Electrochemical Characterization of a Supercapacitor Flow Cell for Power Production from Salinity Gradients

Bruno B. Sales,^{1,2#} Fei Liu,^{1,2#} Olivier Schaetzle,² Cees J. N. Buisman,^{1,2} Hubertus V. M.

Hamelers^{2}*

¹Department of Environmental Technology, Wageningen University, Bornse Weiland 9, 6708 WG Wageningen, The Netherlands. ²Wetsus, Centre of Excellence for Sustainable Water Technology, Agora 1, 8932 CJ Leeuwarden, The Netherlands.

Both authors contributed equally to the work described in this manuscript.

*To whom correspondence should be addressed. E-mail: bert.hamelers@wetsus.nl

Footnote: Corresponding Author Phone: +31582843000; Fax: +31582843001; e-mail: bert.hamelers@wetsus.nl; Address: Wetsus, Centre of Excellence for Sustainable Water Technology, Agora 1, 8932 CJ Leeuwarden, The Netherlands.

ABSTRACT

Salinity gradients could be a great source of energy in the future. Capacitive energy extraction based on Donnan Potential (CDP) is a new technique to directly convert this energy into electricity. CDP uses a supercapacitor-like device combining ion exchange membranes and capacitive materials to adsorb and desorb ions with the Donnan Potential of the membranes as only driving force. The resulting current can be extracted through an external load. In this study, traditional electrochemical techniques: galvanostatic charge-discharge and cyclic voltammetry were used to investigate intrinsic properties of this open

system. This study demonstrate the feasibility to characterize the capacitive behavior of the cell in low concentration (0.5 M). Presence of membranes, as well as the possibility of having the electrolyte flowing through the cell was investigated. In the studied cell, the presence of membranes showed a limitation by the anion exchange membrane at low current densities but no effect at high current densities. The flow rate did not influence the capacitance of the system either.

Keywords: Salinity Gradient Energy; Supercapacitor; Renewable energy; Specific capacitance; Activated Carbon

1. Introduction

Renewable energy can be harvested from the salinity gradient difference between river and sea water. The mixing of fresh and sea water increases the entropy of the mixture and dissipates free energy. Globally, the total flow of rivers into the seas has a power potential of 2.6 TW [1]. Different methods were studied to extract energy from this source [2-4], all facing great technical challenges. Recently, capacitive techniques have been developed to extract this energy [4-7] . Among these techniques, the Capacitive energy extraction based on Donnan Potential (CDP), a technique combining carbon electrodes and ion-exchange membranes in a supercapacitor flow cell was proposed with desirable advantages [5]. Figure 1 illustrates the working principle of this technique. First, when a concentrated salt solution (e.g. sea water) is flushed in the cell, ions diffuse through the ion exchange membranes into the capacitive electrodes. An electronic current is generated from the anion-adsorbing electrode to the cation-adsorbing electrode through an external load (Figure 1A). When the system reaches equilibrium, a diluted salt solution (river water) is flushed in the system. The adsorbed ions are diffusing out of the electrodes generating an electronic current flowing from the cation-desorbing electrode to the anion-desorbing electrode (Figure 1B). When the system reaches equilibrium the complete cycle can start over by switching back to sea water.

Figure 1. Working principle of CDP. A. sea water is flushed in the system allowing ions to diffuse in the electrodes and thus generate a current in the external load. B. River water is flushed in the system allowing ions to diffuse out of the electrodes and thus generate an opposite current.

Similar to a capacitor, the total electrical energy extracted and stored in a CDP device is directly proportional to the capacitance and voltage squared of this device. The overall performance of CDP increases with the optimization of these parameters. The electrolytes are restricted to neutral aqueous solutions simulating river and sea water, theoretically having a practical operating voltage about 0.6 –

0.8 V [8]. In our proposed operation, the operating voltage (< 0.2 V) is determined by the Donnan equilibrium potential [9] present due to the use of membranes, which acts solely as the driving force for the process without any energy input. Therefore the selection of electrode material and construction of electrodes becomes a major path leading to breakthroughs for this technology.

