

Electrochemical Flow System for Li-Ion Battery Recycling and Energy Storage

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ABSTRACT

The wide applications of energy storage systems in consumer electronics, electric vehicles, and grid storage in the recent decade has created an enormous market globally. The electrochemical flow system has many applications in Li-ion battery recycling and energy storage system design. First, research work on a scalable electrochemical flow system is presented to effectively restore the lithium concentration in end-of-life Li-ion cathode materials. An effective recycling process for end-of-life lithium-ion batteries could relieve the environmental burden and retrieve valuable cathode battery materials. The design is validated in a static configuration with both cathode loose powder and cathode electrode sheet. Materials with comparable electrochemical performance to virgin cathode materials are produced after post heat treatment. Second, research contributions in sulfur-based flow battery systems for long-duration energy storage are presented. Sulfur-based redox flow batteries are promising due to their high theoretical capacity, low cost, and high abundance. The speciation of aqueous sulfur solutions with different nominal concentrations, sulfur concentrations, and pH are studied by Raman spectroscopy. Next, a promising aqueous manganese catholyte to couple with the sulfur anolyte for a full flow battery is investigated. Test protocols and quantification metrics for the catholyte are developed. The stability of the catholyte, including self-discharge rate and precipitation rate, is measured via *ex-situ* characterizations. The electrochemical performance of the catholyte is investigated and optimized via *in-situ* experiments. The reaction pathway for the precipitation of catholyte is discussed and several mitigation strategies are proposed. Finally, a semi-solid sodium-sulfur flow battery is developed. The electrochemical performance of the sodium-sulfur battery is studied first in a static configuration at an intermediate temperature (150°C). Then a Na-S semi-solid flow cell is assembled and cycled under the two-aliquots and three-aliquots intermittent flow.

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GENERAL AUDIENCE ABSTRACT

The market of energy storage systems has been expanding dramatically in recent years due to their wide applications in portable electronics, electric vehicles, and large-scale grid storage. First, the research on the development of an electrochemical flow system in the Li-ion batteries (LIB) recycling process is presented. The improper disposal of end-of-life LIBs will generate flammable hazardous waste. Recycling spent LIBs could ease the environmental burden and replenish valuable resources such as lithium, cobalt, and nickel, and reduce the cost of battery manufacturing. In this study, an electrochemical flow system is designed to restore the end-of-life cathode materials in LIBs. The design has the potential to scale up and is validated with a static configuration. The recycled materials show comparable electrochemical performance to virgin battery cathode materials. Life cycle analysis shows that the recycling process consumes less energy and is more environmentally friendly. Second, the research contribution in sulfur-based flow battery systems for long-duration energy storage is presented. The aqueous sulfur solutions with different nominal concentrations, sulfur concentrations, and pH are studied by Raman spectroscopy. Next, a promising aqueous manganese catholyte to couple with the sulfur anolyte for a full redox flow battery is investigated. The chemical stability of the catholyte, including self-discharge rate and precipitation rate, is measured via *ex-situ* characterizations. The electrochemical performance of the catholyte is studied and optimized via *in-situ* experiments. The reaction mechanisms for the precipitation of aqueous manganese solutions are discussed. Finally, a semi-solid sodium-sulfur (Na-S) flow battery is developed. The electrochemical performance of the sodium-sulfur battery is studied first in a static cell at intermediate temperature. Then a Na-S semi-solid flow cell is demonstrated and cycled under the two-aliquots and three-aliquots intermittent flow.

Dedication

To my grandfather who passed away in Aug of 2021.

He would be delighted to see this day.

To my mother Jia Yang and my grandmother Qilin Yang,

Without whom none of this would be possible.

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Time flies so fast that I still remembered when I first came to the US in 2016. The 5 years journey towards my Ph.D. degree has many twists and turns. I couldn't accomplish these without the supports I received from countless people. The experience through my Ph.D. study changes my life and will be remembered forever. I apologize for leaving some people out in this acknowledgment

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Chapter 1 - Introduction

1.1 Direct recycling of Li-ion battery

Due to its wide applications in everything from mobile phones to laptops and electric vehicles, lithium-ion battery (LIB) technology wins the Nobel prize in chemistry in 2019. The invention of the lithium-ion battery can date back to the 1970s when Stanley Whittingham introduced titanium disulfide which, at a molecular level, has spaces that can house – intercalate – lithium ions. Based on John Goodenough's demonstration of cobalt oxide cathode, Akira Yoshino created the first commercially viable lithium-ion battery in 1985.[1] Comparing with other battery systems such as metal hydride-nickel and lead-acid batteries, lithium-ion batteries offer high energy and power density, long cycle life, and low self-discharge rate.[2-4] These advantages enable LIBs to dominate the power source market for consumer electronics for decades.

The growing number of LIBs in the market also brings growing pressure on the environmental impact of solid waste disposal. In the consumer electronics sector, there are over 1.2 billion shipments of smartphones globally since 2014 which implies 24,000 tons of lithium-ion battery cathode materials that need to be recycled in 2017 and roughly \$1 billion in market size for the recycled materials.[5] In the EV sector, approximately 2 million EV lithium-ion battery packs in the US and China will reach their EOL by 2020 which translates to roughly 20,000 tons of EOL lithium-ion battery cathode materials, and this recycling market growth will accelerate with the proliferation of EVs and the increasing use of lithium-ion batteries.[6] A spent LIB without proper treatment contains

heavy metals like Co, Ni, and Mn which would contaminate soil and underground water. The battery electrolyte easily reacts with water to release harmful gas such as hydrogen fluoride (HF). The deposited Li on the anode can react with water to release hydrogen gas (H₂) and produce lithium hydroxide (LiOH). Furthermore, the residual electric power tends to cause explosions or fire accidents. [7]

Currently, End-of-life (EOL) LIBs are only collected and recycled at a rate of less than 5%, in the absence of strong government regulation and economic incentives for recycling. [8] The composition of LIBs varies from different chemistry systems, but they all contain hazardous heavy metals, inorganic and organic compounds, all associated with significant environmental and health risks. [9, 10] Recycling LIBs can ease the environmental burden by reducing the disposal of hazardous battery materials and greenhouse gas emissions, and replenish valuable natural resources such as lithium, cobalt, and nickel, significantly cutting down energy consumption during battery production.

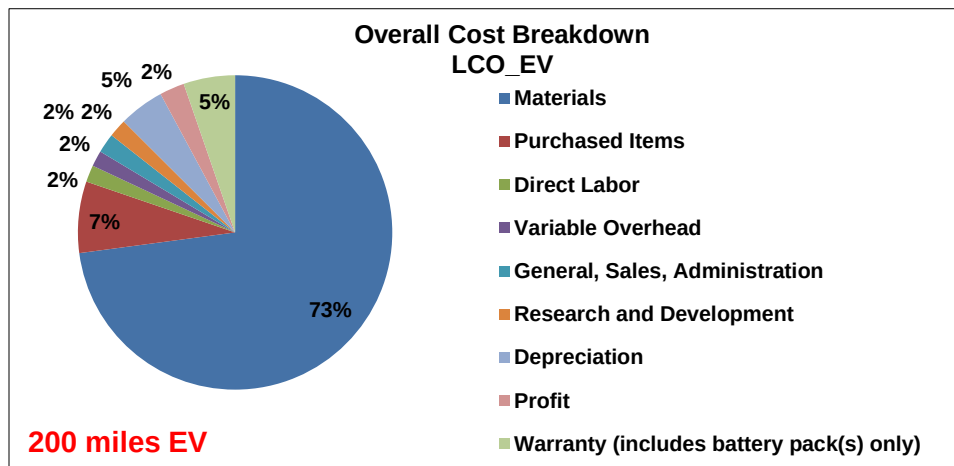


Figure 1.1. 1 Overall cost breakdown for a 200 miles electric vehicle. Assuming using lithium cobalt oxide as cathode active material, calculate using BatPac model.[11]

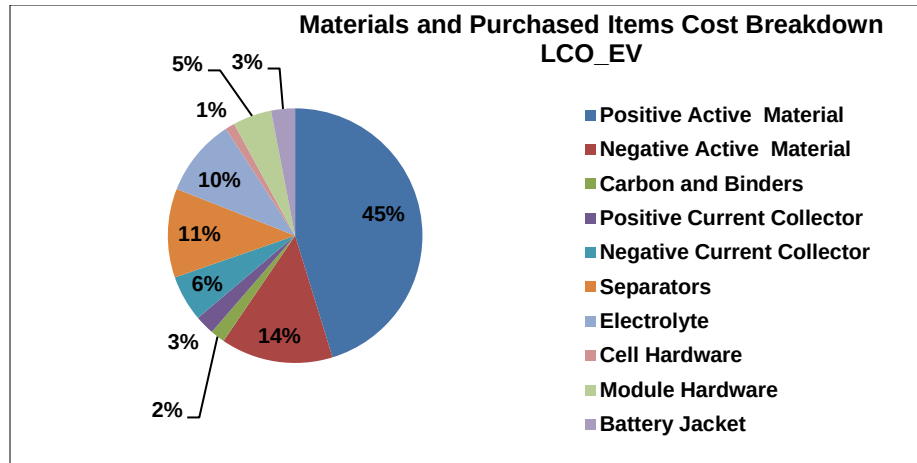


Figure 1.1. 2 Materials and purchased items cost breakdown for a 200 miles electric vehicle. Assuming using lithium cobalt oxide as cathode active material, calculate using BatPac model.[11]

Recycling of the cathode active material is the key step during the recycling process since it is the most valuable component in a LIB. Figure 1.1.1 and 1.1.2 shows the cost breakdown estimated for a 200-mile electric vehicle using the BatPac model. The material cost for a battery pack of a 200-mile electric vehicle takes up 73%. Among the cost of materials and purchased items, the cathode active material takes up to 45%. While government mandates for recycling LIBs are slowly enforced throughout the world, an economically viable recycling approach has to be developed for the industry to grow sustainably. [12-16]

The commercialized recycling approaches for LIBs are pyrometallurgical (Figure 1.1.3) and hydrometallurgical (Figure 1.1.4) processes or a combination of the two. [14, 16-22] These two methods are also defined as indirect recycling or incumbent recycling approaches where the battery components are degraded into elemental constituents and recycled as secondary raw materials.[22] A pyrometallurgical recycling process smelts the end-of-life battery materials and recovers some of the useful metals in alloy forms, though

notably, lithium and aluminum are not typically recovered. A hydrometallurgical process utilizes acid leaching and solvent extraction. It recovers lithium as Li_2CO_3 and other major materials as polymetallic compounds. While the hydrometallurgical process does not involve high temperature and therefore consumes less energy, both methods destroy the structure and morphology of the cathode material, which is the most valuable and takes up to 55% manufacturing cost of LIBs (for the LiCoO_2 case) [11]. Most importantly, both pyrometallurgical and hydrometallurgical methods rely on the recovery of expensive cobalt to make a profit, or to compensate the cost at the very least. As the cathode chemistry gradually shifts away from cobalt to more abundant elements such as iron and manganese, these approaches may not be economically self-sustainable and may require government regulations to force the recycling.

