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Study on Organic Redox Flow Battery Mechanism Using TEMPO and FMN-Na Solutions

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Abstract

Among numerous energy storage technologies, redox flow battery is one of the promising technologies that can be used to supply reliable continuation of electricity to electricity grids with a scale up to MW or MWh. In this paper, the process mechanism and optimization of redox flow battery using organic solution such as Riboflavin-5'-phosphate sodium salt dihydrate (FMN-Na) as anolyte and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as catholyte were investigated. Sodium and chloride ions in salt feed were moved respectively to anolyte and catholyte by electrochemical reaction of electrolytes during the charge process and return to the feed during the discharge process. The study was carried out by given electric current with different voltage to graphite electrode range 1,5-10,5 volts and TEMPO concentration 0,02-0,08 M. The result shows that the optimum voltage is 7,5 volts with the concentration of TEMPO 0,06 M. The result also confirms the role of TEMPO solutions in the cathode. In addition to that, the FTIR and SEM analysis to the sedimentation generated during the process also revealed the change of the anolyte and catholyte after charging process.

Keywords: *Organic; Flow Battery; TEMPO; FMN-Na; energy storage*

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INTRODUCTION

Renewable energy such as wind and solar energy is the one of strategy to minimize the dependency of traditional fossil fuels. Nowadays, utilization of renewable energy has been intensified widely in all over the world, but the recent challenge is how to develop a large-scale electrical energy-storage (EES) systems (Park et al., 2016 and Singh et al., 2019). Energy storage technology is a long-desired technique in the development of power systems. However, the traditional battery cannot meet the requirement of regular wind or solar power output due to its short discharge duration. The redox flow batteries have attracted attention because of large-scale of electricity by storing the electro-active species outside the battery container itself (Liang, 2018).

A redox flow battery (RFB) employ redox-active materials in its liquid form to be circulated to stores energy. This mechanism adds the advantages of redox flow battery process as it increases the scalability compared to traditional and modern batteries (Wei et al, 2014). The RFBs is divided into positive and negative electrode electrolytes, which are separated by membranes. The liquid redox electrolytes are pumped through the cell where charged or discharged and returned to the external electrolyte tanks. The RFBs realize the mutual conversion of electrical energy and chemical energy through the redox reaction of the active material (Liang,2018). In this study, the organic solution as electrolyte to produce clean energy, TEMPO as catholyte and FMN-Na as anolyte were used with salt bridge as replacement of ion exchange membrane part with the same function. On the other hand, sodium chloride salt in the bridge salt is to enhance conductivity. In order to increase the solubility of FMN-Na, vitamin B3 (nicotinamide) was added. During the charge process, chloride ions transports to catholyte and sodium ions are moved to anolyte by redox reaction. On the contrary, chloride and sodium ions are released from electrolytes to bridge salt during the discharge. This organic redox flow battery with integration bridge sodium chloride salt exhibits the cost-effective renewable energy storage than using inorganic materials and ion exchange membrane.

MATERIALS AND METHODS

Materials

In this experiment, 4% hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as catholyte and riboflavin-5'-phosphate sodium salt (FMN-Na) as anolyte were purchased from Alibaba Group and were used directly without further treatment. Other chemicals such as nicotinamide 99%, sodium chloride 99.5% were obtained from Aladdin Co. Ltd.

Experimental setup

The redox flow battery used in this experiment consist of power supply cellkit 1502 plus, 20 x 20 x 25 cm acrylic chambers as cathode and anode, connected with salt bridge and sets of cables and galvanometers. The chambers also connected with small tank and peristaltic pump BT 101S for circulation as shown in Figure 1.

Experimental procedures

The anolyte in the form of solution was made by 0.02 N FMN-Na, 0.08 M nicotinamide and 1 M NaCl in 100 mL aquadest. Meanwhile as catholyte TEMPO 0.02 N was mixed with 1 M NaCl in 100 mL aquadest. Each solution is set to a pH of 12. In addition, the preparation of salt bridge is following the procedure stated in other reference (Liang et al., 2018).