In supercapacitors studies, different optimization techniques are suggested to improve the capacitance of the electrodes [10-14], but with non standardized measurement methods. These different reports lead to a wide variation in published values [15]. For that reason a reliable characterization cell and methodology to test and confirm the performance of suitable materials for CDP is still needed.

CDP has several characteristics very different from traditional supercapacitors. First, CDP uses ion-exchange membranes (anion exchange at one side and cation exchange at the other) that are of course completely absent in traditional supercapacitors. Second, the electrolytes used have low concentrations compared to traditional supercapacitors (0.017 M and 0.5M for CDP compared to typically several molar for supercapacitors). Finally, the system is open, allowing an hydraulic flow between the electrodes.

In this study, we investigated the use of two electrochemical characterization methods commonly used with supercapacitor systems as well as the possible effects of the presence of membranes, the salt concentration and the flow. The cell used during our previous study [6] presented several drawbacks like uneven flow repartition and water leakages between the membrane and the electrode. Thus, we designed a new flow through cell different from the previously reported one by a more linear flow pattern and by a better integration of the different components.

2. Experimental

2.1. Carbon electrodes

Carbon electrodes were prepared with the composition of 90% activated carbon (Super 30, Norit, the Netherlands) and 10% polyvinylidene fluoride (PVDF) (KYNAR HSV 900, Arkema Inc. Philadelphia,

USA). The production procedure was as follows: a carbon slurry was obtained by mixing activated carbon powder with a solution of PVDF in 1-methyl 2-pyrrolidone (NMP) (Merck Schuchardt OHG, Hohenbrunn, Germany) in a ball mill grinder (PM 100, Retsch, Haan, Germany) for 30 min at 450 rpm to produce a carbon slurry. The carbon slurry was casted with the Doctor Blade method on a graphite paper foil (1.0 g/cm^3 density, 99% purity, Coidan Graphite Products Ltd., York, UK) and was dried for 24 h in a fume hood.

2.2. Research Setup

The CDP flow-through cell used in this study consisted of a flow through compartment ($10 \times 2.2 \times 1.5 \text{ cm}$). At each side of the cell a stack containing an ion exchange membrane, a capacitive electrode and a current collector was placed. At one of the side a cation exchange membrane is used (FKS, Fumatech, Germany) and at the opposite side an anion exchange membrane is used (Fumasep FAS, Fumatech, Germany). Graphite plates were used as current collectors (Muller&Rossner GmbH, Troisdorf, Germany). The total amount of activated carbon material in the cell was around 2 g and the total geometric area of the electrode was 44 cm^2 for one cell. Figure 2 shows a picture and a drawing of the experimental set-up.

A **B**

Figure 2. Drawing (A) and picture (B) of the CDP cell used in this study.

2.3. Operation

The electrolyte solutions were synthetic 0.5 M NaCl solution (concentrated salt solution) and 0.017 M NaCl solution (diluted salt solution), which were fed into the cell alternatively with three flow rates, 0 ml/min, 60 ml/min, and 450 ml/min. All the experiments were conducted at 25 °C in a thermostatic incubator (Friocell, MMM Medcenter, Munich, Germany). NaCl was from ESCO-salt (Harlingen, The Netherlands).

2.4. Electrical measurement and analyses

In this study, the cell was investigated by cyclic voltammetry and galvanostatic charge-discharge, using a potentiostat (IviumStat, Ivium Technologies, the Netherlands). Cyclic voltammetry measurements were performed at 1 mV/s from 0.4 V to -0.4V between both electrodes. Capacitance was calculated in each case by integrating the current between 0.0 V and +0.3V where all the obtained voltammograms showed good capacitive behavior.

Galvanostatic charge-discharge was done at different current densities: 0.45 A/m², 11 A/m², 22.7 A/m² and 45.4 A/m². The internal resistance was calculated by using the voltage drops before and after each charging/discharging step. The capacitance was calculated by dividing the amount of charges stored or released during each step by the corresponding ΔV according to the formula:

$$C = Q / \Delta V$$

Where C is the capacitance (F), Q the amount of charges (C) and ΔV (V) the difference between the potential before and after the charging/discharging step.