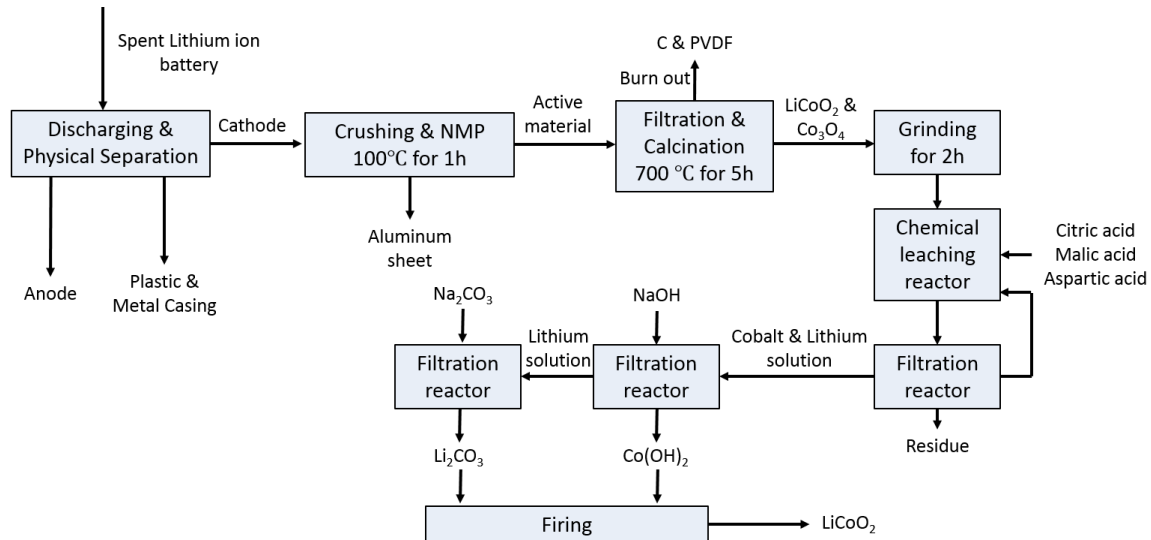


Figure 1.1. 3 Process flow chart of a hydrometallurgical recycling process for LiCoO_2 Li-ion batteries.[22]

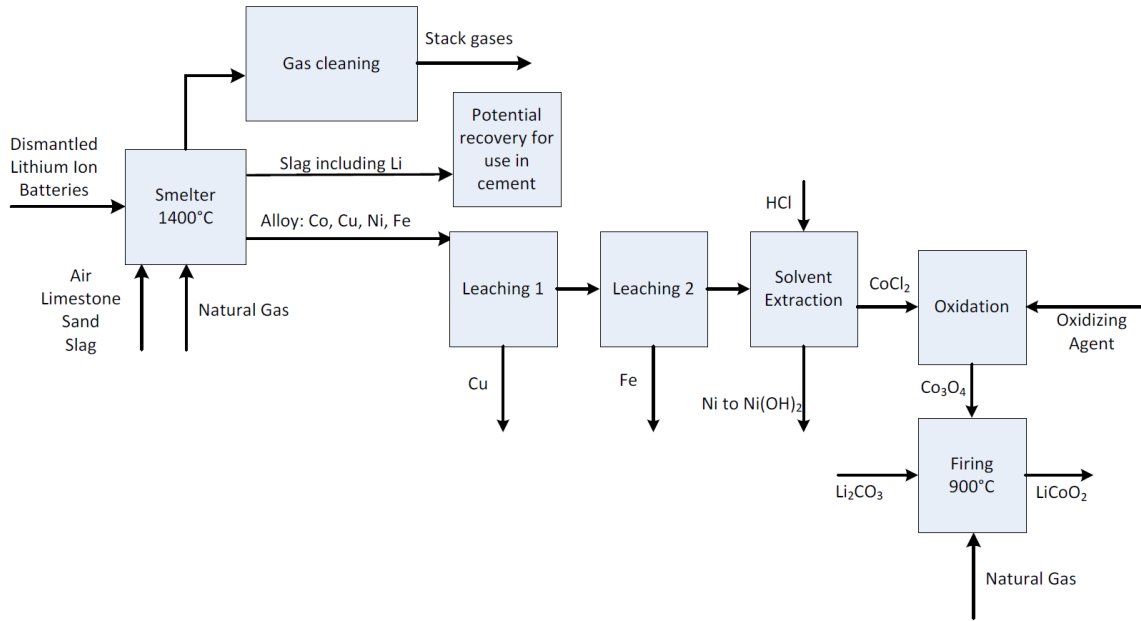


Figure 1.1. 4 Process flow chart of a pyrometallurgical recycling process for LiCoO_2

Li-ion batteries.[23]

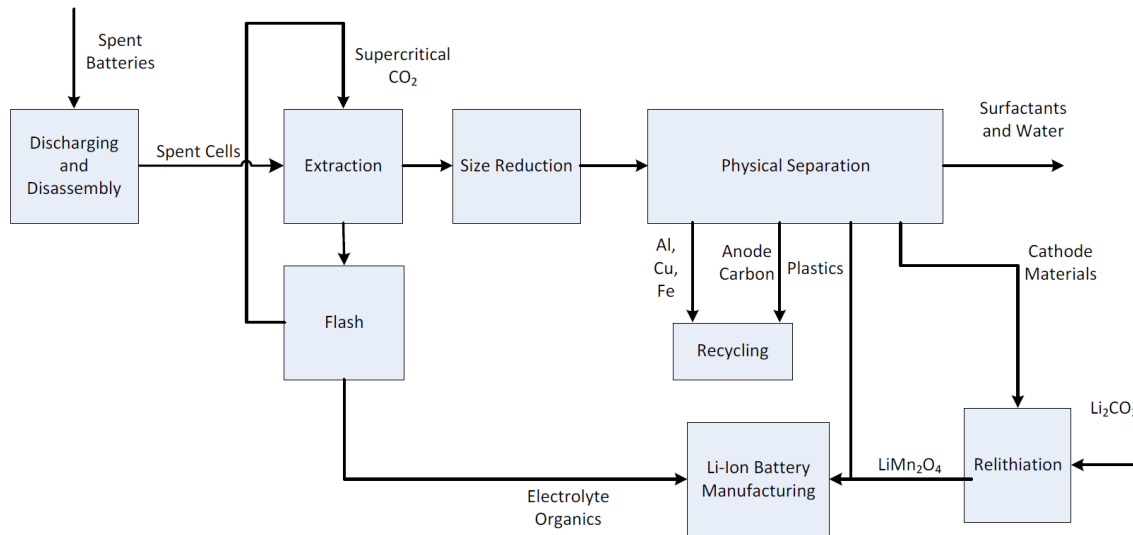


Figure 1.1. 5 Process flow chart of a pyrometallurgical recycling process for spinel

LiMn_2O_4 Li-ion batteries.[24]

For a direct recycling approach (Figure 1.1.5), the outputs of such a process can be reincorporated into a new battery with little additional processing.[25] During direct

recycling, the battery components including the packaging materials, anode, separator, and cathode are separated for individual treatment. The polymer, carbon, and metals from the packaging, anode, and separator can be recycled or reused. The most valuable cathode active material is then treated and restored to its virgin state. In contrast with the incumbent recycling technologies, the direct recycling process retains the structure, morphology, and purity of the cathode materials, which yields resalable high-value materials to the battery manufacturers. It is estimated that battery-grade cathode materials are 2-10 times more valuable than their corresponding elemental constituents depending on the chemistries used. [13]

Understanding the fabrication of the cathode, the nanostructure of the cathode, and the degradation mechanism of the cathode is important to design an efficient recycling process for the cathode active material. Conventional battery manufacturing fabricates the cathode by coating an aluminum foil with a mixture of active material, carbon, and binder. The active material is lithium transition metal oxide or phosphate. The binder is usually polyvinylidene difluoride (PVDF), which dissolves in an organic solvent such as N-methyl-2-pyrrolidone (NMP) to bind the powder mixture and Al substrate together. NMP will be evaporated, and the dried cathode is used for battery assembly. During battery operation, the cathode material deteriorates due to several degradation mechanisms, including irreversible lithium loss during the solid electrolyte interface (SEI) formation or lithium plating on the anode side, defect formation, and particle cracking and isolation.[26-28] Among these degradation mechanisms, the lithium consumption due to solvent reduction and formation of the SEI at the anode side is considered the major cause of

capacity fade, which results in a lithium deficiency of the EOL cathode material compared to their virgin form.

An efficient direct recycling method must address the complex physical and chemical history of the EOL cathode material. Normally the EOL powder was harvested by physical or chemical means before being sintered together with a certain amount of lithium salt to make up for the lithium deficiency caused by extended cycling. [29, 30] The sintering process burns off residual binder and C, heals micro-cracks, and restores the cathode materials to their virgin state. Cycling damage that sometimes occurs at the cathode such as micro-cracking and surface layer formation can be healed and removed during the heat treatment. [31]

Great efforts have been made to find a simple and efficient relithiation/regeneration method that can enable cost-effective direct recycling.[29, 32-38] Solid-state synthesis has been investigated for cathode material regeneration.[32] In such a method, EOL LiCoO_2 is calcined with a pre-determined amount of supplementary Li_2CO_3 powder to yield material that has compatible physical, chemical, and electrochemical properties with commercial LiCoO_2 . This approach is potentially inefficient for scale-up because each cell may have different lithium loss and therefore the lithium addition needs to be quantified for each batch of material processing. A similar regeneration process by direct heat treatment is also investigated for LiFePO_4 and $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$. [29, 35, 36] Electrochemical relithiation of LiFePO_4 was demonstrated by Ganter et al. with organic electrolyte and lithium as the counter electrode.[37] This method is also difficult to scale up, as the system is air-sensitive and cost-prohibitive. A hydrothermal relithiation approach followed by short annealing is developed to recycle degraded LiCoO_2 . [33] The hydrothermal treatment

happens in an autoclave at 180-220 °C. Increased rate capability is observed compared with the solid-state synthesis approach. Shi et al.[38] report an ambient-pressure relithiation process for degraded $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ via eutectic Li solutions. Combining such a relithiation process with a thermal annealing step, the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ can be regenerated to their original composition and structure. An electrochemical relithiation process for recycling cathode materials in a lithium-ion battery is reported.[34] Lithium deficient cathode material is mixed with a solution containing lithium ions. The relithiation of the cathode material happens with an electron-conductive working electrode and a lithium metal counter electrode. This device can efficiently restore the stoichiometry of the cathode material, but safety issues may arise from the lithium metal used in the counter electrode. This potentially hinders the scale-up of the recycling process. In general, a simple and effective relithiation process that allows easy scale-up for mass production and applies to different commercial li-ion cathode materials is still needed.

1.2 Redox flow battery for energy storage

The use of fossil fuels such as coal, petroleum, and natural gas have played an important role in the Industrial Revolution. The burning of fossil fuels, generating carbon dioxide and water, could produce significant amounts of energy. However, it also causes several negative environmental impacts. The burning of fossil fuels generates greenhouse gases, sulfuric and nitric acids. Some fossil fuels also contain radioactive materials. The detrimental environmental effects and the depletion of fossil fuels urge a transition from fossil fuels to renewable and environmentally sustainable energy. As of 2018, the world's

main primary energy sources consisted of petroleum (34%), coal (27%), and natural gas (24%), amounting to an 85% share for fossil fuels in primary energy consumption in the world. Non-fossil sources included nuclear (4.4%), hydroelectric (6.8%), and other renewables (4.0%, including geothermal, solar, tidal, wind, wood, and waste). [39] The share of renewables (including traditional biomass) in the world's total final energy consumption was 18% in 2018. [40]

Among the renewable energies, wind and solar energy are so far the most attractive ones because they are abundant and readily accessible. However, due to the nature of wind and solar energy, these power sources only provide an intermittent supply from the environment. Therefore, renewable energies are perceived to be grid unstable and the contribution level is limited. The integration of more than 20% intermittent renewables could endanger the stability of the grid without required storage.[41] On the other hand, the mismatch between the power generation and the customer demand has resulted in a waste of a large amount of power generation. The installation of a large-scale energy storage system would level the power load of the grid by storing the power during the off-peak hours and discharging the power during peak hours.

Redox flow batteries have recently been studied intensively because they demonstrated the ability to provide large-scale energy storage. Figure 1.2.1 shows a typical design of a redox flow battery. Redox is the short combination of reduction and oxidation. A redox flow battery is a type of rechargeable battery where the chemical components are dissolved in liquids and stored in external tanks. During charging/discharging, the catholyte and anolyte in the tanks will be pumped to a power stack (Figure 1.2.2) where the reversible conversion between electrical and chemical energy happens via redox reactions. Inside the power stack

usually contains the electrodes, current collectors, and the separator which avoid the cross-contamination of the electrolytes but only allow for the cross of charge-carrying ions. (e.g. H^+ , Cl^- and OH^-) The reversible nature of the redox reactions qualifies the redox flow batteries as secondary batteries. For redox flow batteries, the energy capacity is determined by the size of the catholyte/anolyte storage tanks, and the power capacity is determined by the active area in the power stack. Therefore, RFBs have decoupled energy and power capacity. The unique operating mechanism of RFBs endows them several advantages. They can store energy and power up to megawatt-hours (MWh) and megawatts (MW) levels. The design of RFBs can be tailored for energy storage applications at different levels and purposes such as load-leveling, standby power supply, power quality and peak shaving, and renewable energy management & integration. [42]

