

AN ALKALINE DIRECT CHLORO ETHANOL FUEL CELL WITH A CATION EXCHANGE MEMBRANE

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ABSTRACT

A barrier that limits the performance of anion exchange membrane (AEM) direct chloro ethanol fuel cells (DCLEFCs) is that state of the art AEMs do not allow the fuel cell to operate at high temperature (< 60°C). Here we describe an alkaline DCLEFC that employs a cation exchange membrane (CEM) and show that this type of CEM-DCLEFC can stably discharge with a high power density at an operating temperature as high as 90°C.

KEYWORDS: DCLEFC, AEM, CEM, EOR, Membrane

INTRODUCTION

Anion exchange membrane direct chloro ethanol fuel cells (AEM-DCLEFCs) have received ever-increasing attention, mainly due to increased performance as a result of fast electrochemical kinetics at both the anode and cathode in alkaline media [1] [2]. Typical like a proton exchange membrane (PEM) based fuel cell, an AEM-DCLEFC is composed of an anode, an AEM and a cathode, as shown in figure 1a. On the anode chloro ethanol reacts with hydroxide ions (OH⁻) that migrate from the cathode according to:

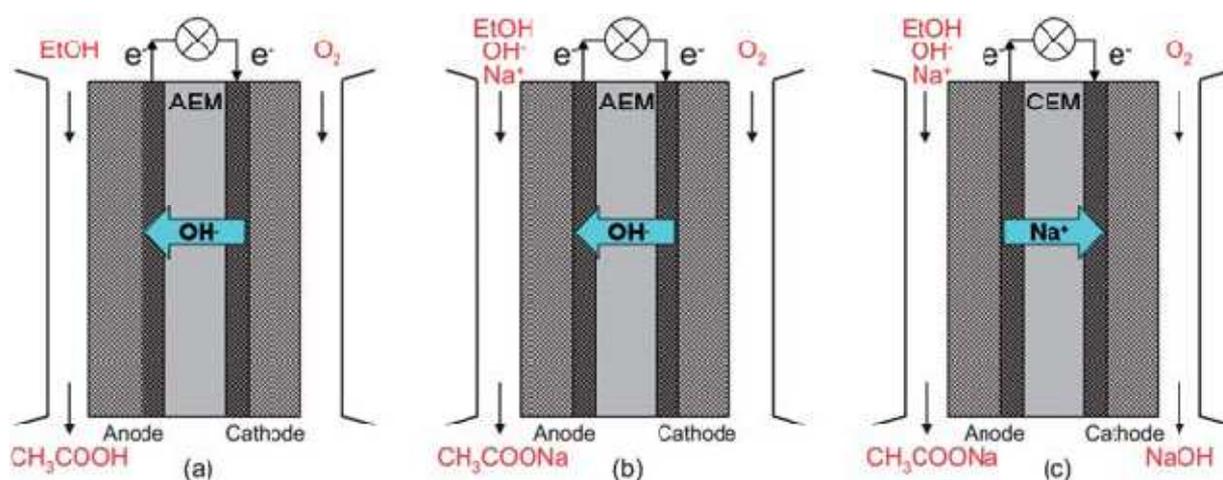
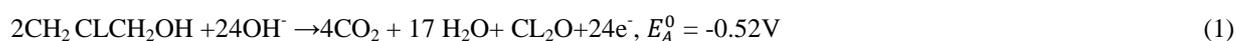


Figure 1: Schematic of Anion and Cation Exchange Membrane Direct Chloro Ethanol Fuel Cells

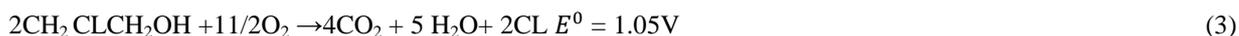


The produced electrons pass through an external electrical load and arrive at the cathode. Note that the above reaction is based on the assumption that the final product is carbon dioxide. It has been proven that with existing

