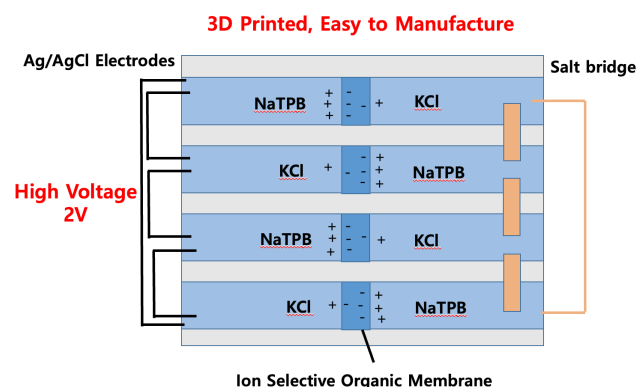# Membrane Batteries: Utilizing Galvani Potential to Store Energy

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'Supporting Information.docx'

ABSTRACT: Organic batteries are spotlighted as one of the substitutes for lithium-ion batteries as they are cheap and cause fewer environmental problems. Here, we introduce a novel membrane-based organic battery that can stand harsh conditions, create high voltage, and is extremely easily fabricated using a 3D printer which improves some of the traits of conventional organic batteries. This battery stores energy as the phase difference of two solutions, using permselective polyvinylchloride (PVC) organic membranes to create a phase boundary potential. In this paper, we show how to increase the voltage of the battery by changing the inner and outer solutions. We also decreased the resistance by (1) making the membrane thinner, (2) adding electrolytes, and (3) changing the compositions of materials. We demonstrated 3D printing battery frames to create a series of batteries that can produce a higher voltage. The high voltage, the simple manufacturing process, and the small size are promising, but the high membrane resistance and degrading battery capacity are still remaining problems to solve. To improve the battery, we additionally propose (1) increasing the concentration of the solutions and (2) stacking membranes to increase the voltage, and (3) replacing PVC with a conductive polymer to decrease the resistance. Also, a spiking attitude of voltage was observed within charging in thin membranes, and additional research is proposed to explain the phenomenon.

Batteries, a great source to store energy, are receiving increased attention along with the approach of the renewable energy era. Due to the lithium-ion batteries (LIB) high recharge stability, energy density, and low self-discharge rate, they gained popularity in fields including batteries for cars, electronic devices, and energy storage systems.[1] However, some complications with the LIB include having thermal issues and a negative impact on the environment.[2,3] Since the LIB was commercialized in 1991, these complications were always tagged along with the batteries. The continuous issues of LIB stressed scientists, precipitating the development of substitute batteries. Organic batteries were introduced as one of the substitutes for LIBs as they cause much fewer environmental problems, and the resources needed to make them are abundant and cheap. However, organic batteries are facing many problems such as fading capacity, high resistance, and low energy density.[4]

Here, we introduce a novel membrane-based organic battery. This battery can stand harsh conditions, create high voltage, and be extremely easily fabricated using a 3D printer. The battery can be manufactured in simple steps. After printing the frame for the battery, a membrane cocktail is injected and left overnight. After filling the inner filling solution (IFS) and the outer filling solution (OFS), the battery can be used. The battery stores energy by utilizing the Galvani potential, an electric potential difference that happens between the interface of two phases,[5] using polyvinylchloride (PVC) plasticized membrane. Sensing ions through liquid-liquid interfaces is the main flow of research utilizing Galvani potential. Obtaining the concentration of certain ions using ion-selective electrodes is promising and repeatedly performs well in trials.[6] However, we tried to use the Galvani potential to create a rechargeable, cheap battery that withstands high voltages and high temperatures. The battery consists of cation-excluding membranes and anion-excluding membranes, and solutions that create potential. (Figure 1)
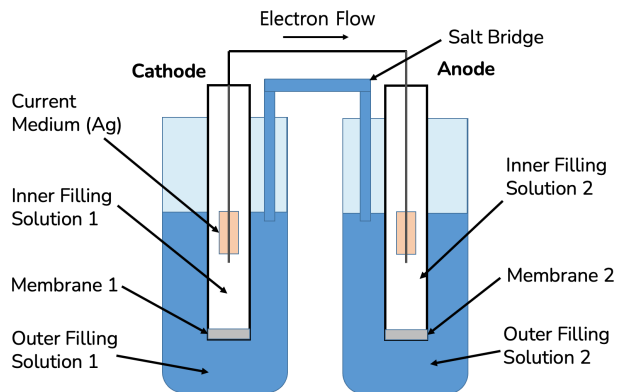
Figure 1. Diagram of the membrane cell