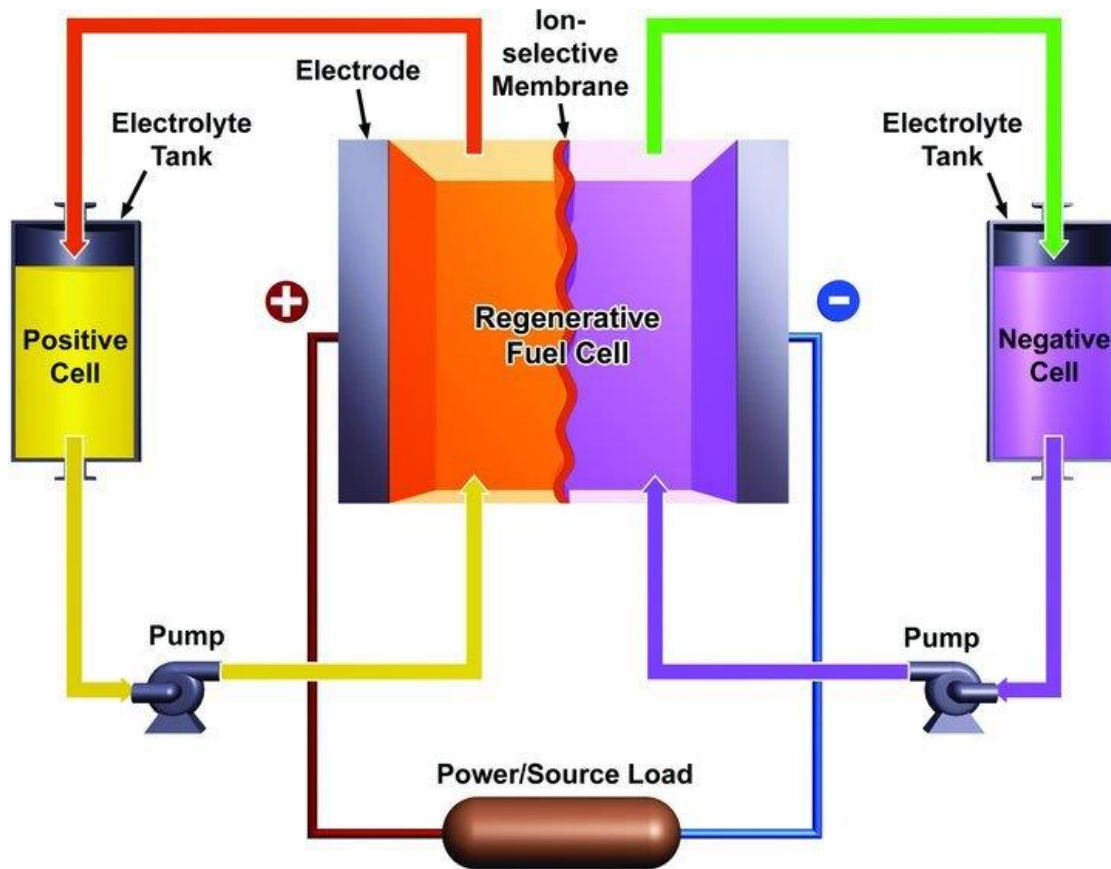


Figure 1.2. 1 Schematic of the structure of a redox flow battery. Reproduced with permission. [43]

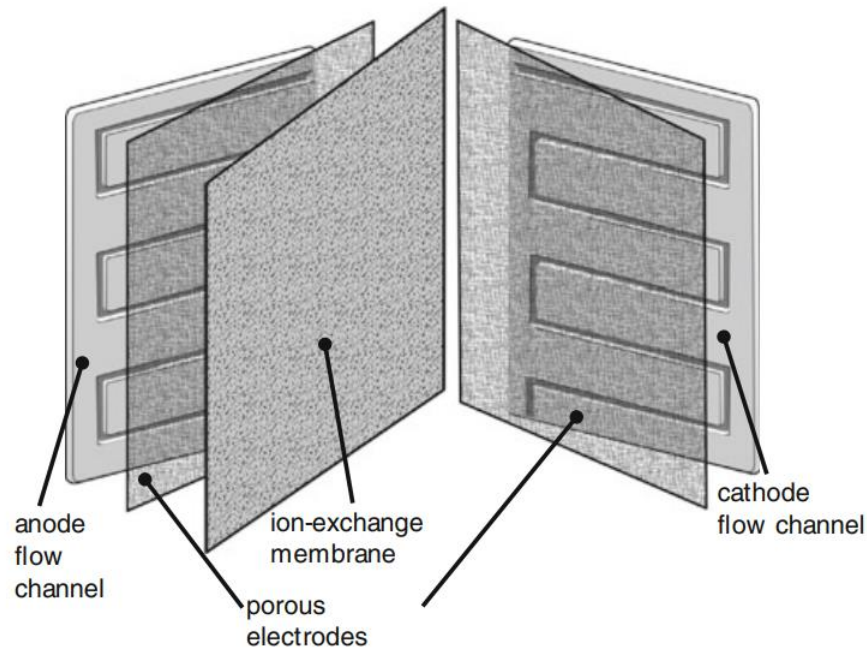
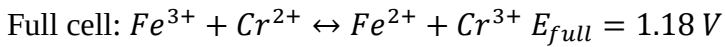
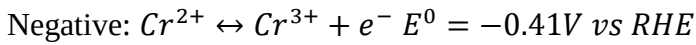
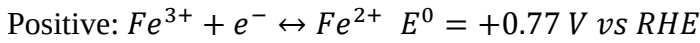


Figure 1.2. 2 Schematic diagram of standard RFB cell with flow channels, porous electrodes, and ion-exchange membrane.[42]

The electrodes in RFBs only provide an interfacial surface for the electrochemical reactions, comparing to traditional solid-state electrodes which usually have complex microstructures. The simple working mechanisms bring long cycling life and easier maintenance and easier manufacturing of the RFBs.

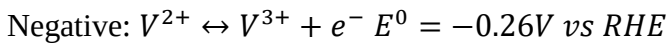
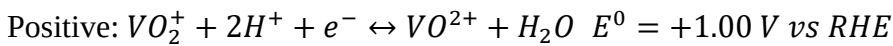
1.2.1 Non-sulfur based redox flow batteries

The invention of RFBs dates back to the 1970s and is credited to Lawrence Thaller at the National Aeronautics and Space Administration (NASA).[44] A Fe/Cr system was demonstrated in aqueous solutions. The redox reactions on each electrode can be described as:



The cell has a standard potential of 1.18 V and could operate with either a cation or anion exchange membrane as the separator. The slow kinetics of the Cr^{2+}/Cr^{3+} redox couple requires an electrocatalyst to improve the electrochemical activity. The cell is often operating at elevated temperatures (65 °C) to further facilitate the Cr^{2+}/Cr^{3+} redox reaction.[45]

Maria Skyllas-Kazacos and co-workers at the University of New South Wales invented the all-vanadium redox flow batteries in the 1980s and made further development since then.[46-51] The all-vanadium system employs four different oxidation states of vanadium and has two vanadium-based redox reactions. The redox reactions on positive and negative electrodes are expressed as:



With the use of all-vanadium-based redox couples, the cross-transport of the active materials will only result in a decrease in coulombic efficiency but not an irreversible decrease in cell capacity.

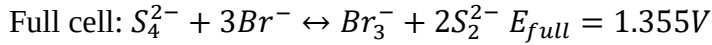
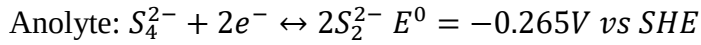
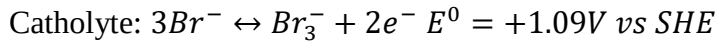
Other redox flow battery systems have also been developed, for example, the zinc/bromine system [52-56] and the iron/vanadium system.[57, 58]

1.2.2 Sulfur based redox flow batteries

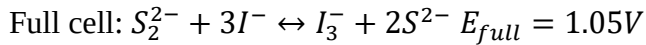
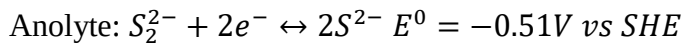
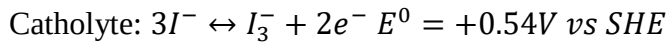
The main motivations for using sulfur as battery electrode material are its high theoretical capacity, low cost, and high abundance in nature. Sulfur ranks 14th among the abundance of chemical elements in Earth's crust.[59] It is widely available as a byproduct of natural gas and petroleum refining. Sulfur also has the lowest cost per stored charge of known redox materials and is close to water and air (in US\$/kAh: sulfur 0.15, zinc 3.66, graphite 32.27, and LiCoO₂ 292.14). [60] Polysulfide redox species have demonstrated high solubility in both aqueous and non-aqueous solutions and have been intensively studied in sulfur-based RFBs.[61, 62] The speciation in aqueous polysulfide solution is complicated, and often contains alkali-metal cations (Li⁺, Na⁺, or K⁺), H₂O, OH⁻, H⁺, H₂S, HS⁻, S²⁻, S₂²⁻, S₃²⁻, S₄²⁻, and S₅²⁻. For polysulfide redox couples applied in RFBs, the reversible reactions are usually between different polysulfide species (S₂²⁻, S₄²⁻, S₈²⁻, S₈⁰ and S²⁻). Polysulfide redox based RFBs have a great potential for high energy density and ultralow chemical cost energy storage.[60, 63-69] Aqueous based polysulfide RFBs have lower cost but also limited voltage window due to the electrolysis of water molecules. The use of organic solvents enables a wider voltage window but also increase the system cost. Besides, the organic solvents based polysulfide solutions also show lower ionic conductivity and higher viscosity, which is not favorable in terms of the kinetics of the redox reaction.[70] For

example, 1 mol dm⁻³ tetraethylammonium tetrafluoroborate in acetonitrile has an ionic conductivity of 55.5 mS cm⁻¹, which is 65%, 27% and 14% that of sodium chloride (85.76 mS/cm), potassium hydroxide (209 mS/cm) and sulfuric acid (394.5 mS/cm) at the same concentration, respectively.[71] For polysulfide organic solutions, the higher-order polysulfides have a higher solubility and the ionic conductivity of the solution is around 0.2 - 35 mS/cm. For polysulfide aqueous solutions, the lower order polysulfides have a higher solubility and the ionic conductivity of the solution is around 127 mS/cm.[72]

The bromine-polysulfide flow battery was reported [63, 73] where the anolyte is the sodium polysulfide and the catholyte is sodium bromide. The working principle of the polysulfide/bromine flow cell can be described as follows:



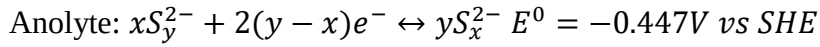
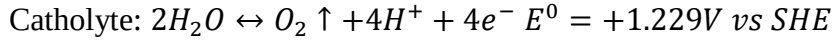
The $\text{Br}^-/\text{Br}_3^-$ redox couple can also be replaced by the I^-/I_3^- redox couple which has much faster kinetics. The working principle of the polysulfide/iodide flow battery can be described as follows[64]:



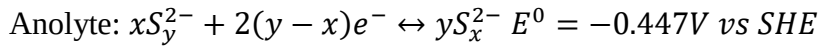
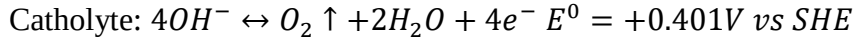
Recently, the polysulfide anolyte is also reported to couple with oxygen reduction reaction (ORR) or oxygen evolution reaction (OER) to build an energy storage system with ultralow-cost and long-duration.[60] In this design, polysulfide anolyte is paired with an oxygenated/aerated salt solution as the catholyte and the working ion can be Li^+ or Na^+ .

Unlike the conventional redox couples, the configuration in this design does not share a common working ion. A Li/Na ion conductive Li-/Na-SICON membrane is used to separate the anolyte and catholyte. The working principles of the flow cell at acidic and alkaline conditions are described as follows:

Acidic Catholyte



Alkaline Catholyte



The chemical cost of the active materials in the system is estimated to be $\sim \$1 \text{ kWh}^{-1}$ when using sodium polysulfide as the cathodic active material.

Chapter 2 - Design of an electrochemical flow system for direct recycling of cathode material in Li-ion batteries

Disclosure

The major part of this chapter has been published by Wiley-VCH: Yang, Tairan, Yingqi Lu, Liurui Li, Dayang Ge, Heng Yang, Weinan Leng, Hui Zhou, et al. "An Effective Relithiation Process for Recycling Lithium-Ion Battery Cathode Materials." *Advanced Sustainable Systems* 4, no. 1 (2020): 1900088.

In this chapter, an electrochemical flow system is proposed for the direct recycling of cathode materials in Li-ion batteries. In section 2.1, an efficient relithiation approach for cathode materials in Li-ion batteries is demonstrated with lithium cobalt oxide. The morphology, crystal structure, and electrochemical performance of the recycled materials are studied and compared with the virgin cathode materials. In section 2.2, the energy consumption for producing virgin lithium cobalt oxide and producing from recycling is compared. In section 2.3, the proposed electrochemical flow system is described in detail.

2.1 Direct recycling of cathode material by electrochemical relithiation

In this section, lithium cobalt oxide from the EOL Li-ion battery is restored to its original lithium stoichiometry by an efficient electrochemical relithiation process. The relithiation process is demonstrated with 2 forms of EOL lithium cobalt oxide (LCO): loose powder and electrode sheet. In the following text, the EOL lithium cobalt oxide is denoted as Li_xCoO_2 (where $x < 1$).