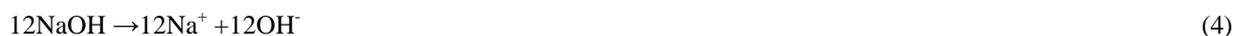
electro catalysts at low temperatures the final product of the ethanol oxidation reaction (EOR) is predominated by acetic acid with a rather small amount of CO₂ [3,4]. On the cathode, O₂ reacts with water and electrons to form hydroxide ion (OH⁻), i.e



Combining the EOR given by eq (1) and the oxygen reduction reaction (ORR) given by eq(2) result in an overall reaction in an AEM-ADCLEFC:



With state of the art AEMs and the electrodes formed with relevant ionomer material, previous investigation [5][6]. Showed that the performance of AEM-DCLEFCs was generally low, To increase the AEM conductivity and to further enhance the EOR kinetics, a base, (e.g. KOH, NaOH) need to be added to the chloro ethanol solution in state- of- the- art AEM –DCLEFCs [7]. As NaOH is added to chloro ethanol solution, anions OH⁻ will are formed at the anode according to:



In addition to those that migrate from the cathode. The fuel cell system with an added base is shown in figure 1b, in which the increased OH⁻ concentration at the anode not only increases the PH value at the anode, thereby speeding up the kinetics of the EOR, but also improves the AEM conductivity. For this reasons, it has been demonstrate that the addition of a base to chloro ethanol solution can tremendously boost the cell performance [8-11]. On the other hand, it is noticed from eqn (4) that in the fuel cell system shown in figure 1b, there also exit cations Na⁺ at the anode. The presence of cations Na⁺ at the anode leads us to think that it is also possible to use a cation exchange membrane (CEM) to conduct cations Na⁺ from the anode to the cathode to close the internal circuit. As such, a new fuel cell system shown in figure 1c is devised. Here after, we refer to the system shown in figure 1c as the CEM-DCLEFCs. The electrochemical reactions in the CEM-DCLEFCs are as follows. At the anode, OH⁻ dissolved from the base, as indicated in equ.4, reacts with chloro ethanol according to equ (1). At the cathode there exist two reaction: i) O₂ reacts with water and electrons to produced OH⁻ according to eqn.(2) and ii) the produced OH⁻ combines to form NaOH. In summary, the above discussion suggest that for the current membranes based alkaline DCLEFCs system with an added base to the anode there exist two options for electrolyte membranes: AEM or CEM. Accordingly, two different fuel cell systems are formed: one is the AEM-DCLEFCs shown in figure 1b and the other is the CEM-DCLEFCs shown in figure 1c. Question that arise are whether this newly proposed CEM-DCLEFCs work or not, and if yes, how it perform as compared with that of the AEM-DCLEFCs. The objective of this work was to answer these questions.

EXPERIMENTAL

Fuel Cell Setup and Instrumentation

Each MEA was fixed between an anode and a cathode flow field. Both flow field were made of 316L stainless steel plate, in which a single serpentine flow channel, 1.0mm wide, 0.5mm deep, and 1.00mm, wide grooved by the wire-cut technique. At the anode, an aqueous fuel solution containing 3.0 M chloro ethanol and 5.0M NaOH was fed into the flow channel by a peristaltic pump at a flow rate of 2.0ml min [9] at the cathode, 99.7 % pure oxygen at ambient pressure with a flow rate of 100 standard cubic cm/p, (sccm) was fed without humidification. Additionally, the cell temperature was