On both sides of the cell, Galvani potential exists due to the phase difference between the membrane and the solution. Figure 2 illustrates the mechanism of the anode in the membrane cell. In the anode of the cell, a perm-selective cation-exchanging membrane is used,[7] and both solutions include organic cations and aqueous anions. This allows the organic cation to partially penetrate the membrane, causing a potential. A bigger difference in the partition coefficients of the ions in the IFS and OFS creates bigger potential in the interface. Normally, the potential difference between the outer interface and the inner interface is preferred, causing the use of two different solutions. A similar potential happens in the cathode, creating a full cell.

The model can be explained by the Nernst equation:

$$E_{\text{Interface}} = E^{\circ}_{\text{Interface}} + \frac{RT}{zF} ln \frac{a_{Cation^+(aq_{bulk})}}{a_{Cation^+(org_{bulk})}} \quad (1)$$

When a cation-exchanging membrane is used, the $a_{Cation^+(org_{bulk})}$ becomes constant, letting the $a_{Cation^+(aq_{bulk})}$ become the independent variable of the potential. We intend to increase $a_{Cation^+(aq_{bulk})}$ to increase the potential of the battery. Also, the temperature in the Nernst Equation was accounted for when the temperatures are changed.
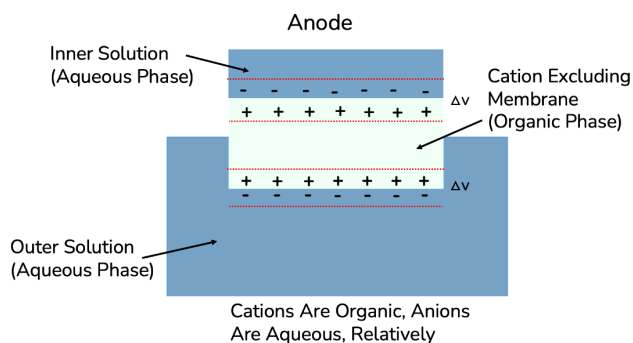
Figure 2. Simplified diagram of the anode

We focused on two main factors to increase the voltage in the phase boundary model battery, (1) changing the types and concentrations of the solution and (2) changing the temperature of the environment. As con-

centration increases, the potential difference also increases which leads to an overall increase in the voltage in the cell. By increasing the number of carbons to increase the difference between the partition coefficients of the inner and outer filling of the electrode, we will observe the contribution of the partition coefficient and the concentration to the voltage. Finally, we will mix and match the solutions to find the high voltage half cells. Also changing the temperature impacts the partition coefficient, the Nernst equation (1), and the maximum concentration that will affect the potential of the model.

The resistivity of the membrane is one of the main factors that decrease the current. Therefore, minimizing the resistance is essential for the ISE to work as an effective battery. Experiments to reduce resistivity were conducted by (1) adding electrolytes, (2) modifying the thickness of the membrane, and (3) changing the membrane composition.

Tetrabutylammonium hexafluorophosphate (TBAH) works as an electrolyte in nonaqueous electrochemistry.[9] Addition of tetrabutylammonium hexafluorophosphate increases the mobility in the membrane, leading to the decrease of the resistivity. Modifying the thickness of the membrane also decreases resistivity in the membrane.

$$\rho = R\frac{A}{l} \quad (2)$$

According to the relationship between resistivity and resistance, by increasing the cross-section area of the membrane, the resistance is reduced (Equation 2). Therefore, decreasing l, the thickness of the membrane, reduces the resistance. Decreasing the ratio of PVC shows similar consequences. PVC has a characteristic of high resistivity, and by decreasing the ratio of it, a lower value of the overall resistivity is derived. A change of membrane plasticizer would also improve the current in this model. We used 2 types of plasticizers, dioctyl sebacate (DOS) and 1-(2-nitrophenoxy) octyl ether (NPOE). By comparing the two plasticizers, we maximize the current in the given voltage.

