *Science*, 305(5686):968–972, 2004. PMID: 15310891.
- [2] B E Logan and M Elimelech. Membrane-based processes for sustainable power generation using water. *Nature*, 488:313–319, 2012.
- [3] *Key World Energy Statistics 2015.* International Energy Agency, 31-35 rue de la Federation 75739 Paris Cedex 15 France, 2015.
- [4] Mark A Shannon, Paul W Bohn, Menachem Elimelech, John G Georgiadis, Benito J Marinas, and Anne M Mayes. Science and technology for water purification in the coming decades. *Nature*, 452(7185):301–310, 2008.
- [5] Jian Xu, Fred J Sigworth, and David A LaVan. Synthetic protocells to mimic and test cell function. Advanced Materials, 22(1):120–127, 2010.
- [6] Jan W Post, Hubertus VM Hamelers, and Cees JN Buisman. Energy recovery from controlled mixing salt and fresh water with a reverse electrodialysis system. *Environmental science & technology*, 42(15):5785–5790, 2008.
- [7] Wei Guo, Ye Tian, and Lei Jiang. Asymmetric ion transport through ion-channelmimetic solid-state nanopores. Accounts of chemical research, 46(12):2834–2846, 2013.
- [8] Kah Peng Lee, Tom C Arnot, and Davide Mattia. A review of reverse osmosis membrane materials for desalinationdevelopment to date and future potential. *Journal* of Membrane Science, 370(1):1–22, 2011.
- [9] Shuren Chou, Rong Wang, Lei Shi, Qianhong She, Chuyang Tang, and Anthony Gordon Fane. Thin-film composite hollow fiber membranes for pressure retarded osmosis (pro) process with high power density. *Journal of membrane science*, 389:25–33, 2012.

- [10] Joost Veerman, Michel Saakes, Sybrand J. Metz, and G. Jan Harmsen. River water by reverse electrodialysis: A first step from the laboratory to a real power plant. *Environmental Science & Technology*, 44(23):9207–9212, 2010.
- [11] Joost Veerman, Michel Saakes, Sybrand J Metz, and G Jan Harmsen. Electrical power from sea and river water by reverse electrodialysis: a first step from the laboratory to a real power plant. *Environmental science & technology*, 44(23):9207–9212, 2010.
- [12] Jae-Hwan Choi, Hong-Joo Lee, and Seung-Hyeon Moon. Effects of electrolytes on the transport phenomena in a cation-exchange membrane. *Journal of colloid and interface science*, 238(1):188–195, 2001.
- [13] Isao Kumagai, Makoto Kataoka, and Yuji Kinoshita. Cation exchange membrane, May 5 1987. US Patent 4,663,013.
- [14] Gab-Jin Hwang, Haruhiko Ohya, and Toshiyuki Nagai. Ion exchange membrane based on block copolymers. part iii: preparation of cation exchange membrane. *Journal of Membrane Science*, 156(1):61–65, 1999.
- [15] Géraldine Merle, Matthias Wessling, and Kitty Nijmeijer. Anion exchange membranes for alkaline fuel cells: A review. *Journal of Membrane Science*, 377(1):1–35, 2011.
- [16] Jun Fang and Pei Kang Shen. Quaternized poly (phthalazinon ether sulfone ketone) membrane for anion exchange membrane fuel cells. *Journal of Membrane Science*, 285(1):317–322, 2006.
- [17] Michael R Hibbs, Cy H Fujimoto, and Christopher J Cornelius. Synthesis and characterization of poly (phenylene)-based anion exchange membranes for alkaline fuel cells. *Macromolecules*, 42(21):8316–8321, 2009.
- [18] Nicholas J Robertson, Henry A Kostalik IV, Timothy J Clark, Paul F Mutolo, Héctor D Abruña, and Geoffrey W Coates. Tunable high performance cross-linked alkaline anion exchange membranes for fuel cell applications. *Journal of the American Chemical Society*, 132(10):3400–3404, 2010.
- [19] RE Pattle. Production of electric power by mixing fresh and salt water in the hydroelectric pile. *Nature*, 174(4431):660–660, 1954.
- [20] RE Pattle. Electricity from fresh and salt waterwithout fuel. *Chem. Proc. Eng*, 35:351–354, 1955.
- [21] Isabel C Escobar and Andrea Schäfer. Sustainable water for the future: Water recycling versus desalination, volume 2. Elsevier, 2009.
- [22] Gurmukh D Mehta and Sidney Loeb. Internal polarization in the porous substructure of a semipermeable membrane under pressure-retarded osmosis. *Journal of Membrane Science*, 4:261–265, 1978.

- [23] James N Huckins, Jim D Petty, and Kees Booij. Monitors of organic chemicals in the environment: semipermeable membrane devices. Springer Science & Business Media, 2006.
- [24] John K Hsiao, Beth Ann Ball, Paul F Morrison, Ivan N Mefford, and Peter M Bungay. Effects of different semipermeable membranes on in vitro and in vivo performance of microdialysis probes. *Journal of neurochemistry*, 54(4):1449–1452, 1990.
- [25] Sapna N Makhija and Pradeep R Vavia. Controlled porosity osmotic pumpbased controlled release systems of pseudoephedrine: I. cellulose acetate as a semipermeable membrane. *Journal of Controlled Release*, 89(1):5–18, 2003.
- [26] Guy Z Ramon, Benjamin J Feinberg, and Eric MV Hoek. Membrane-based production of salinity-gradient power. *Energy & environmental science*, 4(11):4423–4434, 2011.
- [27] Thor Thorsen and Torleif Holt. The potential for power production from salinity gradients by pressure retarded osmosis. *Journal of Membrane Science*, 335(1):103–110, 2009.
- [28] Andrea Achilli and Amy E Childress. Pressure retarded osmosis: From the vision of sidney loeb to the first prototype installationreview. *Desalination*, 261(3):205–211, 2010.
- [29] Andrea Achilli, Tzahi Y Cath, and Amy E Childress. Selection of inorganic-based draw solutions for forward osmosis applications. *Journal of Membrane Science*, 364(1):233–241, 2010.
- [30] Sidney Loeb. Method and apparatus for generating power utilizing pressure-retarded osmosis, March 18 1980. US Patent 4,193,267.
- [31] Robert L McGinnis and Menachem Elimelech. Global challenges in energy and water supply: the promise of engineered osmosis, 2008.
- [32] Fabio La Mantia, Mauro Pasta, Heather D Deshazer, Bruce E Logan, and Yi Cui. Batteries for efficient energy extraction from a water salinity difference. *Nano letters*, 11(4):1810–1813, 2011.
- [33] Jun Gao, Wei Guo, Dan Feng, Huanting Wang, Dongyuan Zhao, and Lei Jiang. Highperformance ionic diode membrane for salinity gradient power generation. *Journal of the American Chemical Society*, 136(35):12265–12272, 2014.
- [34] Hong Liu, Ramanathan Ramnarayanan, Bruce E Logan, et al. Production of electricity during wastewater treatment using a single chamber microbial fuel cell. *Environmental science & technology*, 38(7):2281–2285, 2004.
- [35] Hong Liu and Bruce E Logan. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environmental science & technology*, 38(14):4040–4046, 2004.

- [36] Korneel Rabaey, Geert Lissens, Steven D Siciliano, and Willy Verstraete. A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency. *Biotechnology letters*, 25(18):1531–1535, 2003.
- [37] Aaron K Neufeld, Ivan S Cole, Alan M Bond, and Scott A Furman. The initiation mechanism of corrosion of zinc by sodium chloride particle deposition. *Corrosion Science*, 44(3):555–572, 2002.