measured with a thermocouple located at the anode current collector, and two electrical heating rods were installed in the cell fixtures to control the operating temperature. An Arvin BT2000 electrical load interfaced to a computer was employed to control the condition of discharging and record the voltage- current curves. The voltage current services were collected by consecutive current step from the zero current to high current. For each discharging current point along the 1-V curve, a 30-s waiting time was needed to obtain the stable voltage at the last second. The internal resistance of the cell was measured by the built- in function of the Arbin BT2000. Anode polarization data for this present fuel cell were obtained by employing an Hg/HgO (MMO) reference electrode. Cathode polarizations were derived by subtracting anode polarization values from the respective cell polarization data. To measure the ionic conductivities of both the CEM and AEM, selected membrane were dipped in 5 M NaOH solution, and then washed by DI water to remove the alkaline solution from the membrane surface. Prior to measurements, each was kept at a desired temperature for at least 10 min. AC impedance was tested in a frequency range of 100 KHz-10Hz with an amplitude of 5mV using auto lab PGSTAT30 electrochemistry workstation(Eco Chemie B.V, the Netherlands). Both samples were measured at least three times, and an average value was then obtained. The ionic conductivity was determined by:

$$\sigma = \frac{d}{RS} \quad (5)$$

Where σ is ionic conductivity ($S\text{ cm}^{-1}$), d is the thickness of membrane (cm), R is the measured impedance of the membrane (Ω) and S is the area of membrane (cm^2)

Membrane Electrode Assembly

Two membrane electrode assemblies (MEAs) one with an AEM and other with CEM, were prepared in this work. The AEM (A201) with a thickness of 28 μm , was provided by Tokuyama, while the CEM was a Nafion 211 membranes, (25 mm thick), which was treated as a cation conductor. The procedure of treating the Nafion membranes included: [12]. i) immersing it in 10 wt% NaOH solution: ii) heating it to 80 $^{\circ}\text{C}$ for 1h and iii) washing it by dionized (DI) water several times. Both AEM- and CEM- MEAs had the same anode and cathode and the same active area of 1.0*1.0 cm. The cathode was a single- side electrode consisting of a fe-CoK-14 HYPERMECTM_ catalyst (ACTA) with a loading of 1.0 mg cm^{-2} , which was attached to a baking layer made of carbon cloth (ETEK). The anode was formed by following the steps: i) a catalyst ink was prepared by mixing a homemade PdNi/C with a loading of 1.0 mg cm^{-2} , chloro ethanol as the solvent and 5 wt% PTFE as the binder [13]. ii) The anode catalyst ink was stirred continuously in an ultrasonic bath for 20 min. such that it was well dispersed; and iii) the anode catalyst ink was brushed into a piece of nickel foam (Hohsen Corp. Japan) that served as the backing layer.

RESULTS AND DISCUSSIONS

Cell Performance at 90 $^{\circ}\text{C}$

Previous studies [16] showed that state of the art AEMs became unstable when the operating temperature became higher than 60 $^{\circ}\text{C}$. However, CEMs (e.g. Nafion) are stable below 100 $^{\circ}\text{C}$. To confirm this point, we tested the AEM and CEM-DCLEFC at 90 $^{\circ}\text{C}$. During the experiment we found that the AEM-DCLEFC could not discharge stably at 90 $^{\circ}\text{C}$ and its cell performance kept degrading all the time. However, the CEM-DCLEFC could run very stably and the measured performance was repeatable. In the following, we chose the best performance of the AEM-DCLEFC to compare with that of the CEM-DCLEFC.

Figure 2 shows a comparison of the cell performance between the AEM-DCLEFC and CEM-DCLEFC at 90°C. It can be seen that the CEM-DCLEFC yield a peak power density of 135 mW cm⁻², which is higher than the best value of the AEM-DCLEFC (115 mW cm⁻²). The performance difference between the AEM-DCLEFC and the CEM-DCLEFC can be explained by the measured anode and cathode potential shown in figure 3b. Like the case at 60°C, the anode potential of the CEM-DCLEFC is lower than that of the AEM-DCLEFC in the whole range of current density, and the difference in the anode potential between the AEM-DCLEFC and the CEM-DCLEFC is gradually enlarged with the current density, however the situation for the cathode potential at 90°C is different from that 60°C: the cathode potential of the CEM-DCLEFC is almost the same as that of the AEM-DCLEFC in the whole range of current densities at 90°C. Due to the similar ohmic loss of the AEM-DCLEFC (315 mΩ) and the CEM-DCLEFC (350 mΩ) this result can mainly be attributed to the fact that at such a high temperature (90°C), the permeation rate of NaOH through the AEM can be high. As in the CEM-DCLEFC where the NaOH produced at the cathode can lower the cathode potential, the permeated NaOH from the anode to the cathode in the AEM-DCLEFC can also reduce the cathode potential.