The EOL Li_xCoO_2 materials were harvested from a lithium-ion pouch cell (MTI) with a LiCoO_2 cathode. The pouch cell was galvanostatically cycled between 3.0 - 4.2 V at 1.5 A until around 10% capacity was left (Figure 2.1.1). The EOL pouch cell was manually dismantled in an argon-filled glovebox. The EOL cathode sheet was obtained by unfolding the electrode core. The cathode sheet was then washed with dimethyl carbonate (Sigma) to remove the residual electrolyte on it to make sure the harvested Li_xCoO_2 did not contain any lithium salt impurities. To collect the EOL Li_xCoO_2 powder, the EOL cathode sheet was immersed in NMP and sonicated for 10 min at room temperature. The powder was effectively separated from the Al foil after sonication and suspended in NMP. The Al foil was then removed, and the remaining suspension was centrifuged at 1600 rpm for 20 min. The top dilute liquid layer was decanted afterward. The centrifuge washing process was repeated twice to remove the majority of the PVDF binder. After decanting the top dilute layer of NMP for the second time, the centrifuge tube with the remaining suspension was dried at 100°C for 8 hrs. The powder was then collected and ground. The same procedures were applied to obtain the powder from relithiated LiCoO_2 cathode sheets.

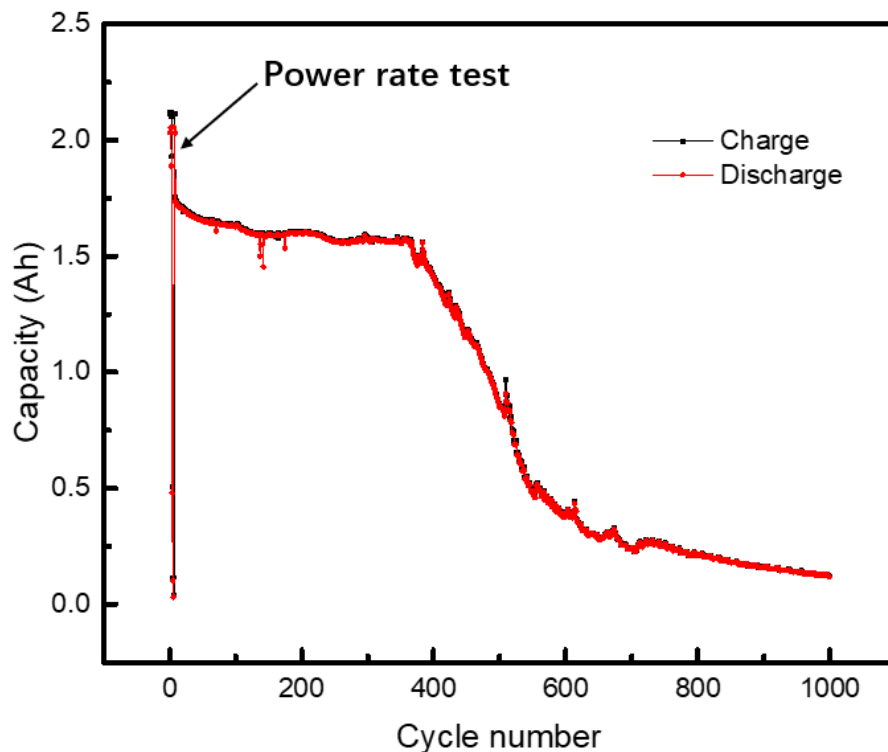


Figure 2.1. 1 Cycling history of the end-of-life Li-ion pouch cell with LiCoO₂ cathode.

2.1.1 Relithiation of Li_xCoO₂ loose powder

A customized half H-cell is shown in Figure 2.1.2. The cell consists of a small chamber on the right for the working electrode (WE) and a bigger chamber on the left for the counter electrode (CE) and reference electrode (RE). An Ag/AgCl gel-type RE was used for the relithiation experiments. A porous polymer membrane was sandwiched between the two glass chambers. The electrochemical relithiation process was conducted by a Biologic SP-150 potentiostat.

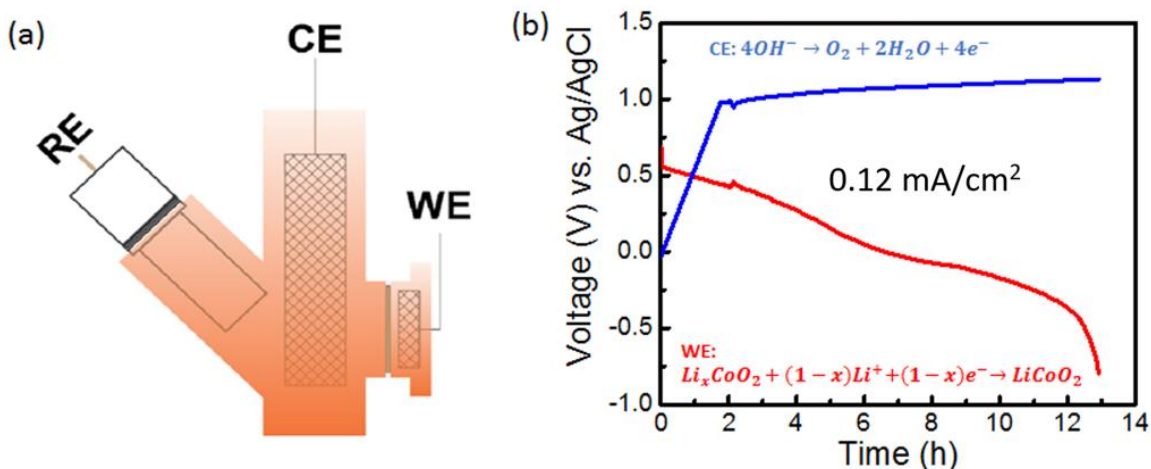


Figure 2.1. 2 (a) The schematic drawing of the H-cell for relithiation. (b) The voltage profiles of the relithiation reaction on the EOL Li_xCoO_2 suspension (WE) and the oxygen evolution reaction on the Pt (CE) electrode at 0.12 mA/cm^2 . The RE is an Ag/AgCl gel-type reference electrode.

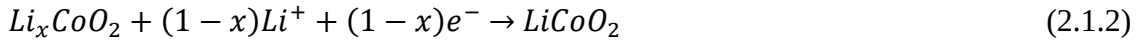
The redox reactions and the voltage profiles of the WE and CE for the relithiation of EOL Li_xCoO_2 powder are shown in Figure 2.1.2(b). In this experiment, the WE current collector was a stainless-steel rod attached to the small chamber which was filled with a suspension composed of 50 vol% EOL Li_xCoO_2 powder in 1.5 M Li_2SO_4 + 0.5 M LiOH aqueous solution. A Pt mesh CE and an Ag/AgCl RE were immersed in the left chamber filled with the same aqueous solution. A constant cathodic current (0.12 mA/cm^2) was applied to the WE until the cut-off voltage of -0.8 V vs. Ag/AgCl (this is around 2.5 V vs. Li^+/Li in organic electrolytes) was reached when Li_xCoO_2 is assumed to be fully converted to $LiCoO_2$.

As shown in Figure 2.1.2(b), the potential of the Pt CE quickly rises from 0 to 1 V vs. Ag/AgCl in the first two hours of reaction, before reaching a gradually increasing potential

plateau for the rest of the experiment. The high voltage polarization (> 1 V) on the CE is due to the slow kinetics of the oxygen evolution reaction (OER) (Equation 2.1.1). Small bubbles were observed on the surface of the CE which indicated the generation of oxygen gas.



On the other hand, the WE potential gradually drops for 13 hours to the cut-off potential at -0.8 V, corresponding to the relithiation of the EOL Li_xCoO_2 powder (Equation 2.1.2). The relatively steep voltage drop indicates high reaction impedance due to poor electrical contacts for the suspension-type electrode. The relithiated $LiCoO_2$ suspension was washed with deionized water and dried to obtain the relithiated $LiCoO_2$ powder.



2.1.2 Relithiation of Li_xCoO_2 electrode sheet

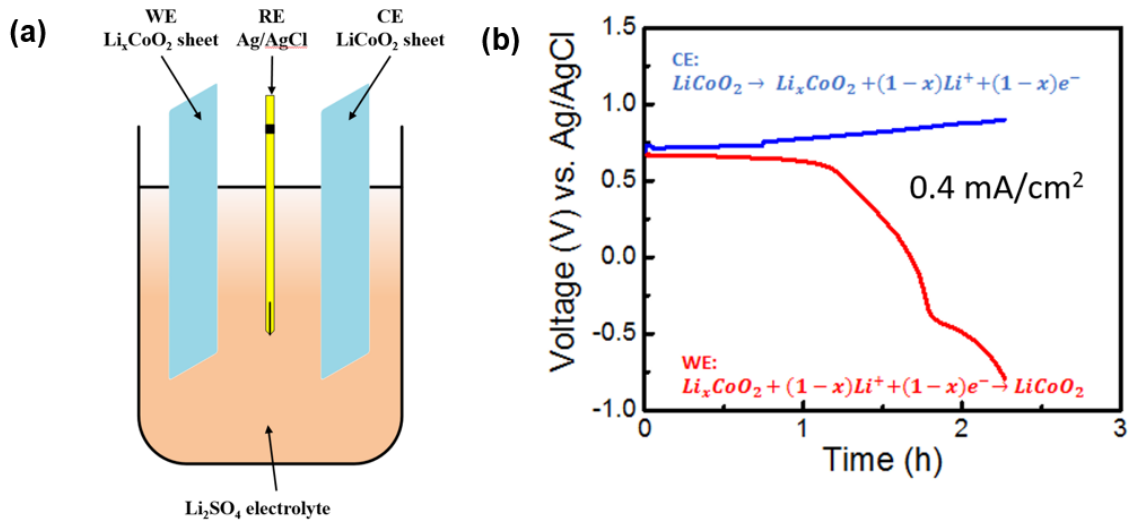


Figure 2.1. 3 (a) The schematic drawing for relithiation of the EOL Li_xCoO_2 electrode sheet. (b) The voltage profiles of the relithiation reaction on the EOL

Li_xCoO_2 electrode (WE) and a new LiCoO_2 electrode (CE) at a higher current density (0.4 mA/cm^{-2}). The RE is an Ag/AgCl gel-type reference electrode.

The second electrode combination employs the EOL Li_xCoO_2 cathode sheet as the WE (Figure 2.1.3). The Pt CE is replaced by a pristine LiCoO_2 cathode sheet to explore the possibility of reducing the energy consumption during relithiation. All three electrodes are immersed in a $1.5 \text{ M Li}_2\text{SO}_4$ aqueous solution. This cell resembles a $\text{LiCoO}_2/\text{LiCoO}_2$ symmetric cell, but the lithium content in the WE is undetermined. For the EOL Li_xCoO_2 cathode sheet, most of the lithium deficient Li_xCoO_2 are still electrically connected and attached to the Al current collector. The reaction on the WE is the same as shown in Equation 2.1.2. And the reaction on the CE is the reversed form of Equation 2.1.2.

Figure 2.1.3(b) shows the voltage profiles for the EOL Li_xCoO_2 cathode sheet (WE) and the pristine LiCoO_2 CE. While the voltage of WE decreased to cutoff voltage (-0.8 V vs. Ag/AgCl), the voltage of CE increased gradually from 0.7 V to 0.9 V vs. Ag/AgCl (around 3.9 V to 4.1 V vs Li/Li^+ in organic electrolytes). No bubbles were observed in this symmetric relithiation process, indicating the process did not consume the OH^- or H^+ in the solution. The Li_2SO_4 electrolyte remained neutral throughout the whole electrochemical process and no Al corrosion on the WE was observed. This is important to reduce the content of Al impurity in the relithiated LiCoO_2 . Since the electrode powder is still attached to the aluminum current collector with conductive carbon, this approach was found to improve the charge transfer and enable the use of a higher current density (i.e., 0.4 mA/cm^2) for relithiating the Li_xCoO_2 (Figure 2.1.3). This relithiation strategy not only shortens the time to fully restore the lithium stoichiometry but also significantly reduces the polarization

at the WE. In addition, the pristine LiCoO_2 cathode sheet used as the CE in this case further reduces the voltage hysteresis.

Notice that the LiCoO_2 electrode sheet used here just serves as a lithium reservoir to demonstrate the concept for relithiating the lithium-deficient materials Li_xCoO_2 . Cheaper lithium sources like lithium-ion salt solution (e.g., Li_2SO_4 , LiNO_3) can be used to scale up the relithiation process by electrolyzing the lithium-ion-containing solution at the CE side and driving the lithium-ion intercalation reaction at the WE side with Li_xCoO_2 electrode sheet.

