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Electrochemistry Evaluation of Chromocene in Organic Solvents for Non-Aqueous Organic Redox Flow Electrolyte

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Abstract. The redox flow battery (RFB) is kind of energy storage device for large scale energy storage system. It has many advantages for large scale energy storage system. But, conventional electrolyte has low energy density. So, for overcoming this problem, the chromocene, which is kind of metallocene and has high standard voltage, is studied for RFB. In this paper, the solvents (1-dioxolane, 2-tetrahydrofuran, 3-N,N-dimethylformamaide, 4-benzene, 5-hexane, 6-toluene, 7-heptane, 8-acetotrile, 9-propylene carbonate, 10-N-methyle-2-pyrrolidinone) for chromocene is researched. Solubility, electrical conductivity, electrochemistry properties determined by many experiments. As a result, N-metyle-2-pyrrolidinone has highest conductivity and toluene has highest solubility for using chromocene. Also, N-metyle-2-pyrrolidinone has suitable redox reaction and electrochemical property for RFB. Synthetically, N-metyle-2-pyrrolidinone is determined that it is proper for solvent of chromocene in RFB.

Keywords: redox couple, chromocene, metallocene, non-aqueous electrolyte, flow battery

1. Introduction

Recently, as increasing demand of electricity and renewable energy, Energy storage devices are interested by industry and researchers. Many kind of Energy storage device (Li-ion battery [1], super capacitor [2], redox flow battery, [3]-[5] Sodium-sulfur battery [6], etc.) are compete for energy storage market. Among them, the Redox Flow Battery (RFB), which have high scalability, high flexibility, low safeness issue, has become as much a part of the energy storage market. But, low energy density is a sticking point of the RFB. So, many researchers carried out a research about energy density enhancing method of RFB for using new redox couple in the non-aqueous electrolyte.

Byunghyun Hwang carried out the new non-aqueous Redox Flow Battery for enhancing energy density. The ferrocene and cobaltocene, which is kind of a metallocene, are used for new redox couple for redox flow battery [3]. Also, Yu Ding carried out the research about lithium based redox flow battery using metallocene [4]. And Christo S. Sevov used organic materials for persistent, cyclable electrolyte for flow battery [5].

Chromocene, which is kind of a metallocene compound with formula $(C_5H_2)_2Cr$, considered as redox couple for flow battery. Because it has high standard potential [4] for redox reaction for overcoming low energy density. In the RFB, electrolyte has to have high electrical conductivity and high solubility for high voltage efficiency of the battery. Also, good reversibility and proper electrochemical properties are required for electrolyte of RFB. So, 10 type of solvents (1-dioxolane, 2-tetrahydrofuran, 3-N,N-dimethylformamaide, 4-benzene, 5-hexane, 6-toluene, 7-heptane, 8-acetotrile, 9-propylene carbonate, 10-N-methyle-2-pyrrolidinone) is studied for optimizing for a chromocene as a redox couple. And electrochemical and mechanical properties of chromocene according to each solvent was studied for high performance of RFB.

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2. Experimental

2.1. Electrolyte

Electrolyte was prepared by many kind of solvents. For determine a solubility and conductivity, 10 type of solvents (1-dioxolane, 2-tetrahydrofuran, 3-N,N-dimethylformamaide, 4-benzene, 5-hexane, 6-toluene, 7-heptane, 8-acetotrile, 9-propylene carbonate, 10-N-methyle-2-pyrrolidinone) is researched using chromocene.

2.2. Solubility

For determine a solubility of the chromocene in each solvent, 0.1g of chromocene is dissolved in 10mL of each solvent during 24h using mechanical stirrer at the room temperature. After 24h, the electrolyte pour through filter paper for finding insoluble component. After that, the insoluble slurry is evaporated by air at the room temperature until to evaporate perfectly. And the weight of insoluble component (chromocene) are measured.

2.3. Conductivity

Also, conductivity of saturated solution which is dissolving chromocene is measured. Each solution used 10 kind of solvent (1-dioxolane, 2-tetrahydrofuran, 3-N,N-dimethylformamaide, 4-benzene, 5-hexane, 6-toluene, 7-heptane, 8-acetotrile, 9-propylene carbonate, 10-N-methyle-2-pyrrolidinone). And it stirred during 24h by mechanical stirrer. Conductivity of each electrolyte are measured 30times. And eventually, average of conductivity is calculated.