In summary, the performance tests show that the CEM-DCLEFC could discharge stably with a higher power output at 90°C, but the performance of the AEM-DCLEFC kept degrading at high temperatures.

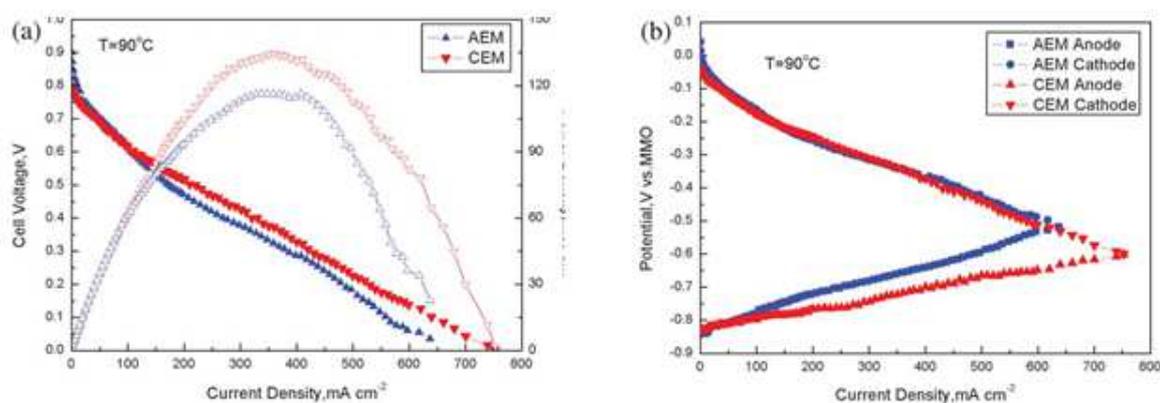
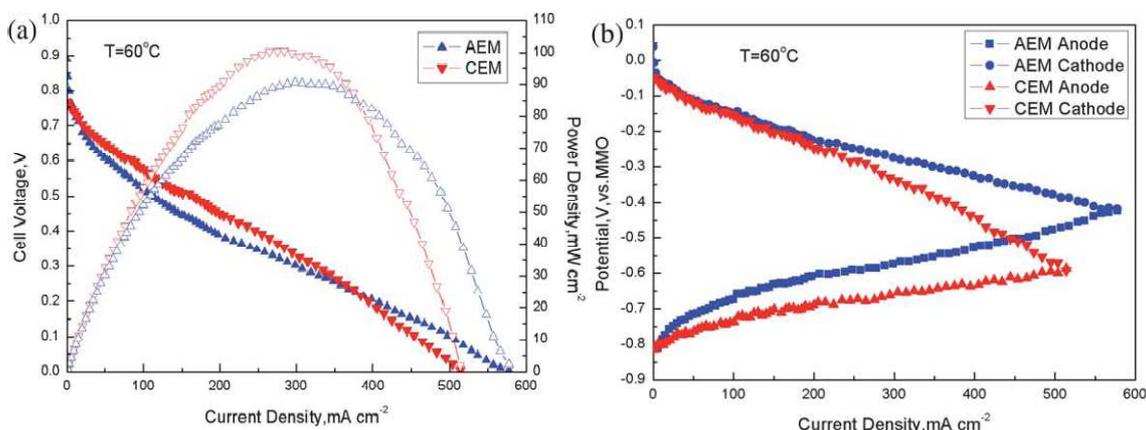