After the electrochemical relithiation process as shown in Figure 2.1.3, the relithiated LiCoO_2 cathode sheet was immersed in NMP and sonicated for 10 min at room temperature. The powder was effectively separated from the Al foil after sonication and suspended in NMP. The remaining suspension was centrifuged at 1600 rpm for 20 min. The top dilute liquid layer was decanted afterward. The centrifuge washing process was repeated twice to remove the majority of the PVDF binder. After decanting the top dilute layer of NMP for the second time, the centrifuge tube with the remaining suspension was dried at 100°C for 8 hrs. The relithiated LiCoO_2 powder was then collected and ground.

2.1.3 Characterization and electrochemical test for the recovered LiCoO₂

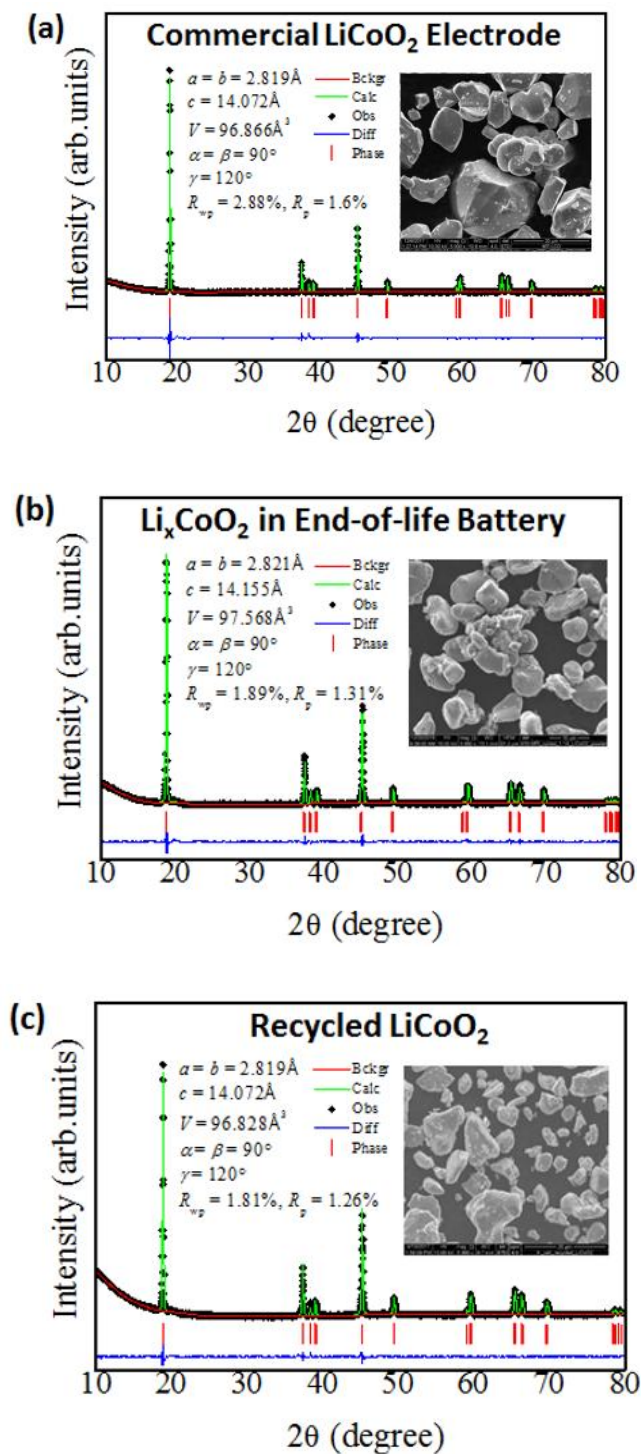


Figure 2.1. 4 The comparison of XRD patterns and SEM morphologies for (a)commercial LiCoO_2 , (b) Li_xCoO_2 in EOL lithium-ion batteries, and (c)recycled LiCoO_2 .

Recovered LiCoO_2 powder from both experiments (Figure 2.1.2 and 2.1.3) was collected separately and was further pressed into pellets by a hydraulic press. The pellets were then sintered at 700 °C in the air for 6 hrs to burn off the residual binder and carbon. The sintering process was done in a KSL-1100X-S-UL-LD muffle furnace (MTI). The sintering step completes the recycling process. Both electrochemical set-ups (Figure 2.1.2 and 2.1.3) yield recycled LiCoO_2 powder with no observable difference in microstructure and X-ray diffraction patterns. The x-ray diffraction (XRD) pattern was recorded using a Panalytical X'pert Pro PW 3040 diffractometer with $\text{Cu } \alpha$ radiation. The morphology of the samples was examined by a Scanning Electron Microscopy (FEI Quanta 600 FEG). Raman spectra were recorded using a confocal Raman microscope (WITec alpha 500R) equipped with a 100 x Olympus objective lens. Laser excitation (~ 1 mW at the sample) was provided by a 633 nm He-Ne laser. Each spectrum was obtained as an average of 3 accumulations of 60 s each.

Figure 2.1.4 shows the comparison of XRD patterns and SEM morphologies for the commercial LiCoO_2 , EOL Li_xCoO_2 , and recycled LiCoO_2 . All diffraction patterns show a single-phase layered rock-salt structure. Compared with the XRD pattern of recycled materials, the 006 diffraction peak (around 38.5 deg) shifts to the left and the intensity of the peak decreases in EOL Li_xCoO_2 , indicating the degradation of a layered structure in Li_xCoO_2 . After going through the relithiation and sintering process, the 006 diffraction

peak shifts back to the right, and the intensity increases in recycled LiCoO_2 . The Rietveld refinement results show that both the a and c lattice parameters in the recycled LiCoO_2 closely match with those of commercial LiCoO_2 , indicating full restoration of the crystal structure. The lattice parameter and unit cell volume are also consistent with those reported. [74] SEM images in the corresponding inset figures show that the morphology and the particle size distribution of the recycled LiCoO_2 are very similar to those of the virgin cathode materials and are retained throughout the physical separation and chemical relithiation processes. It should be noted that micro-cracks were not observed in the EOL materials in this study.

Comparing with the commercial and recycled LiCoO_2 , the EOL Li_xCoO_2 shows a slightly larger a and a much larger c lattice parameter. The evolution of the lattice parameters and unit cell volume of LiCoO_2 has been well documented. The refinement results are therefore compared with those reported, which suggests an x value in the EOL Li_xCoO_2 to be between 0.85 to 0.95.[74] The loss of lithium on the cathode side is mostly consumed on the anode graphite surface during battery cycling to form the solid electrolyte interface (SEI), or plated as metallic lithium.[27] However, as shown in Figure 2.1.3, an accurate determination of the lithium deficiency is not necessary as the extent of the reaction is controlled by the cut-off potential.

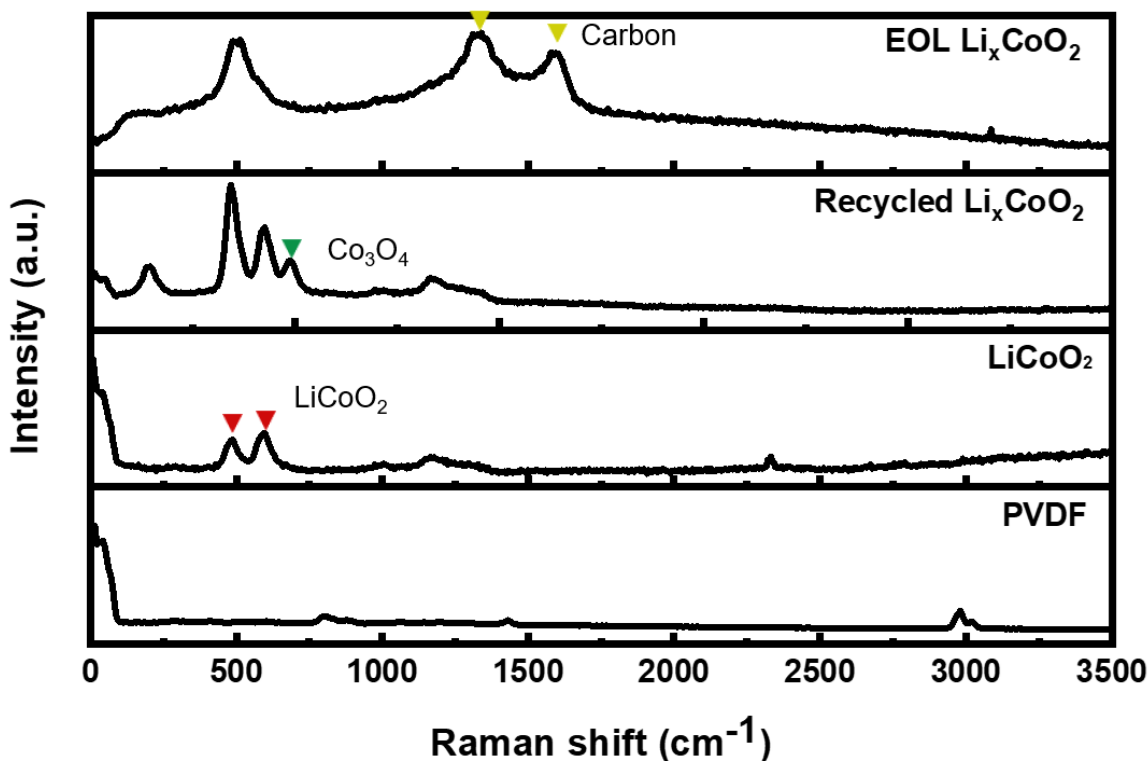


Figure 2.1. 5 Raman spectra for the EOL Li_xCoO_2 , recycled LiCoO_2 , and commercial LiCoO_2 and PVDF powder.

The Raman spectra for the EOL Li_xCoO_2 , recycled LiCoO_2 , commercial LiCoO_2 , and PVDF are shown in Figure 2.1.5. Spectroscopically identified compounds and Raman band assignments are listed in Table 2.1.1. Two carbon bands at 1328 and 1593 cm^{-1} are observed in the EOL powder, which disappears in the recycled powder, indicating that carbon was effectively burned off during sintering. Raman bands of the PVDF binder are not observed for the EOL Li_xCoO_2 sample, possibly because of its low abundance. The two Raman bands at 487 and 596 cm^{-1} are the main fingerprints of the layered rock-salt crystalline structure of LiCoO_2 , corresponding to the Co-O stretching (A_{1g}) and O-Co-O bending (E_g) mode, respectively.[75] The recycled and commercial LiCoO_2 both show

these two peaks. The recycled LiCoO_2 shows two additional peaks at around 205 and 685 cm^{-1} , which are assigned to the F_{2g} and A_{1g} mode of Co_3O_4 , respectively. The E_g peak at 481 cm^{-1} for Co_3O_4 partly overlaps with the A_{1g} peak of LiCoO_2 , probably adding to the peak intensity of the A_{1g} peak for the recycled LiCoO_2 . It should be noted that Co_3O_4 is not detected in the XRD analysis for the recycled LiCoO_2 (Figure 2.1.4), probably because of its very low phase abundance. These results suggest that electrochemical relithiation and post sintering process restore the majority of Li_xCoO_2 to the LiCoO_2 phase, with a trace amount of Co_3O_4 impurity, which is likely formed on the particle surface during the recycling process.

Table 2.1. 1 Raman band assignments

Reference [cm^{-1}]				Raman band assignments
LiCoO_2	Co_3O_4	PVDF Binder	Carbon	
		3020 2980		CH stretching
			2655 1593	2D G mode
		1431	1328	D mode
1159 993		878 804		
	685			A_{1g} O-Co-O bending (E_g)
596				Co-O stretching (A_{1g})
487				
	481			E_g
	205			F_{2g}

The electrochemical performance of the recycled LiCoO_2 (Figure 2.1.6 and Figure 2.1.7) was tested and compared with commercial LiCoO_2 . All samples were tested in CR2032-type coin cells using an MTI 8-Channel Battery Analyzer (0.02 -10 mA, 5V). The cathode slurry was prepared by mixing 80 wt % of active material, 10 wt % of conductive carbon black, and 10 wt % of PVDF binder in NMP homogeneously. The slurry was cast onto an Al foil with a doctor blade and dried at 100°C for 4 hrs. The cathode sheet was then cut into discs (12.7 mm diameter) and further dried in a vacuum oven at 90°C overnight before coin cell assembly. The loading of the active material was around 4.0 - 5.3 mg cm^{-2} . The electrolyte was 1M LiPF_6 (lithium hexafluorophosphate) in a mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) with a 3:7 volume ratio (MTI Corporation, USA). Coin cells were assembled in an argon-filled glovebox with oxygen and moisture content below 1 ppm.