Flow cell test for optimum parameters

The performance level of the TEMPO FMN-Na flow was measured using the galvanostat. Cell flow tests include: The optimum voltage test, which is used to find the optimum voltage from the flow battery, where the optimum voltage obtained is used to test the optimum concentration of cells operated with variations in voltage 1.5 V; 3.0 V; 4.5 V; 6.0 V; 7.5 V; 9 V; and 10,5 V for 3 hours. And two solutions (0.02 M TEMPO + 1 M NaCl and 0.02 M FMN-Na + 1 M NaCl) were used as anolites and catholites for the charge-discharge test. On both the positive and negative sides of the battery 25 μL electrolytes are pumped with a flow rate of 25 ml/min.

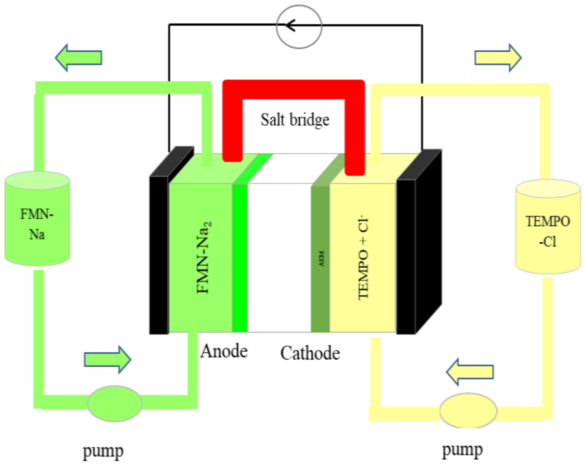


Figure 1. The schematic diagram of TEMPO-FMNNa redox organic flow battery

The optimum concentration test, which is used to find the optimum concentration of the flow battery. The cell is operated with the optimum voltage obtained in the previous cell test for 3 hours. And TEMPO + NaCl and FMN-Na + NaCl solutions were used as anolite and catholite for the charge-discharge test, with variations in the concentration of 97% TEMPO solution, FMN-Na 97%, each 0.02 M; 0.04 M; 0.06 M; and 0,08 M. On both the positive and negative sides of the battery pumped 25 μL electrolytes with a flow rate of 25 ml/min.

Characterization

Qualitative testing was conducted by using Scanning Electron Microscope (SEM) and Fourrier Transform Infra Red (FTIR). Scanning image electronmicroscope (SEM, JEOL-6700F) from negative electrodes with different charge states (SOCs) was used to reveal the morphology of TEMPO compounds inside the electrode. Mapping elements with FTIR in the 4000–400 cm − 1 range in a solid state was also carried out to see the distribution of TEMPO compounds and carbon in the porous electrode, identifying the composition of the product load on the anolite after filling.

RESULTS AND DISCUSSIONS

The voltage was varied to find out the optimum voltage to be used in the redox flow battery charging process. As shown in Figure 2, current enhancement was observed every 30 minutes at all voltage parameter.

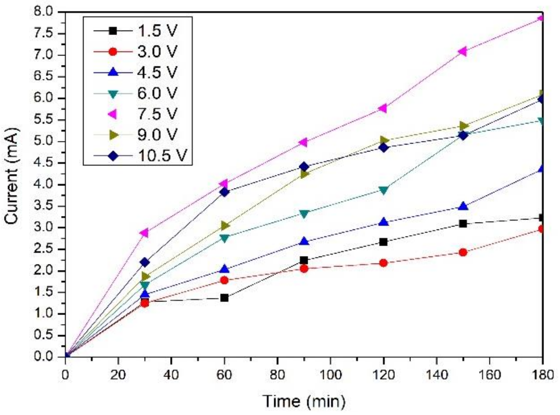


Figure 2. The effect of voltage to current of flow battery

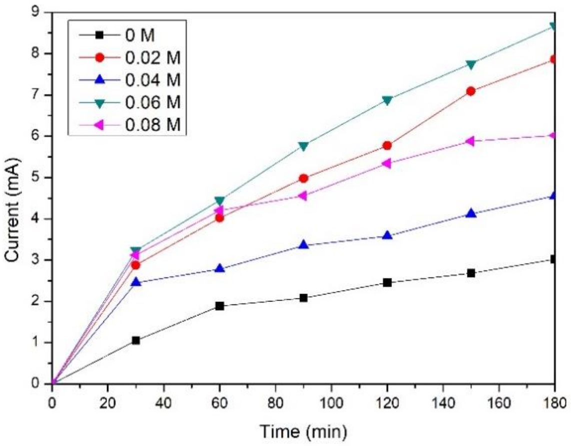


Figure 3. The effect concentration of electrolyte to current of flow battery

Based on Ohm's law theory states that the voltage or voltage (V) is directly proportional to the electric current (I) so that if the voltage is enlarged, the stronger the current generated is greater (Koyun, 2012). But the larger enhancement is in 7,5 volts.