Figure 2: Performance of the AEM and CEM-DCLEFC at 90°C, (a) Polarization and Power Density Curve, (b) Anode and Cathode Potentials

Cell Performance Cell at 60°C

Figure 3 shows a comparison of the cell performance between AEM-DCLEFC and CEM-DCLEFC at 60°C. It can be seen that the CEM-DCLEFC can yield a peak power density of 100 mW cm⁻² which is higher than the AEM-DCLEFC (90 mW cm⁻²). The performance difference between the AEM-DCLEFC and the CEM-DCLEFC can be explained by the measured anode and cathode potential shown in figure 2b. Note that as the voltage = cathode potential – anode potential, a higher cathode potential and a lower anode potential mean a higher voltage. It can be seen that the anode potential of the CEM-DCLEFC is lower than that of the AEM-DCLEFC in the whole range of current densities and the difference in the anode potential between the CEM-DCLEFC and the AEM-DCLEFC becomes larger with an increase in current density. The reason why CEM-DCLEFC yield a lower anode potential than AEM-DCLEFC does is explained as follows. As mentioned above, the final product of the EOR is predominated by acetic acid (CH₃COOH) in the alkaline DCLEFC system according to: [3] [4].





**Figure 3: Performance of the AEM and CEM-DCLEFC at 60°C,
(a) Polarization and Power Density Curve, (b) Anode and Cathode Potentials**

In AEM-DCLEFC as Na⁺ ions neither reacts nor migrate to the anode, Na⁺ concentration at the cathode can be maintained at the feed value (5.0 M). In the CEM-DCLEFC, however, Na⁺ ions can migrate through the membrane to the cathode, which in turn increase the chloro ethanol adsorption on the active sites, thereby improving the anode performance. Also as the Na⁺ migration rate linearly increase with the current density, the anode potential of the CEM-DCLEFC is lowered with the current density as shown in figure 2b. It should be recognized that the OH⁻ concentration at the anode can also affect the EOR kinetics. In this regard the OH⁻ concentration at the anode of the CEM-DCLEFC can be higher than that at the anode of the AEM-DCLEFC due to the fact that OH⁻ ions can migrate from the cathode to the anode in addition to the OH⁻ ions resulting from the added alkali. This reasoning suggests that the EOR kinetics of the AEM-DCLEFC is faster than that of the CEM-DCLEFC. However a previous study showed that when the added alkaline exceeded 3.0M the effect of OH⁻ concentration on the EOR kinetics become negligible.[9].

Let us now focus our attention on the cathode potential shown in figure 2b. It is shown that the cathode potential of the CEM-DCLEFC is lower than that of the AEM-DCLEFC at high current densities. It should be mentioned that the cathode potential loss includes the cathode over potential and the internal resistance loss (ohmic loss). On the other hand, the lower cathode potential is mainly attributed to the fact that NaOH is produced at the cathode of the CEM-DCLEFC and its production rate is proportional to the current density. Previous study [14] [15] showed that the presence of NaOH in the cathode of the alkaline DCLEFC system lowered the ORR kinetics and reduced the cathode active side. On the other hand, the internal resistance of the CEM –DCLEFC (344m Ω) is higher than the AEM-DCLEFC (247m Ω) at 60°C, lowering the cathode potential in the CEM-DCLEFC. At low current densities (< 200mA cm⁻²) the cathode potential for both cell are almost the same, mainly because at low current densities the NaOH production rate in the cathode of the CEM-DCLEFC and the ohmic loss are low. In summary, the performance shown in figure 2 confirm that the alkaline DCLEFC which uses a CEM works and its power output is slightly higher than that of the AEM-DCLEFC at 60°C.