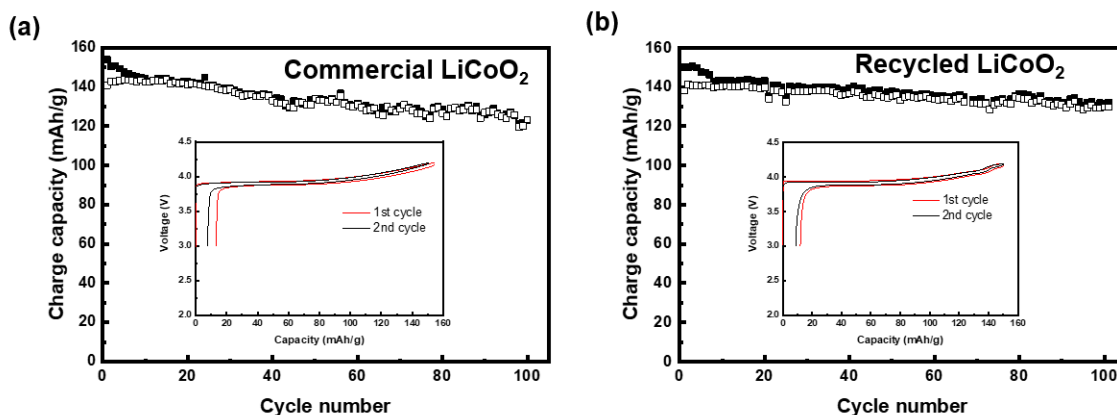


Figure 2.1. 6 The cycling performance of (a)Li/commercial LiCoO_2 coin cell and (b)Li/recycled LiCoO_2 coin cell at C/10 current rate. The inset figure shows the voltage profiles of the first two cycles.

Figure 2.1.6 shows the cycle stability curve over 100 cycles, with the voltage profiles for the first two cycles shown as the inset figures. The experiments were conducted at a C/10

rate. Both recycled and commercial LiCoO_2 show very similar voltage profiles during charge and discharge. The first cycle charge and discharge capacities for both materials are around 150 and 140 mAh/g, respectively, indicating a successful relithiation of the recycled material. After 100 cycles, the recycled LiCoO_2 shows slightly better capacity retention (93%) than that of the commercial LiCoO_2 (87%).

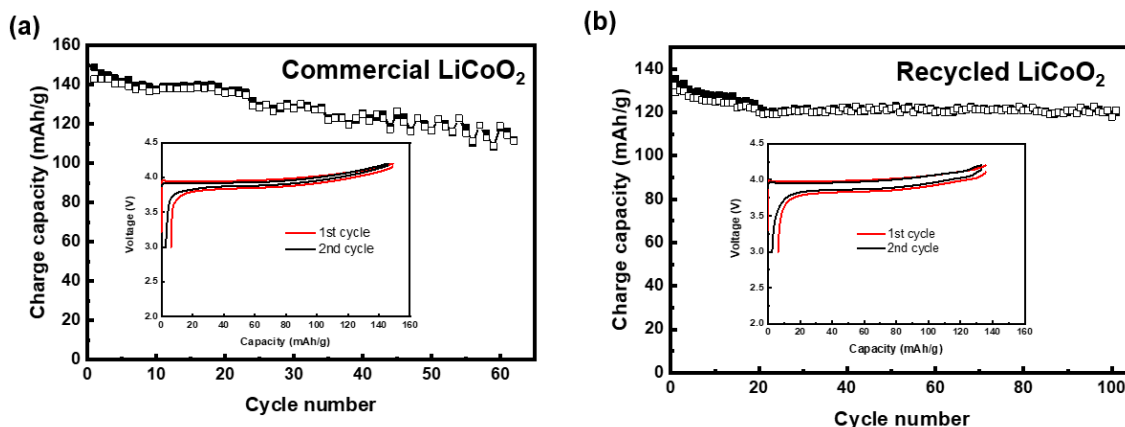


Figure 2.1. 7 The cycling performance of (a) Li/commercial LiCoO_2 coin cell and (b) Li/recycled LiCoO_2 coin cell at C/5 current rate. The inset figure shows the voltage profiles of the first two cycles.

When cycled at a higher rate (C/5, Figure 2.1.7), the recycled LiCoO_2 shows a first cycle discharge capacity of around 130 mAh/g, slightly lower than commercial LiCoO_2 (142 mAh/g). We suspect the formation of surface Co_3O_4 mildly affects the rate of performance. The mechanism of Co_3O_4 formation and its impact on electrochemical performance require further investigation.

2.2 Energy cost benefit of the direct recycling process for LiCoO_2 case

The execution of LIB recycling must take the economic, environmental, and technological factors during the entire recycling process into consideration. Here in this section, the energy cost of the three common recycling methods, pyrometallurgical, hydrometallurgical, and direct recycling, respectively are calculated assuming the cathode active material is LCO.

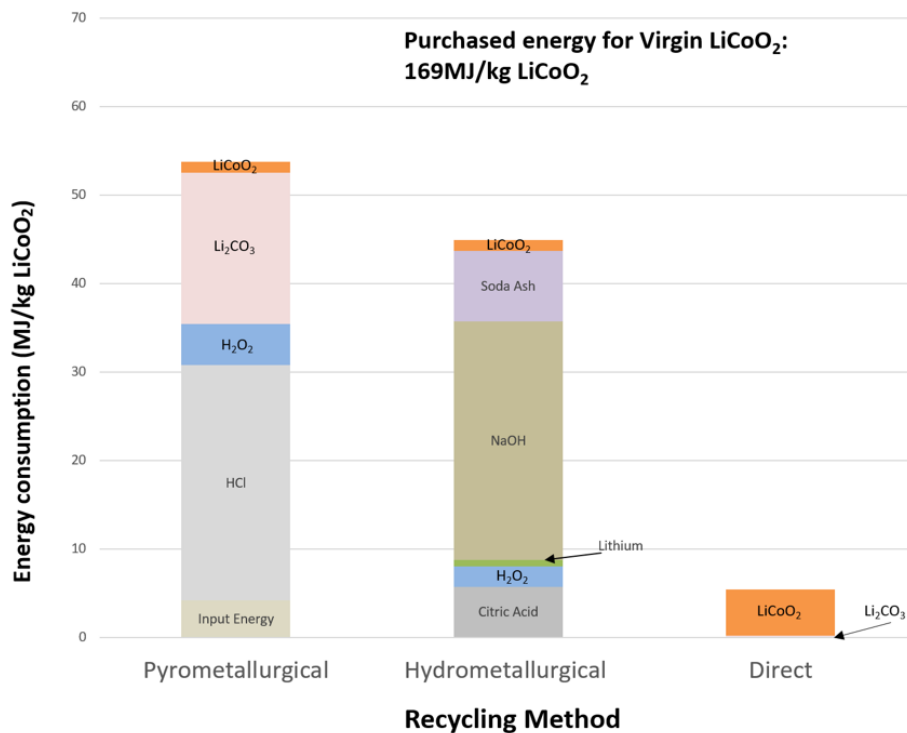


Figure 2.2. 1 Comparison of energy consumption for the pyrometallurgical, hydrometallurgical, and direct recycling methods for the LiCoO_2 material.

Life-cycle analysis is performed on the three recycling methods using Argonne National Laboratory's Greenhouse gases, Regulated Emissions, and Energy use in Transportation

(GREET) model[76] and BatPaC model[11]. The energy consumptions analysis of LiCoO_2 in three recycling methods was conducted using the same methodology as described in previous work.[25] Typical pyrometallurgical, hydrometallurgical, and direct recycling processes were also summarized previously.[77] All the energy consumptions calculation for LiCoO_2 recycling in this work were based on these recycling processes. Such process-level calculation of energy flows used purchased energy data from the GREET model.[76] Figure 2.2.1 compares the energy consumption per kilogram of LiCoO_2 produced by the three recycling approaches. Recycling LiCoO_2 by any of these three methods saves a significant amount of energy compared to producing virgin LiCoO_2 . Among the three recycling approaches, direct recycling demands the lowest energy consumption, thus more profitable than the other two recycling methods. The cost benefit for direct recycling is even larger when manufacturers shift away from expensive cobalt. In addition, the direct recycling method produces battery-grade materials as the end product and generates fewer emissions and waste.[13] It is therefore obvious that direct recycling is the optimum route for sustainable use of the cathode materials if a cost-effective strategy can be implemented for scale-up production. Detailed energy consumptions are listed in Table 2.2.1.

Table 2.2. 1 Energy consumptions for virgin LCO and recycled LCO

	Virgin	Recycled LCO		
	LCO	Pyrometallurgical	Hydrometallurgical	Direct
Energy Consumption				
[MJ Kg ⁻¹ LCO]	169	53.8	41.6	6

2.3 Design of a scalable electrochemical flow system for cathode recycling

Herein we propose a novel relithiation approach for direct recycling based on the preliminary results presented in this work and knowledge that semi-solid flow batteries have been well developed. This approach aims at continuously producing a large quantity of recycled cathode powder with minimum energy cost. The idea is summarized in a schematic shown in Figure 2.3.1.

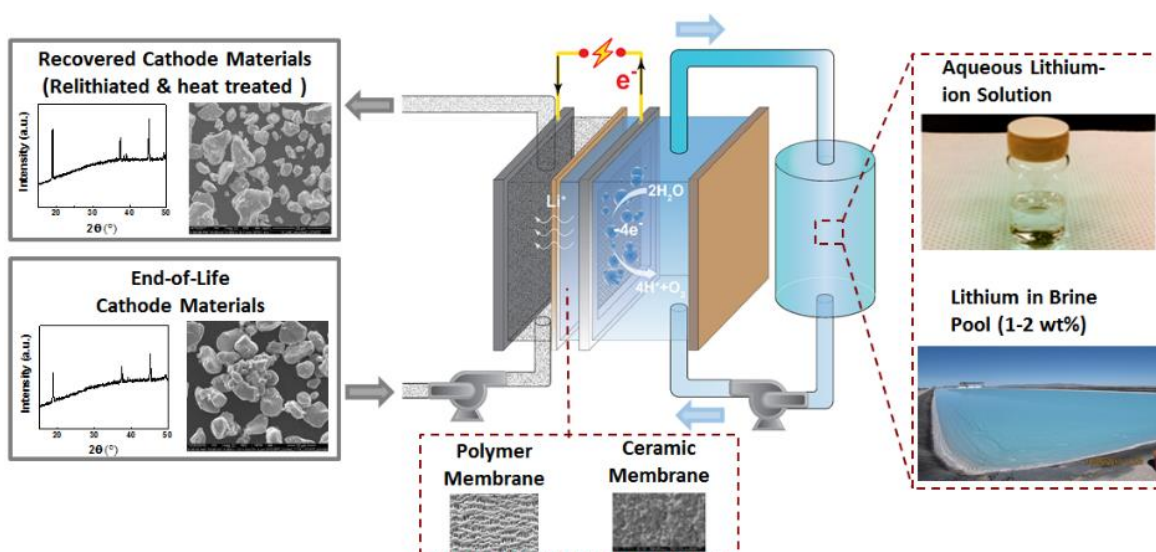


Figure 2.3. 1 A scalable electrochemical flow system that restores lithium stoichiometry of the used lithium deficient cathode and yields battery-grade cathode materials with post heat treatment. Two chambers are either separated by a porous polymer membrane or a lithium-ion conducting ceramic membrane. Using lithium-ion conducting ceramic separator with ion-selectivity enables lithium-containing brine or even seawater-derived solutions as the lithium-ion source in the right chamber.