Electrochemical impedance spectroscopy (EIS) is a technology used for the analysis of interfacial properties.[10] Generally, efficiency experiments for batteries are conducted while charging and discharging, and the conditions including time, temperature, and voltage are measured to be used as criteria for evaluating the state of a battery. This method lacks the precision that voltage alone cannot reflect the detailed characteristics inside the battery. To analyze the battery accurately and quickly, EIS is generally used nowadays. In this paper, EIS was used to view the Nyquist plots and the data was compared.

Table 1. Open circuit potentiometry of various half cells
*Abbreviations in the experimental section

IFS	Membrane	OFS	Half Cell Voltage (V)
TMAN	PTPB	THAN	0.675
STPB	TDMAC	KCl	0.601
TMAN	PTPB	TBAN	0.431
TMAN	PTPB	TPAN	0.325
TMAN	PTPB	TEAN	0.207
TMAN	PTPB	TMAN	0.099
Reference Electrode			≈ 0
STPB	TDMAC	STPB	-0.180
THAC	PTPB	TMAC	-0.407
KCl	TDMAC	STPB	-0.578

Experimental Section

Materials and Instruments

Tridodecylmethylammonium chloride (TDMAC), sodium tetraphenylborate (STPB), polyvinylchloride (PVC), potassium tetrakis(4-chlorophenyl) borate (PTPB), nitrophenyl-octyl-ether (NPOE), tetrahydrofuran (THF), petri dish, 2 cm diameter plastic tube, potassium nitrate (KNO_3), tetramethylammonium nitrate (TMAN), tetramethylammonium chloride (TMAC), tetraethylammonium nitrate (TEMN), tetrapropylammonium nitrate (TPAN), tetrabutylammonium nitrate (TBAN), tetrahexylammonium nitrate (THAN), tetrahexylammonium chloride (THAC), 2 cm diameter puncher, potassium chloride (KCl), balance, reference electrode, EMF 16 (Lawson), Bis(2-ethylhexyl) sebacate (DOS), Ag/AgCl wires, Pt wires

Preparation of electrodes

NPOE and PTPB electrodes were prepared by mixing 330 mg PVC, 10 mg PTPB, 660 mg NPOE, and 10mL THF and leaving it to solidify at room temperature for 24 hours. The membrane was punched out with a 1.5 cm diameter circular puncher and attached to the plastic tube by dipping the tube into THF and placing the membrane on the tube. IFS and the OFS were filled, the electrode was equilibrated overnight, and an Ag/AgCl wire was inserted into the membrane. Other membranes were prepared by replacing the corresponding material, and electrolytes were added to the membranes if needed. The composition of the cocktail was equally maintained.

Electrochemical Preparation

Open circuit potentiometry is done with a two-electrode model, with a reference electrode connected to the EMF16, and the A.C. Impedance and amperometry were done by a three-electrode preparation, including a counter platinum wire, and a reference electrode. Additional experimental information will be explained near the results.

Figure 3 is a schematic diagram to explain the two-electrode model used for potentiometry.
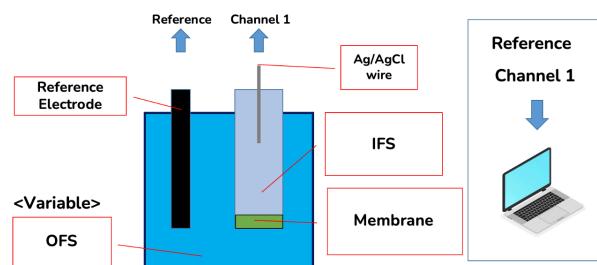
Figure 3. A schematic of the half-cell experiment

Results and Discussion

Increasing the Voltage

The Galvani potential of the membrane happens proportionally to the log P value difference of the ions in the solution.[11] Here, log P refers to the partition coefficient, the measure of the dissolve rates in different phases. To create the difference, an ion has to be easily soluble in one state, and the counterpart should be easily soluble in another state. We have studied the relationship between the number of carbons in the organic ion and the potential of the interface. Figure S1 is s schematic of the experiment to explain the relationship between increasing carbons and the increasing hydrophobicity and increasing potential. Figure S2 illustrates the results obtained from the experiments. These results indicate shows that the theoretical relationship is true, explaining the importance of the log P values of the solutions.