2.4. Cyclic voltammetry

Cyclic voltammetry is carried out for determining electrochemical properties of each electrolyte. The 3 electrode system is used. Pt-wire, Standard Calomel Electrode (SCE), Carbon felt are used for counter electrode, standard electrode, working electrode, respectively. 10mV/s of scan rate is injected from -1.8V to -0.9V. And 4 cycle of cyclic voltammetry are carried out. Each electrolyte prepared by 0.1M of chromocene and each solvent.

3. Discussion

3.1. Solubility

The toluene has the highest solubility for using chromocene among them. And the tetrahydrofuran has lowest solubility. 10 kinds of solvents are studied and the solubility was shown by table 1.

Table 1: Solubility of chromocene following each solvents (1-dioxolane, 2-tetrahydrofuran, 3-N,N-dimethylformamaide, 4-benzene, 5-hexane, 6-toluene, 7-heptane, 8-acetotrile, 9-propylene carbonate, 10-N-methyle-2-pyrrolidinone).

Solvent	1	2	3	4	5
Solubility(g/l)	4.42	2.39	5.55	4.65	3.06
Solvent	6	7	8	9	10
Solubility(g/l)	5.90	4.25	4.37	3.78	4.25

3.2. Conductivity

Table 2: Conductivity of electrolyte following each solvents (1-dioxolane, 2-tetrahydrofuran, 3-N,N-dimethylformamaide, 4-benzene, 5-hexane, 6-toluene, 7-heptane, 8-acetotrile, 9-propylene carbonate, 10-N-methyle-2-pyrrolidinone).

Solvent	1	2	3	4	5
conductivity(μS/cm)	0.000	0.000	0.247	0.000	0.000
Solvent	6	7	8	9	10
conductivity(μS/cm)	0.000	0.000	0.217	0.084	0.268

According to conductivity experiment, N-methyle-2-pyrrolidinone has highest conductivity and propylene carbonate has lowest conductivity. It can be shown at the table 2. Also, dioxolane, tetrahydrofuran, benzene, hexane, toluene, heptane has 0 μS/cm of conductivity. It means that chromocene doesn't exist as an ionic condition in that solvents. So it can't be solvent as electrolyte of RFB. So, dioxolane, tetrahydrofuran, benzene, hexane, toluene, heptane fall out in the cyclic voltammetry measurement.

3.3. Cyclic Voltammetry

For determining electrochemical properties, cyclic voltammetry experiment is carried out. As shown by table 3, acetotrile has highest reduction potential and lowest oxidation potential. It means that reversibility of the acetotrile is lowest. Likewise, N-methyle-2-pyrrolidinone has lowest reduction potential and highest oxidation potential. It means that N-methyle-2-pyrrolidinone has highest reversibility. So, it is determined that the N-methyle-2-pyrrolidinone is proper as a solvent using chromocene as a redox couple.

Table 3: Redox potential of (3) N,N-dimethlformamaide, (8) acetotrile, (9) propylene carbonate, (10) N-methyle-2-pyrrolidinone.

Solvent	3	8	9	10
E_{pa}	-1.38	-1.42	No find	-1.28
E_{pc}	-0.91	-0.86	No find	-1.07
$\lvert E_{pa} \rvert - \lvert E_{pc} \rvert$	0.47	0.56	-	0.21