By default, the electrolyte concentration used for these experiments was 0.5 M (e.g. sea water concentration). Concentrations of 1, 2, 3 and 6 M were also investigated.

3. Results and discussion

3.1. Electricity extraction cycle

Before starting the electrochemical characterization of the cell we first investigated its operational performance. For this, we proceeded with the same two steps process as previously reported [6]. Figure 3 displays the evolution of the cell potential over time. In this operation, step one consists of a “charging” step where the cell was filled with the concentrated salt solution. The ions were diffusing through the ion exchange membranes into the electrodes. The charge separation led to an increase of the cell potential known as the Donnan potential. The electrons repelled at the anion exchanging side were flowing through an external load ($R = 15 \Omega$) before reaching the cation exchanging side where they allowed the sodium ions to adsorb. The cell potential is progressively decreasing with the flow of electrons until reaching 0 V. The concentrated salt solution in the cell was then replaced by the diluted salt solution to start the second step of the process. The salinity gradient made the ions to leave the

electrodes and to go through the membranes in the other direction toward the flow channel. This led the cell potential to suddenly decrease toward the negative values. The electrons were then flowing back from the cation adsorbing side, through the load and finally to the anion adsorbing side. The resulting cell potential progressively reached 0V allowing a new cycle to start.

The amount of charges exchanged in a single cycle was 1.17 coulombs during the charging step and 1 coulomb during the discharge. The difference between these values is related to a self-discharge effect common to supercapacitors [16]. The overall performances of the system studied here was the extraction of 75.6 mJ per cycle for a maximum power density of 131.7 mW/m² during the charging step (and 20.3 mW/m² peak power density during the discharging step). The average power produced through the whole cycle was 8.36 mW/m². In comparison, the previous study [6] reported peaks of respectively 60 and 40 mW/m² for the charging and the discharging steps. However, direct comparisons are difficult as cell designs were very different (different amounts of carbon, surface area and channel volume). The large channel used in the present studies explains the rather low average power as the cycle had to last longer due to the distance between the electrodes (the cycles were twice as long as the ones previously reported).

Figure 3 Cell potential versus time and peak power density (mW/m^2) for one cycle with “charging” in the concentrated salt solution and “discharging” in the diluted salt solution.

3.2. Electrochemical characterization of the device

3.2.1. Feasibility of the characterization

As these systems use rather low concentrations of electrolyte compared to supercapacitors (typically 0.5M for the artificial sea water) we first proceeded with preliminary tests of the characterization methods. For this, we used galvanostatic charge-discharge and cyclic voltammetry. Figure 4 shows the obtained results for the studied cell when concentrated salt solution is in the cell compartment and in the absence of flow.

Figure 4. Galvanostatic charge and discharge (2mA) (A) and cyclic voltammetric (1mV/s) (B) investigations of our system in concentrated salt solution without flow.

These methods proved to be very reproducible with our system and gave consistent results. With both methods we could evaluate comparable specific capacitances (4.58 ± 0.05 F/g using the galvanostatic charge, 4.2 ± 0.04 F/g using the galvanostatic discharge and 4.89 ± 0.01 F/g using cyclic voltammetry).

In terms of reproducibility, the standard deviation measured for consecutive duplicates was around 0.05 F/g for galvanostatic charge and discharge and 0.01 F/g for cycling voltammetry. However, when experiments were repeated after one day, the standard deviation for both methods was 0.3 F/g.

Moreover, the galvanostatic charge-discharge method was used to evaluate the internal resistance (through the potential drop before and after charging at constant current). The 2Ω internal resistance that was calculated this way was comparable to the values obtained by directly measuring this resistance with an AC-milliohmeter (Agilent Technologies, mention type meter).

Finally, the capacitance behavior was slightly different during the charging and the discharging step. We systematically obtained lower specific capacitance during the discharge than during the charge (Table 1).