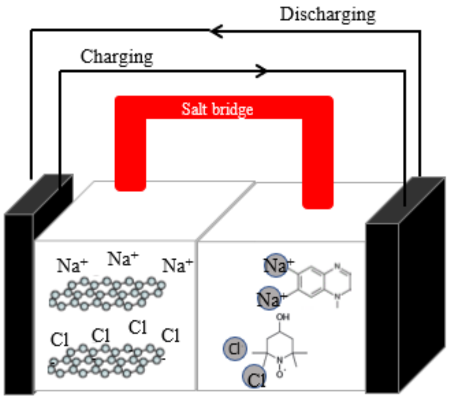
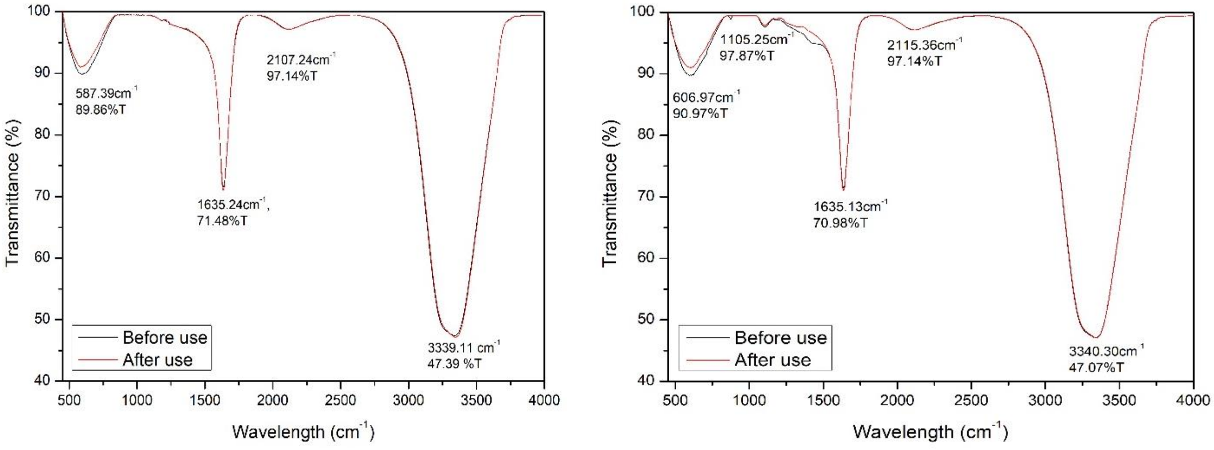


Figure 4. Reaction mechanism of charging and discharging process in redox organic flow battery