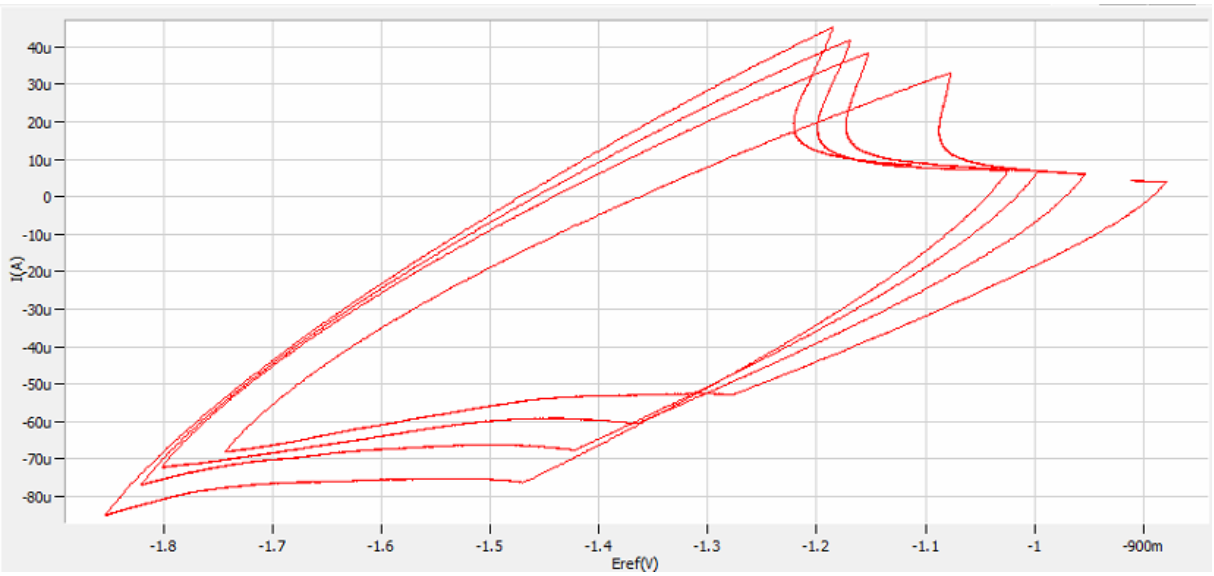

Fig. 1: Cyclic voltagram of chromocene dissolved in N-methyle-2-pyrrolidinone (from 1st cycle to 4th cycle) vs. SCE electrode

The Fig. 1 is the cyclic voltagram of the chromocene dissolved in N-methyle-2-pyrrolidinone. It can be seen in the Figure 1, the cyclic voltagram from 1st to 4th cycle is measured. The stability of the peak potentials are changed according to cycle. At the first cycle, the potential of the reduction is -1.1 V but final reduction potential is -1.2 V. It means that stability of the electrolyte is low. It is the problem of using chromocene and NMP as a redox couple and solvent repectively. It seems that the ionic diffusion velocity of chromocene and the unstable electrolyte according to evaporation of NMP. So, for this overcoming this problem, novel additive and novel synthesis method chromocene and novel functional group are researching by our research group.

4. Conclusion

In this paper, 10 type of solvent (1-dioxolane, 2-tetrahydrofuran, 3-N,N-dimethylformamaide, 4-benzene, 5-hexane, 6-toluene, 7-heptane, 8-acetotrile, 9-propylene carbonate, 10-N-methyle-2-pyrrolidinone) are

researched for using chromocene as a redox couple for redox flow battery. Solubility experiment, conductivity experiment, cyclic voltammetry experiment are carried out for determining solubility, conductivity and electrochemical properties, respectively. In the solubility experiment, all kind of solvent are soluble for chromocene. But, in conductivity experiment, just 4 solvent (N,N-dimethylformamaide, Acetotrile, Propylene carbonate and N-methyle-2-pyrrolidinone) has conductivity for chromocene. It means that chromocene are exist as an ionic state in the 4 solvents. In cyclic-voltagrams, the conclusion that the N-methyle-2-pyrrolidinone is proper solvent for chromocene is concluded. Because, the electrolyte which used chromocene solved in N-methyle-2-pyrrolidinone has good reversibility. So, it is determined that the N-methyle-2-pyrrolidinone is proper as a solvent using chromocene as a redox couple for redox flow battery. But, the peak potential of electrolyte moved as the cycle increases. It means that duarability of electrolyte is low. So, as following this result, another research(novel additives or added functional group with chromocene) has to execute for overcoming this problems.

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6. References

[1] Languang Lu, Xuebing Han, Jiangqiu Li, Jiangfeng Hua, Minggao Ouyang. A review on the key issues for lithium-ion battery management in electric vehicles, *journal of power sources.* 2013, **226** : 272-288.

[2] Ander Gonzalez, Eider Goikolea, Jon Andoni Barrena, Roman Mysyk. Review on supercapacitors : Technologies and materials, *Renewable and Sustainable Energy Revies*, 2016, **58** : 1189-1206

[3] Byunghyun Hwang, Min-sik Park, Ketack Kim. Ferrocene and Cobaltocene Derivatives for Non-Aqueous Redox Flow Batteries, *CHEMSUSCHEM*, 2015, **8** : 310-314

[4] Yu Ding, Yu Zhao, Yutao Li, John B. Goodenough , Guihua Yu. A high-performance all-metallocene-based, non-aqueous redox flow battery. *ROYAL SOCIETY OF CHEMISTRY*, 2017, **10** :491-497

[5] Christo S. Sevov, David P. Hickey, Monique E. Cook, Sophia G. Robinson, Shoshanna Barnett, Shelly D. Minteer, Matthew S. Sigman, Melanie S. Sanford. Physical Organic Approach to Persistent, Cyclable, Low-Potential Electrolytes for Flow Battery Applications, *Journal of the American Chemical Society*, 2017, **139** : 2924-2927

[6] Brian L. Ellis, Linda F. Nazar, Sodium and sodium-ion energy storage batteries, *Current Opinion in Solid State and Materials Science*, 2012, **16** : 168-177