	Galvanostatic charge-discharge 0.45 A/m ²		Galvanostatic charge-discharge 11 A/m ²		Cyclic voltammetry
	Charge	Discharge	Charge	Discharge	
Both membranes					
0 mL/min	4.59	4.24	4.27	3.89	4.32
60 mL/min	4.58	4.2	4.28	3.88	4.89
450 mL/min	4.55	3.9	4.32	3.88	4.96
No membranes (60 mL/min)	4.65	4.31	4.64	4.21	4.56
Only CEM (60 mL/min)	4.65	4.47	4.72	4.42	4.96
Only AEM (60 mL/min)	4.81	4.08	4.45	4.05	5.35

Table 1. Specific capacitances measured with different methods for different flow rate and different cell configurations.

A possible explanation for this is the self discharge of the system. During the charge the self discharge of the system limit the potential increase and thus induce an overestimation of the capacitance. During the discharge however, the selfdischarge induces a higher potential change and thus an underestimation of the capacitance. Assuming that the self discharge is the same during charge and discharge, we can write the following equations:

$$\text{Charge: } \Delta V = C \cdot Q - dV_{\text{self}} \quad (1)$$

$$\text{Discharge: } \Delta V = C \cdot Q + dV_{\text{self}} \quad (2)$$

with ΔV the potential change during the charging/discharging step, C the capacitance, Q the amount of charges adsorbed or desorbed and dV_{self} the self discharge expressed as a potential loss.

With this hypothesis, the average specific capacitance between charge and discharge would indicate a more accurate specific capacitance. Moreover, the difference between this average specific capacitance and the specific capacitances calculated for charge and discharge would give a quantitative estimation of the self-discharge. This hypothesis should be tested and confirmed in future research.

3.2.2. Effect of the concentration

To further address the electrolyte concentration effect, we measured the specific capacitance obtained at different concentrations using galvanostatic charge and discharge. The low concentration at river water concentration inducing high resistive behavior in the cyclic voltammogram, cyclic voltammetry was not used to investigate the effect of concentration. Figure 5 shows the relation between the specific capacitance and the electrolyte concentration. We observed that the specific capacitance slightly increased with the electrolyte concentration. However, the specific capacitance at 6M is only 12.5% higher than the one measured at sea water concentration (0.5 M).

This result suggests that the carbon material can be relatively safely characterized at sea water concentration. This statement is of importance regarding the fact that the operational process of energy production uses these lower concentrations to extract energy.

Figure 5. Specific capacitances measured for different NaCl concentrations.

We also investigated the internal resistances relatively to the electrolyte concentration. Figure 6 shows that the internal resistance is particularly important at the lowest concentration (15.5 ohms at 0.017 M NaCl). Such resistance is directly related to the rather high distances between the electrodes (1.5 cm).

However, the purpose of the studied cell being the characterization of the carbon materials, the internal resistance of the system is of less importance. An actual operating system for energy extraction would need smaller space between the electrodes and thus hydrodynamics of the system would be of particular importance.

Figure 6. Relation between internal resistance and electrolyte concentration.

3.2.3. Effect of the membranes

One of the main differences between the studied system and a traditional supercapacitor is the presence of ion selective membranes. To investigate the effect of the membranes on the capacitive behavior of our system we tested different cell configurations : i) the cell without membrane, ii) the cell with only one anion exchange membrane, iii) the cell with only one cation exchange membrane and iv) the cell with both anion and cation exchange membranes. Figure 7 shows the results obtained by cyclic voltammetry for these 4 configurations.

Figure 7. Cyclic voltammograms obtained at 1mV/s for 4 cell configurations.

The specific capacitances calculated from these measurements did not show very significant differences between the different configurations (Table 1).