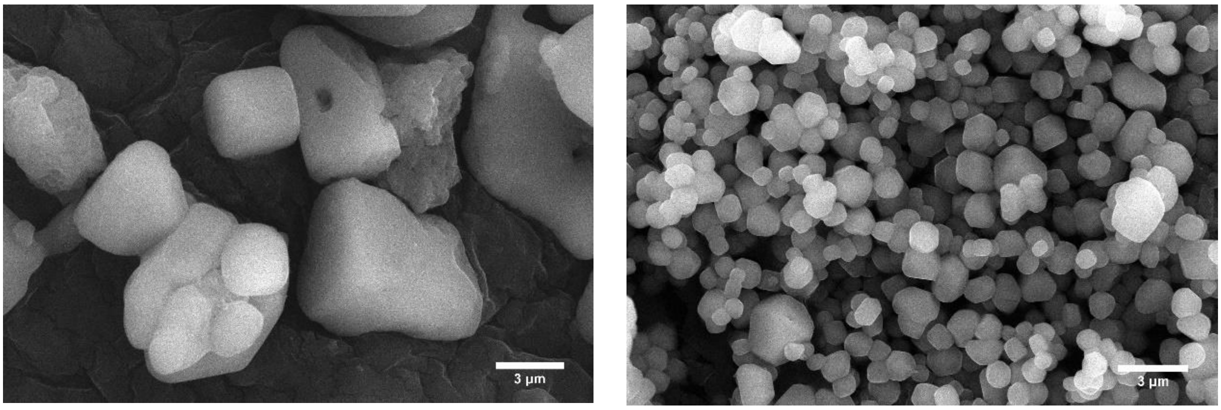
The result of the concentration optimization is shown in Figure 3. Based on the graph above that all of variation of voltage has current enhancement in every 30 minutes. According to 2nd Faraday's law theory states that the mass produced in an electrolysis cell is directly proportional to the electric charge flowing in the cell, so that the higher the mass of the electrolyte which in this case is represented by the concentration of the solution (molarity), the number of ions contained in the solution much so as to increase the electrical conductivity and the value of the current becomes higher (Topayung, 2011). However, other reference states that in solutions that are too concentrated, the movement of ions is more difficult so that the conductivity is lower, whereas in aqueous solution, the ions in the solution move more easily so that the greater conductivity of electricity (Sumar et al., 2014). That is based on this study the optimum concentration of TEMPO is 0.06 N.

This result also affirms the role of TEMPO in the system which is to assist and increase the Na^+ and electron transportation to the anode for energy storage by forming TEMPO-Cl in chatode. The reaction mechanism proposed for this redox flow battery system can be seen in Figure 4.



(a) (b)

Figure 5. FTIR Pattern of (a) TEMPO and (b) FMN-Na before and after the charging process



(a) (b)

Figure 6. SEM images of (a) TEMPO and (b) FMN-Na after the charging process

The flow battery was assembled using aqueous solutions of the redox-active organic FMN-Na/TEMPO as negative/positive electrodes, 1 M NaCl salt as feed. Sodium chloride was used in salt bridge as supporting addition to enhance to conductivity in the electrolyte tanks.

The cell provides an open-circuit voltage of ~0V due to the initial discharge state and tt can be charged and discharged within the potential window of 0.01V-1.10V). Upon charging, the TEMPO radical is oxidized, forming an oxammonium cation (TEMPO+Cl$^-$), while the FMN-Na is reduced to FMN-Na$_2$. The color shift is also observed from orange to yellow (TEMPO) during charging process. The reaction in cathode and anode during charging is summarize as below:

Cathode: TEMPO + Cl- → TEMPO-Cl + e
Anode: FMN-Na + e + Na+ → FMN-Na$_2$

Meanwhile for during the discharge process, the redox reactions can be described as follows:

Cathode: TEMPO-Cl + e → TEMPO + Cl$^-$
Anode: FMN-Na$_2$ → FMN-Na + e + Na$^+$

The characterization analysis using FTIR (Figure 5) in the dried solution of catholyte and anolyte after the charging process revealed that there are a slight change in the solution chemical structure as the difference % of trasmittance was observed in wavelength 587 nm for TEMPO; 606 nm and in the range of 1100-1500 nm for FMN-Na. The phenomena also affirm the reaction mechanism proposed previously and explained the color shift in TEMPO.

SEM image in Figure 6 indicate the morphology of FMN-Na2 and TEMPO-Cl generated during the charging process. The FMN-Na form a big chunk with the size > 5microns, while TEMPO-Cl form a small particle with the size of less than 1 microns.

CONCLUSIONS

Organic flow battery with TEMPO as catholyte and FMN-Na as anolyte was successfully made with capacity 4,298 Wh for 100 ml volume reactor tank and 5,1 Wh for 250 ml volume reactor tank. The result shows that the optimum voltage is 7,5 volts with the concentration of TEMPO 0,06 N. The result also confirms the role of TEMPO solutions in the cathode. In addition to that, the FTIR and SEM analysis to the sedimentation generated during the process also revealed the change of the anolyte and catholyte after charging process. The organic redox flow desalination battery will contribute more in the field of renewable energy and desalination in the future.

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