Constant Current Discharge Behaviors

Figure 5 show that the constant current discharging behavior of AEM –DCLEFC at 90°C. It can be seen that the AEM-DCLEFC underwent strong fluctuation with an amplitude as large as 150mV during the whole discharging process. figure 5b confirm that the periodical fluctuation in the voltage of the AEM-DCLEFC are mainly caused by fluctuation in the cathode potential. The possible reason for performance fluctuation is explained as follows. We found that the amount

of solid NaOH particle at the outlet of the cathode flow channel was significantly higher when the AEM-DCLEFC was tested at 90°C. This fact suggest that the permeation rate of NaOH through the AEM becomes more serious at high temperature operation. As mentioned above, the presence of NaOH at the cathode will lower the ORR kinetics and cover the active sites, thus lowering the cathode performance of the alkaline DCLEFC system.[14] [15]. With time, NaOH particle can gradually accumulate in the cathode flow channel, causing the local pressure of oxygen flow to increase. As in increase in gas pressure increase the gas solubility, the reversible potential and exchange current density for oxygen reduction [21]. However when the amount of NaOH particle is accumulated to a critical value, the oxygen flow stream will blow out the accumulated particles from the flow channel, the oxygen pressure will drop to the normal value and the cathode potential will also undergo a rapid drop, as shown in figure 5b. In addition, the AEM is seriously degraded at 90°C, as a result of the nucleophilic attack and Hoffman elimination mechanisms, rapidly reducing the ion exchange capacity (IEC) of the AEM. [17] [18]. Therefore the degraded AEM can also cause performance fluctuation during the constant current discharging process.

The constant current discharging behavior of the CEM-DCLEFC is shown in figure 6. It can be seen that the CEM-DCLEFC can run stably during 3-h continuous operation, which is mainly attributed to the fact that the CEM can withstand a relatively high temperature operation, which tends to reduce the NaOH permeability through the CEM and thus enhance the operating stability. In summary, the result shown in figure 5 and 6 further suggest that the CEM-DCLEFC can discharge stably with a higher power output at 90°C, but the AEM-DCLEFC cannot run stably at high temperature.

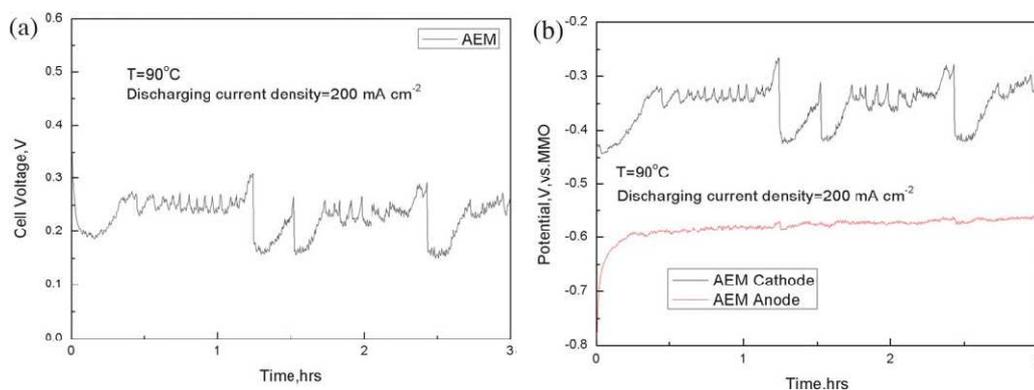


Figure 4: Constant Current Discharging Behavior of the AEM-DCLEFC
a) Voltage b) Anode and Cathode Potential