Table Explanation

Stacking membranes to create a high-voltage half-cell was experimented.

Decreasing the Resistance

One of the limits of membrane batteries is that the membrane shows high resistivity, inducing extremely low currents. To overcome this disadvantage, the addi-

tion of electrolyte, modified thickness, and changing the composition of the membrane was conducted.
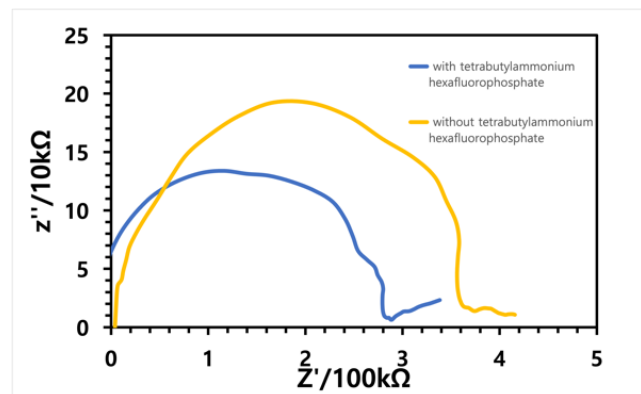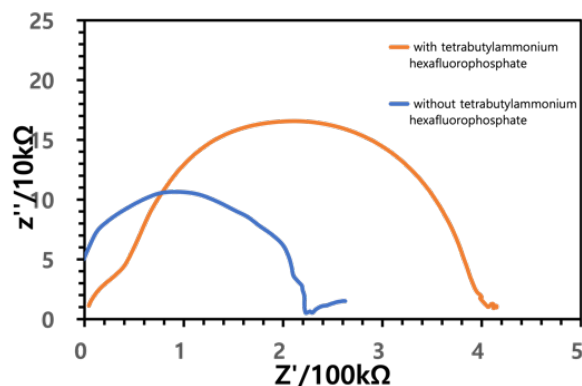
Figure 4. Nyquist plot of ISE with THA as an inner solution, Nyquist plot of ISE with TMA as an inner solution

The sum of ohmic and polarization resistance, which prevents current from flowing, is relatively lower when the membrane contains TBAH. In both cases of the cation-responsive membrane, which has a TPB membrane with THA as an inner solution and TMA as an inner solution, resistivity reduced when 20 mg of TBAH was added. As electrodes with an inner solution of TMA showed lower resistivity, we then increased the amount of electrolyte to the membrane.
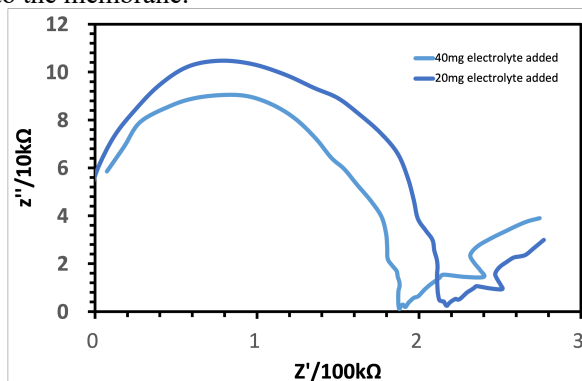
Figure 5. Nyquist plot of ISE with TMA as an inner solution

The result obtained as we increase the amount of the electrolyte, resistivity decreases. However, the value

decreased is relatively lower compared to the difference between membrane containing 0mg and 20mg of TBAH.
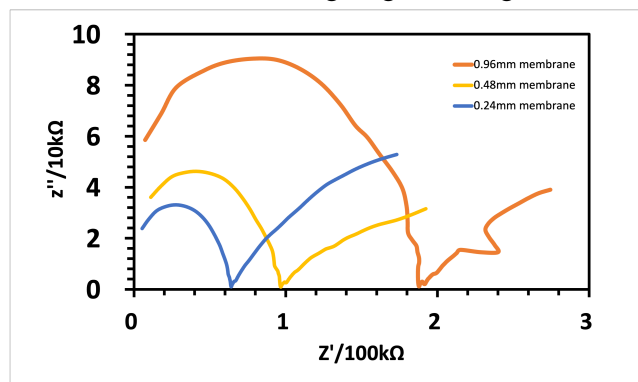