This result is confirmed by the galvanostatic charge-discharge method. Figure 8 shows the results obtained for two different current densities (11 A/m^2 and 0.45 A/m^2). We can observe that in the experiment with the lower current density, the discharge behavior differs slightly between the different cell configurations. We can see that at lower current densities, the discharge step presents lower performances when the anion exchange membrane is present. A possible explanation for this is the lower permselectivity of anion exchange membranes compared to cation exchange membranes. The explanation for this relies in the amount of charge exchanged and the relative effect of the self discharge. Indeed, the amount of charges exchanged at 11 A/m^2 was 10 times higher than the measurement at 0.45 A/m^2 (respectively 4 C and 0.4 C). Thus, if we consider the relation (2), the ratio $dV_{\text{self}} / \Delta V$ is bigger when less charges are exchanged thus allowing to see more effect of the self discharge when less charges are stored.

Figure 8. Galvanostatic charge and discharge for different cell configuration at different current densities: 11 A/m² (A) and 0.45 A/m² (B).

As electricity extraction process has a peak current around 6 mA, the relative limitation of the anion exchange membrane must still be important. Improving either the membrane quality or increasing the current density could improve the overall process (by increasing the amount of charges exchanged and decreasing the amount of charges leaked through time).

Moreover, figure 9 shows the relation between the specific capacitance and the charge-discharge current density. The capacitance slightly decreases with the current but stabilizes around 4 F/g. This again, suggests that increasing the current density in the process could be beneficial for the overall performance of our system. More charges could thus be stored at a higher rate leaving less time to the system to leak charges.

Figure 9. Relation between the specific capacitance (F/g) and the charge/discharge current density (A/m²).

3.2.4. Effect of the flow

Another major difference of such system compared to traditional supercapacitors is the possibility to have the electrolyte flowing through the system.

Figure 10, shows the results obtained by galvanostatic charge-discharge with different flow rates.

We can see that, in the studied system, the flow rate had no influence at all on the performance of the cell. This result suggests that mass transport is not limiting the operation of our system. To verify this we can calculate the thickness of the hydrodynamic boundary layer and thus evaluate the relative amount of salt that adsorbed from this source. This can be calculated to be 257 μm for the sodium adsorbing side and 311 μm for the chloride adsorbing side at 60 mL/min using [17]:

$$\text{Sh} = 3.66(1 + 0.095 \text{D}_T \cdot \text{Pe}/L)^{0.45} \quad (3)$$

$$\text{Pe} = \text{D}_T v/D \quad (4)$$

$$\text{Sh} = k \text{D}_T/D \quad (5)$$

$$\delta = D/k \quad (6)$$

where Sh =Sherwood number (-), D_T =hydraulic diamets (m)= $2WH/(W+H)$ (with W =width=2cm, H =height=1.5cm), L =channel=length=12cm, Pe =Peclet number (-), v =flow velocity=0.36cm/s, D =diffusion coefficient for the considered ion= $1.33 \times 10^{-9} \text{m}^2/\text{s}$ for sodium and $2.03 \times 10^{-9} \text{m}^2/\text{s}$ for chloride [18], k =mass transfert coefficient (m/s), and δ =thickness of the hydrodynamic boundary layer (m). The Reynolds number: $Re=D_T \cdot v \cdot \rho/\mu=69$, where ρ =density= $1 \times 10^3 \text{kg/m}^3$, and μ =viscosity= $8.9 \times 10^{-4} \text{Pa/s}$ insures that the flow is laminar.

First we use (4) to calculate Pe that can then be used to calculate Sh in (3). From this k can then be deducted from (5) and finally δ can be calculated from (6).

With the calculated thicknesses we can determine that in sea water concentrations we have 2.83×10^{-4} moles of sodium and 3.42×10^{-4} moles of chloride available within this boundary. With the amount of charge that we exchanged (maximum of 4 C) during our galvanostatic experiments the corresponding amount of ions would be 4.15×10^{-5} moles. This amount being one order of magnitude less than the amount of salt present in the boundary layer it is no-surprise that the mass transport is not limiting. Moreover, in operation, only 1.17 C was exchanged making the mass transport even less limiting.

In the perspective of an operational device this result is very positive as it implies that less water can be used for the same results, thus increasing the fuel efficiency of the system.

Figure 10. Galvanostatic charge and discharge at 0.45 A/m^2 under different flow rates.

Conclusions

A CDP device was investigated using electrochemical methods traditionally used in the study of supercapacitors. The new cell used showed performances of 131.7 mW/m^2 comparable to the one previously described in the literature.