The isolated cathode powder with a certain amount of residual carbon additive is homogeneously suspended in a lithium-ion-containing aqueous electrolyte, forming a flowable and electrochemically active semi-solid suspension. Similar electrochemically active aqueous and non-aqueous suspensions are widely used in high energy density semi-solid flow batteries and lithium-ion battery manufacturing. The suspension containing the cathode material then flows through the left chamber of the electrochemical flow device (Figure 2.3.1). Meanwhile, a lithium-ion-containing aqueous solution flows through the right chamber. When these two chambers are separated by a simple porous polymer membrane, the same lithium-ion solution must be used in both chambers to avoid cross-contamination. On the other hand, if a selective lithium-ion conducting ceramic membrane is used as the separator, lithium-containing brine or even seawater-derived solutions can serve as the lithium-ion source and flow through the right chamber. Lithium-ion conducting ceramic membranes with the capability of ion-selectivity have been demonstrated in seawater batteries and lithium extraction.^[36] As the cathode material suspension flows through the electrochemical system, a cathodic current is applied to the current collector of the left chamber. While the aqueous solution in the right chamber flows simultaneously and undergoes an OER reaction. During this process, the lithium deficient cathode in the left chamber is lithiated and the amount of lithium-ion intercalation can be precisely controlled by the cut-off potential. In practical operation, the cathode suspension flows intermittently where one batch of suspension enters the left chamber and the lithium deficient cathode materials in the suspension are fully restored to the stoichiometry of the pristine cathode materials before flowing out. In the right chamber, the lithium-ion-containing solution flows continuously to maintain a stable lithium-ion concentration

during operation. The relithiated cathode materials can then be annealed to burn off residue binder and carbon and to heal micro-cracking, after which the material is expected to exhibit physical properties and electrochemical performance similar to virgin commercial material. The proposed direct recycling approach is applicable to recycle most commercial cathode materials (i.e., LiCoO_2 , $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ($x+y+z=1$), LiMn_2O_4 , LiFePO_4). The energy efficiency of such a strategy may be further improved by relithiating EOL cathode sheets and extracting the cathode materials afterward, as demonstrated in Figure 2.1.3. The voltage hysteresis may be further reduced by replacing the OER reaction in the right chamber with a de-intercalation reaction of a less valuable cathode material, LiFePO_4 , for instance. Solid electrode sheets may be delivered into each chamber in a manner similar to a tape recorder. Obviously, there are more engineering challenges if electrode sheets are used, given that semi-solid electrochemical flow systems have already been well understood and developed.

Chapter 3 - Aqueous sulfur flow battery system

3.1 Characterization of aqueous sulfur alkaline solutions

Aqueous sulfur (AqS) solutions have complex equilibrium between different polysulfide species. [78-86] Polysulfide solubility and stability are strongly dependent on pH,[87-90] alkali-metal cations, [82] oxygen concentration,[91] nominal polysulfide speciation and concentration[92, 93] as well as temperature.[93-96] In this section, aqueous sulfur solutions with different nominal compositions, concentrations, and pH are investigated using Raman spectroscopy. The effect of temperature and the stability of the AqS solutions are also studied.

3.1.1 Preparation and characterization

To prepare the alkaline AqS solutions, NaOH stock solutions with different concentrations are prepared first. In this section, concentrations of the AqS solutions are expressed in molality (m , the number of moles of a solute per kilogram of solvent). Table 3.1.1 shows the conversion between molality and molarity of the AqS solutions. Then, sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and sulfur with particular molar ratios are added to the NaOH solution to prepare AqS solution with particular nominal composition. For example, to produce a 0.5m Na_2S_2 + 10 m NaOH solution requires the addition of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and S with a molar ratio of 1:1 to be added to the 10 m NaOH. The solutions are thoroughly mixed to make sure the solids are fully dissolved, except for concentrations that are beyond solubility limits, in which precipitation is expected. Raman spectra were recorded using a

confocal Raman microscope (WITec alpha 500R) equipped with a 100x Olympus objective lens. Laser excitation (~ 1 mW at the sample) was provided by a 633 nm He-Ne laser. Samples were tested in a small semi-transparent plastic container with the lid open. Each spectrum was obtained as an average of 6 accumulations of 30 s each.

Table 3.1. 1 Conversion between molality unit and molarity unit for different sodium polysulfide aqueous solutions.

Molality (m, mol/kg H₂O)	Density (g/cc)	Molarity (M, mol/L solution)
0.5m Na ₂ S + 0m NaOH	1.010	0.4862M Na ₂ S + 0M NaOH
0.5m Na ₂ S + 1m NaOH	1.166	0.5404M Na ₂ S + 1.0808M NaOH
0.5m Na ₂ S + 3m NaOH	1.126	0.4857M Na ₂ S + 2.9141M NaOH
0.5m Na ₂ S + 10m NaOH	1.317	0.4577M Na ₂ S + 9.1550M NaOH
0.5m Na ₂ S ₂ + 0m NaOH	1.033	0.4898M Na ₂ S ₂ + 0M NaOH
0.5m Na ₂ S ₂ + 1m NaOH	1.073	0.4898M Na ₂ S ₂ + 0.9795M NaOH
0.5m Na ₂ S ₂ + 3m NaOH	1.125	0.4788M Na ₂ S ₂ + 2.8729M NaOH
0.5m Na ₂ S ₂ + 10m NaOH	1.298	0.4462M Na ₂ S ₂ + 8.9237M NaOH
0.5m Na ₂ S ₂ + 20m NaOH	1.433	0.3861M Na ₂ S ₂ + 15.4458M NaOH
0.5m Na ₂ S ₃ + 0m NaOH	1.044	0.4876M Na ₂ S ₃ + 0M NaOH
0.5m Na ₂ S ₃ + 1m NaOH	1.082	0.4868M Na ₂ S ₃ + 0.9735M NaOH
0.5m Na ₂ S ₃ + 3m NaOH	1.148	0.4819M Na ₂ S ₃ + 2.8917M NaOH
0.5m Na ₂ S ₃ + 10m NaOH	1.224	0.4159M Na ₂ S ₃ + 8.3182M NaOH
0.5m Na ₂ S ₃ + 20m NaOH	1.464	0.3912M Na ₂ S ₃ + 15.6472M NaOH
0.5m Na ₂ S ₄ + 0m NaOH	1.053	0.4844M Na ₂ S ₄ + 0M NaOH
0.5m Na ₂ S ₄ + 1m NaOH	1.081	0.4796M Na ₂ S ₄ + 0.9592M NaOH
0.5m Na ₂ S ₄ + 3m NaOH	1.144	0.4739M Na ₂ S ₄ + 2.8434M NaOH
0.5m Na ₂ S ₄ + 10m NaOH	1.322	0.4447M Na ₂ S ₄ + 8.8931M NaOH
0.5m Na ₂ S ₄ + 20m NaOH	1.432	0.3795M Na ₂ S ₄ + 15.1818M NaOH
0.2m Na ₂ S ₄ + 0m NaOH	1.002	0.1937M Na ₂ S ₄ + 0M NaOH
0.5m Na ₂ S ₄ + 0m NaOH	1.043	0.4799M Na ₂ S ₄ + 0M NaOH
1.0m Na ₂ S ₄ + 0m NaOH	1.091	0.9296M Na ₂ S ₄ + 0M NaOH
1.5m Na ₂ S ₄ + 0m NaOH	1.143	1.3599M Na ₂ S ₄ + 0M NaOH
2.0m Na ₂ S ₄ + 0m NaOH	1.176	1.7451M Na ₂ S ₄ + 0M NaOH
0.1m Na ₂ S ₄ + 3m NaOH	1.108	0.0975M Na ₂ S ₄ + 2.9235M NaOH
0.2m Na ₂ S ₄ + 3m NaOH	1.112	0.1926M Na ₂ S ₄ + 2.8893M NaOH
0.5m Na ₂ S ₄ + 3m NaOH	1.115	0.4619M Na ₂ S ₄ + 2.7713M NaOH
1.0m Na ₂ S ₄ + 3m NaOH	1.2	0.9277M Na ₂ S ₄ + 2.7830M NaOH
1.5m Na ₂ S ₄ + 3m NaOH	1.222	1.3273M Na ₂ S ₄ + 2.6546 M NaOH
2.0m Na ₂ S ₄ + 3m NaOH	1.255	1.7104M Na ₂ S ₄ + 2.5655M NaOH

Table 3.1. 2 The calculated distribution of species in various concentrated aqueous potassium polysulfide solutions at 25°C. [92]

Nominal concentration (mol/kg H ₂ O)				
K ₂ S	8.8	4.4	2.2	8.5
S	0	4.4	6.6	25.5
Assumed activity coefficients				
<i>F</i>	35.0	4.6	1.5	31.0
<i>A_w</i>	0.14	0.53	0.79	0.16
Calculated concentration (mol/kg H ₂ O)				
H ₂ S	4.0×10^{-10}	1.2×10^{-8}	5.5×10^{-8}	5.4×10^{-10}
HS ⁻	6.3	2.4	0.032	0.0090
S ⁼	2.5	0.012	4.7×10^{-7}	3.8×10^{-6}
S ₂ ⁼	0	0.070	1.3×10^{-4}	8.6×10^{-4}
S ₃ ⁼	0	1.5	0.14	0.70
S ₄ ⁼	0	0.41	1.8	7.1
S ₅ ⁼	0	0.0012	0.24	0.73
S ₆ ⁼	0	2.6×10^{-5}	5.5×10^{-5}	1.1×10^{-4}
OH ⁻	6.3	2.3	0.032	0.0090
H ⁺	6.3×10^{-18}	5.1×10^{-16}	1.7×10^{-13}	6.0×10^{-15}
H ₂ O	7.7	29	44	8.9
K ⁺	17.6	8.8	4.4	17.

3.1.2 Effect of hydroxide concentration on AqS solutions

Nominal Na₂S, Na₂S₂, Na₂S₃, and Na₂S₄ solutions are prepared at hydroxide molalities of 0m, 1m, 3m, 10m, and 20m. The Raman spectra are shown in 2 regions, 200-1200 cm⁻¹ and 2400 - 2800 cm⁻¹ to track the changes of polysulfide species (S_x^{2-} , $1 \leq x \leq 4$).

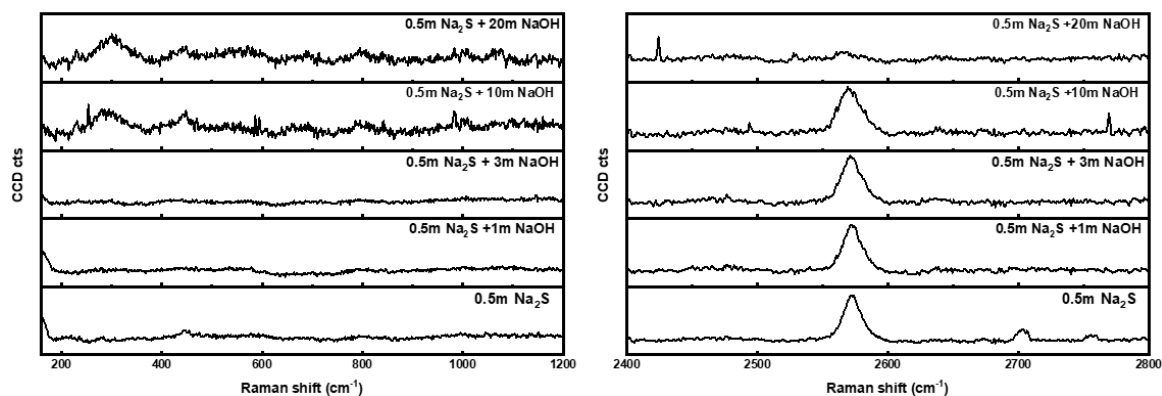


Figure 3.1. 1 Raman spectra of 0.5 m Na₂S solutions at different hydroxide concentrations.

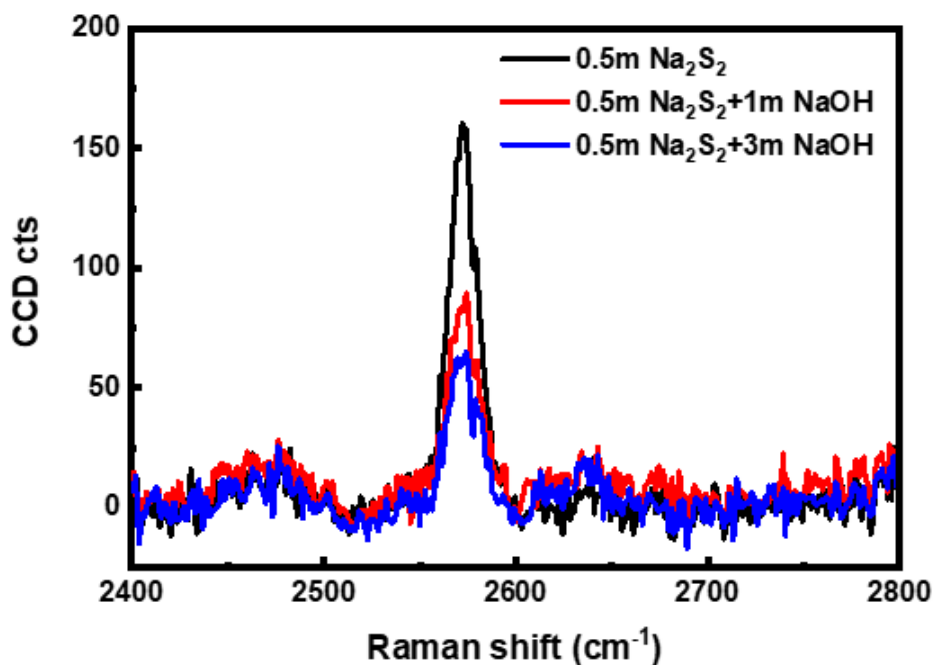


Figure 3.1. 2 Comparison of peak intensity at 2572 cm⁻¹ for Na₂S₂ aqueous solutions.