Figure 6. Nyquist plot of 0.96mm, 0.48mm, 0.24mm membrane

The resistivity of the membrane differed also by the thickness of the membrane. As figure 6 shows, decreasing thickness from 0.96mm to 0.48mm and 0.24mm, the resistivity also showed a decrease in value.
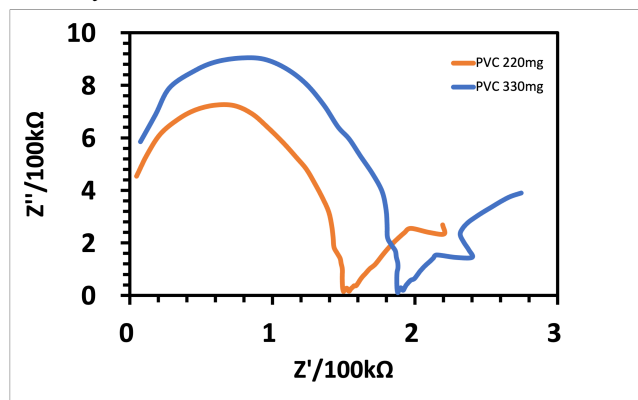
Figure 7. Nyquist plot of PVC 220 mg and 330 mg

As the PVC ratio decreased in the membrane, the resistivity of the overall membrane also showed a decrease.
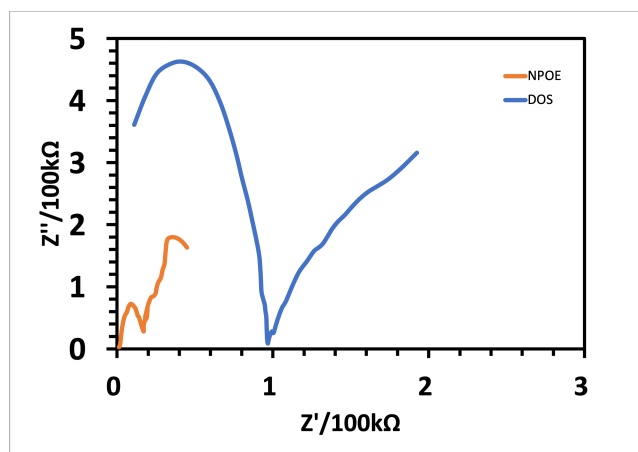
Figure 8. Nyquist plot of membrane made from DOS and NPOE

Lastly, as the plasticizer for the membrane changed from DOS to NPOE, the resistivity of the electrode showed a big drop.

To conclude, we have created a battery cell utilizing the Galvani potential, and gained 0.63 V from a single half-cell, with 0.4 $\mu A\ of$ current. For a cell, we were able to obtain 1.2 V. We were able to increase the voltage by identifying the relationship between the log P values, concentration, and potential. Also, resistance was dropped by adding organic electrolytes (Tetrabutylammonium hexafluorophosphate), making the membrane thinner, and changing the materials. The stacking and fabrication were studied through 3D printing of the frame of the battery. This allowed an easier fabrication of the series of batteries. The final batteries which were connected ----- created 000 V and 000 A. The easily fabricable, environmentally friendly, cheap, high voltage attributes of these membrane batteries make these a promising method to store energy. However, further studies should be done to lower the resistance to create a higher current. Replacing PVC with Nafion or other conductive polymers and making the membranes even thinner will allow even lower, commercializable resistance. Also, understanding the charging process is limited. A sudden increase in potential happens in the charging process as explained in Figure S3. If this phenomenon is understood, even more improvements can happen. This paper has introduced using two different phased solutions to create batteries and presented its advantages and limits. If these are studied deeply, promising results will take place.

ASSOCIATED CONTENT

Supporting Information
The supporting information is available, in the file 'supporting information.docx,' this file includes more potentiometry, amperometry, and more background information.

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