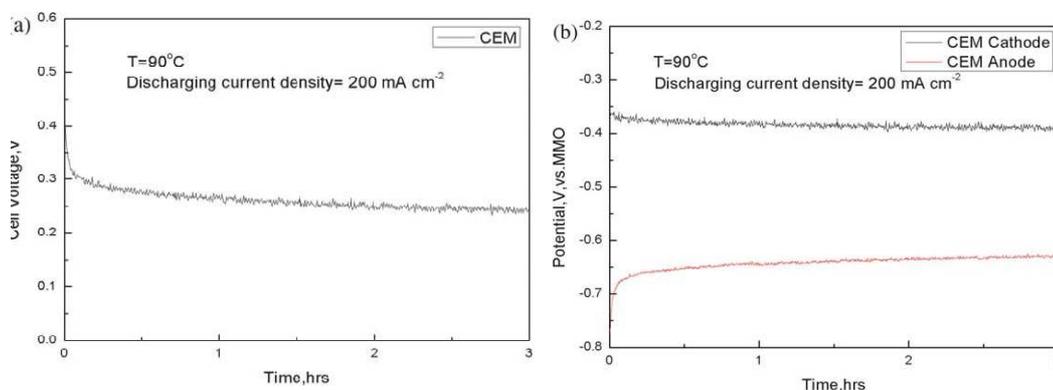


Figure 5: Constant Current Discharging Behavior of the CEM-DCLEFC
a) Voltage b) Anode and Cathode Potential

Ionic Conductivities

Figure 5 shows ionic conductivities of the AEM and CEM at 60 and 90°C as the function of the time period in which the membranes had been soaked in 5.0 M NaOH solution. Generally the charge carrier in the AEM is predominated by the anion (OH⁻), [17]. While cation (Na⁺) is the main charge carrier in the CEM [12]. It can be seen that the AEM shows higher ionic conductivities than the CEM does At both 60 and 90°C within 10 days, indicating that the capability of transporting the OH⁻ through the AEM is higher than transporting the Na⁺ through the CEM in 5.0 M NaOH solution. This result is consistent with the measured internal resistance for both AEM-DCLEFC and CEM-DCLEFC at 60 and 90°C, respectively. It is interesting to note that the ionic conductivities of the AEM at 90°C are lower than those at 60°C in 5.0 M NaOH solution. This is because highly alkaline environments can cause a considerable decrease in the ionic conductivities of the AEM due to nucleophilic attack and Hoffman elimination mechanism, especially at elevated temperature.[17] [18]. However the CEM (e.g Nafion) can be stable in a strong alkaline environment [19] e.g. Nafion membrane employed in the chloro- alkali industry.[20] therefore the CEM-DCLEFC is a promising alternative to the alkaline DCLEFC system, especially at elevated temperatures.

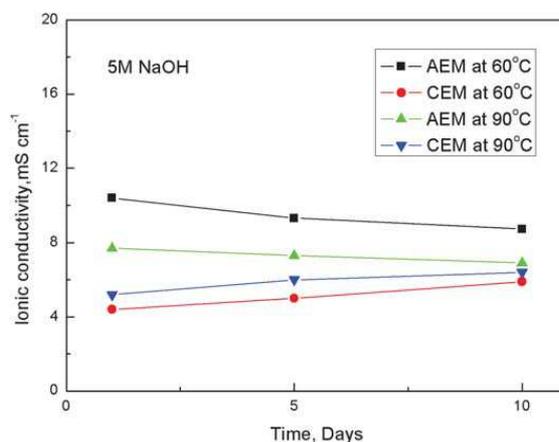


Figure 6: Ionic Conductivities of AEM and CEM

CONCLUDING REMARKS

In this work, we have proposed a new type of DCLEFC that employ a CEM as the ion conductor. Subsequently, we showed that this type of DCLEFC can steadily discharge with a high power density at an operating temperature as high as 90°C. In contrast, as the AEM-DCLEFC become abnormal at 90°C. The significance of the present work lies in the fact that for the first time it reveals that alkaline DCLEFCs can also use cation exchange membranes as the ion conductor to replace original anion exchange membranes. The most striking feature of this CEM-DCLEFC is that it can operate at relatively high temperature which provides plenty of room for boosting the fuel cell performance. Of course like other existing type of fuel cell, there are still some problems such as the formation of NaOH on the cathode that need to be addressed in the future.

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