The characterization methods showed to be very reproducible and allowed to evaluate a specific capacitance of the system around 4.6 F/g . The study of the effect of salt concentration revealed that the system could be reasonably characterized in sea water. The presence of membranes showed no significant effect at higher current and a limitation from anion exchange membranes at lower current. The internal resistance was considerably high under lower concentrations (15 ohms at 0.017 M) because of the considerable distance between the electrodes (1.5 cm). However this is of limited impact on the characterization of the materials and is only of importance for the operation of the device. Future studies will have to compromise between the distance of the electrode and the hydrodynamics of the flow in between.

Finally, the flow showed no effect on the capacitive behavior of the cell. All these results combined suggest that the designed cell is appropriate to test different carbon materials without being influenced by the presence of membranes or the by the flow. Materials can thus be tested in such cell before being implemented in an optimized operational CDP design to be developed in the future.

ACKNOWLEDGMENT. This research was performed in the TTIW-cooperation framework of Wetsus, Centre of Excellence for Sustainable Water Technology. Wetsus is funded by the Dutch Ministry of Economic Affairs, the European Union Regional Development Fund, the Province of Friesland, the City of Leeuwarden, and the EZ/Kompas program of the “Samenwerkingsverband Noord-Nederland”. The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 256868. We thank the members of the research theme “Blue Energy” in Wetsus, in special Odne Burheim and Michel Saakes, for their participation in this research.

REFERENCES

- [1] G.L. Wick, W.R. Schmitt, Marine Technology Society Journal, 11 (1977) 16-21.
- [2] A.T. Jones, W. Finley, O.U.S. Consulting, C.A. San Francisco, Proc. Oceans 2003. Proceedings, 2003.
- [3] J.W. Post, J. Veerman, H.V.M. Hamelers, G.J.W. Euverink, S.J. Metz, K. Nymeijer, C.J.N. Buisman, Journal of Membrane Science, 288 (2007) 218-230
- [4] D. Brogioli, Physical Review Letters, 103 (2009) 058501-1-4
- [5] D. Brogioli, R. Zhao, P.M. Biesheuvel, Energy & Environmental Science, 4 (2011) 772-777.
- [6] B.B. Sales, M. Saakes, J.W. Post, C.J.N. Buisman, P.M. Biesheuvel, H.V.M. Hamelers, Environmental Science & Technology, 44 (2010) 5661-5665.

- [7] N. Boon, R. van Roij, *Molecular Physics*, 109 (2011) 1229-1241
- [8] V. Khomenko, E. Raymundo-Piñero, F. Béguin, *Journal of Power Sources*, 195 (2010) 4234-4241.
- [9] P. Pivonka, D. Smith, B. Gardiner, *Transport in Porous Media*, 69 (2007) 215-237.
- [10] J.-Y. Choi, J.-H. Choi, *Journal of Industrial and Engineering Chemistry*, 16 (2010) 401-405.
- [11] E. Frackowiak, S. Delpeux, K. Jurewicz, K. Szostak, D. Cazorla-Amoros, F. Béguin, *Chemical Physics Letters*, 361 (2002) 35-41.
- [12] J.-S. Kim, J.-H. Choi, *Journal of membrane science*, 355 (2010) 85-90.
- [13] P. Simon, Y. Gogotsi, *Nat Mater*, 7 (2008) 845-854.
- [14] L. Demarconnay, E. Raymundo-Piñero, F. Béguin, *Journal of Power Sources*, 196 (2011) 580-586.
- [15] M.D. Stoller, R.S. Ruoff, *Energy & Environmental Science*, 3 (2010) 1294-1301.
- [16] B.W. Ricketts, C. Ton-That, *Journal of Power Sources*, 89 (2000) 64-69.
- [17] R.E. Hayes, S.T. Kolaczowski, *Chemical Engineering Science*, 49 (1994) 3587-3599
- [18] E. Samson, J. Marchand, K.A. Snyder, *Materials and Structures*, 36 (2003) 156-165