For Na₂S nominal solutions, since sulfur is at the lowest oxidation state, the disproportionation will not happen and the S²⁻ or HS⁻ will be the only speciation in solution. As shown in Figure 3.1.1, the Raman peak at around 2570 cm⁻¹ represents HS⁻. In an aqueous solution HS⁻ and S²⁻ have the following equilibrium:



When the hydroxide concentration increases from 0m to 3m, the intensity of the HS⁻ peak decreases (Figure 3.1.2). When the hydroxide concentration increased to 20m, the HS⁻ peak can no longer be detected by Raman spectroscopy.

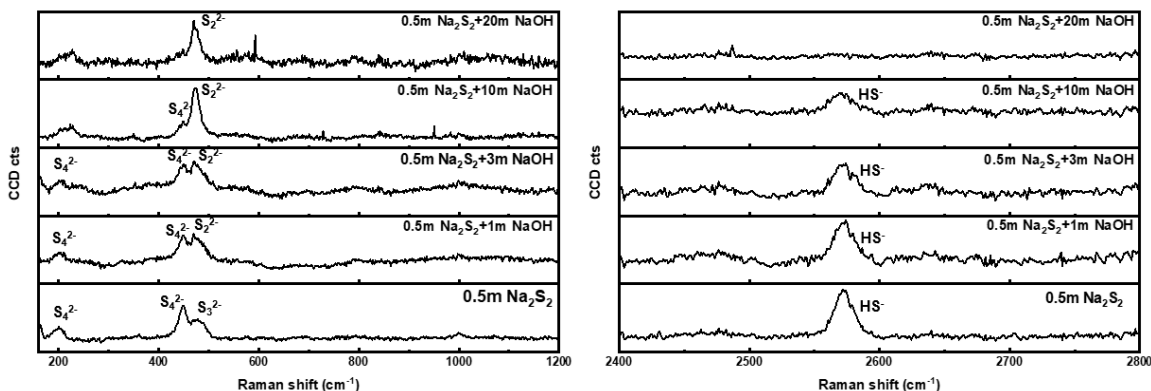


Figure 3.1. 3 Raman spectra of 0.5 m Na₂S₂ solutions at different hydroxide concentrations.

Figure 3.1.3 shows the Raman spectra for nominal Na₂S₂ solutions at different hydroxide concentrations. At low hydroxide concentrations, HS⁻, S₃²⁻ and S₄²⁻ are detected by Raman spectroscopy. This agrees with the calculated distribution of species for AqS solutions (Table 3.1.2). With the increase of hydroxide concentration, peaks of S₄²⁻ and S₃²⁻ gradually disappear and the peak for S₂²⁻ appears. Same as in Na₂S solutions, the intensity of the HS⁻ peak decreases when hydroxide concentration increases and can not be detected when the hydroxide concentration reaches 20m.

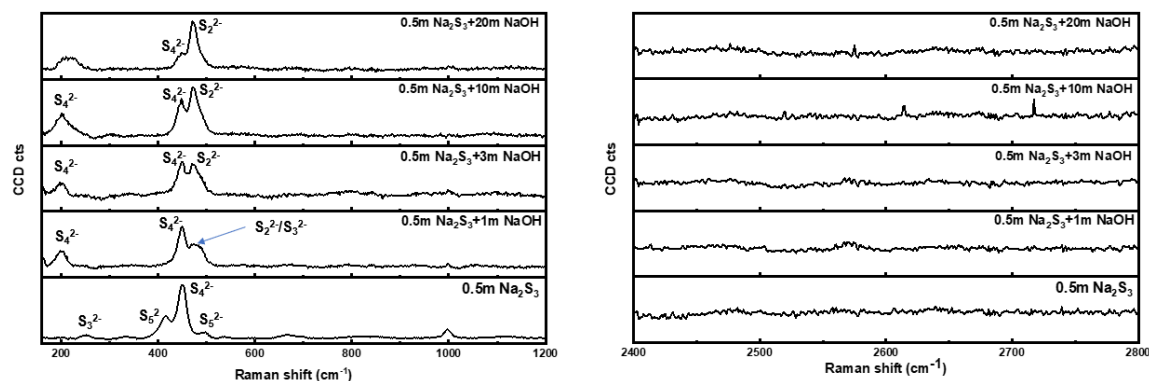


Figure 3.1. 4 Raman spectra of 0.5 m Na₂S₃ solutions at different hydroxide concentrations.

For nominal Na_2S_3 solutions, S_2^{2-} , S_3^{2-} , S_4^{2-} , and S_5^{2-} are the dominant sulfur species characterized by Raman (Figure 3.1.4). When the hydroxide concentration is 0 m, the peak of S_2^{2-} is not present in the Raman spectrum but only peaks of S_3^{2-} , S_4^{2-} , and S_5^{2-} . With the increase of hydroxide concentration, the two peaks of S_5^{2-} disappear. The S_4^{2-} peak at 414 cm^{-1} disappears and a new S_4^{2-} peak appears at 197 cm^{-1} . S_3^{2-} was also detected with increasing hydroxide concentration. At 20 m NaOH, the peak of S_2^{2-} becomes the strongest one. The peak of HS^- cannot be detected at all hydroxide concentrations.

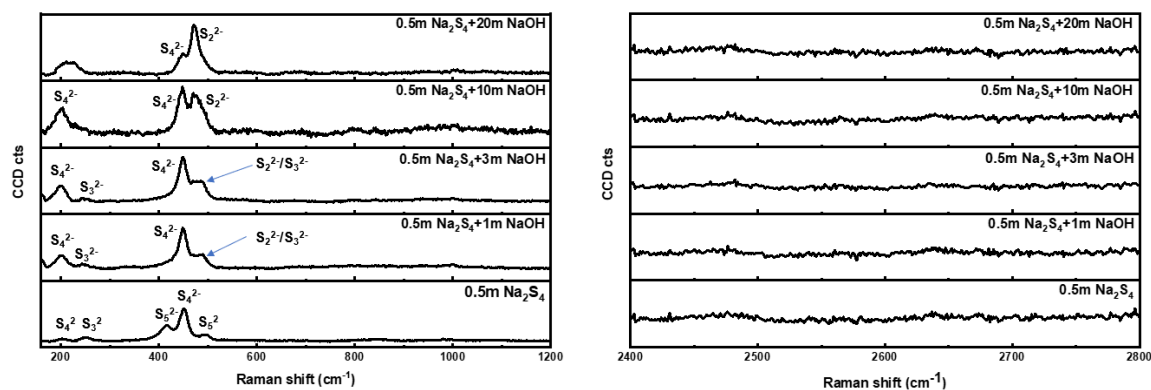


Figure 3.1. 5 Raman spectra of 0.5 m Na_2S_4 solutions at different hydroxide concentrations.

For nominal Na_2S_4 solutions, S_2^{2-} , S_3^{2-} , S_4^{2-} , and S_5^{2-} are the dominant sulfur species characterized by Raman (Figure 3.1.5). The distribution of sulfur species over different hydroxide concentrations is similar to that of nominal Na_2S_3 solutions. At 0 m NaOH, only peaks of S_3^{2-} , S_4^{2-} , and S_5^{2-} appear in the Raman spectrum. When the hydroxide concentration increases to 1m, the S_5^{2-} peak disappears and the peak for S_3^{2-} appears. With the further increase in the hydroxide concentration, the peak intensity of S_3^{2-} decreases, and

the intensity of S_2^{2-} increases. At 20m NaOH, the peak of S_2^{2-} becomes the strongest one. The peak of HS^- cannot be detected at all hydroxide concentrations.

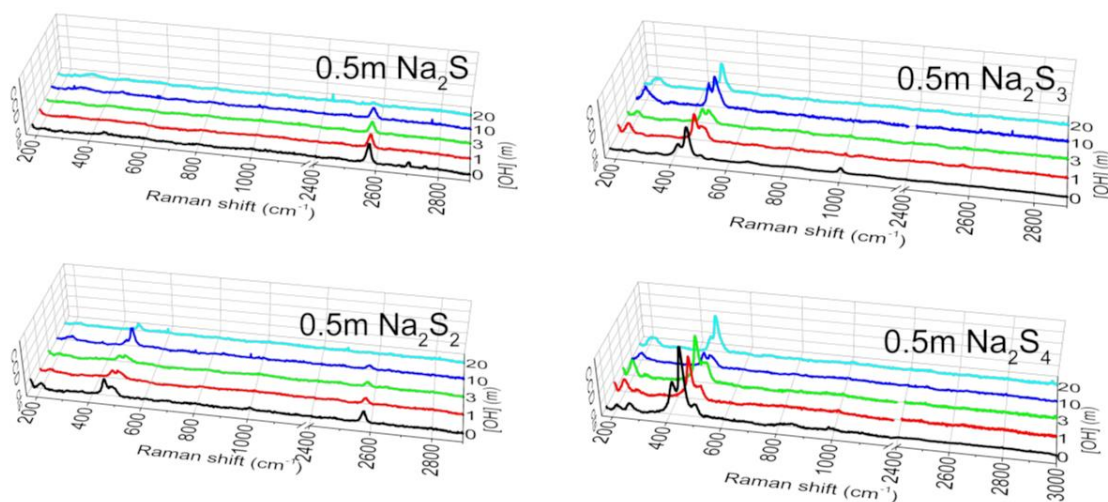


Figure 3.1. 6 3-D plot of Raman spectra for 0.5 m sodium polysulfide solutions at different hydroxide concentrations.

3.1.3 Effect of polysulfide concentrations

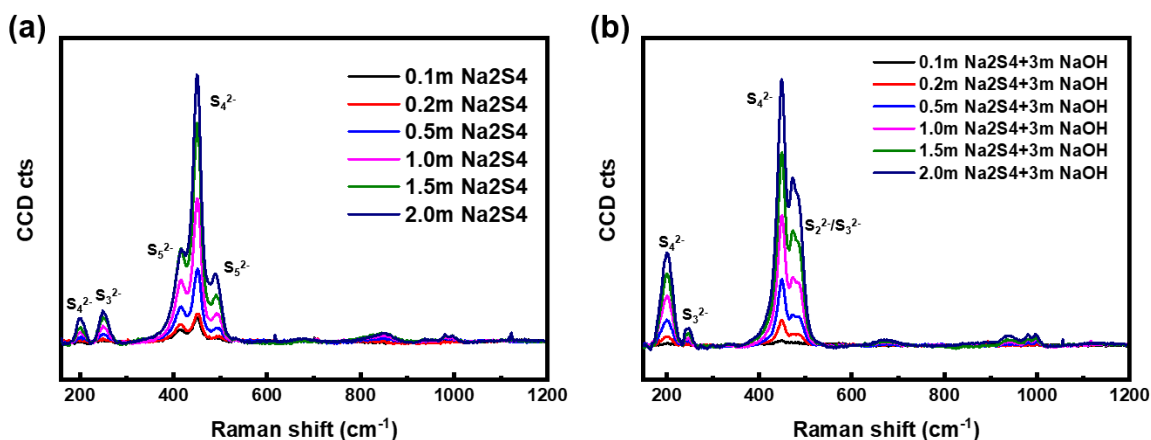


Figure 3.1. 7 Raman spectra of nominal Na_2S_4 solutions at different sulfur concentrations.

In Figure 3.1.7, Na_2S_4 nominal solutions with different sulfur concentrations are studied. In figure 3.1.7a, three polysulfide peaks, corresponding to S_3^{2-} , S_4^{2-} and S_5^{2-} , are detected. With changes in sulfur concentration, peaks do not shift but the intensity of these peaks increases as the concentration increases. When the Na_2S_4 solutions are prepared in 3M NaOH (Figure 3.1.7b), peaks of S_2^{2-} , S_3^{2-} and S_4^{2-} are detected. A combined peak of S_2^{2-} and S_3^{2-} is identified at around 470 cm^{-1} . As the concentration of sulfur increases, the peak intensity ratio of $\text{S}_2^{2-}/\text{S}_3^{2-}$ also increases. For other single peaks at around 200 cm^{-1} , 245 cm^{-1} , and 425 cm^{-1} , the peak intensity simply increases with the increase of sulfur concentration.

3.1.4 Saturated solutions: Nominal Na_2S_5 solution

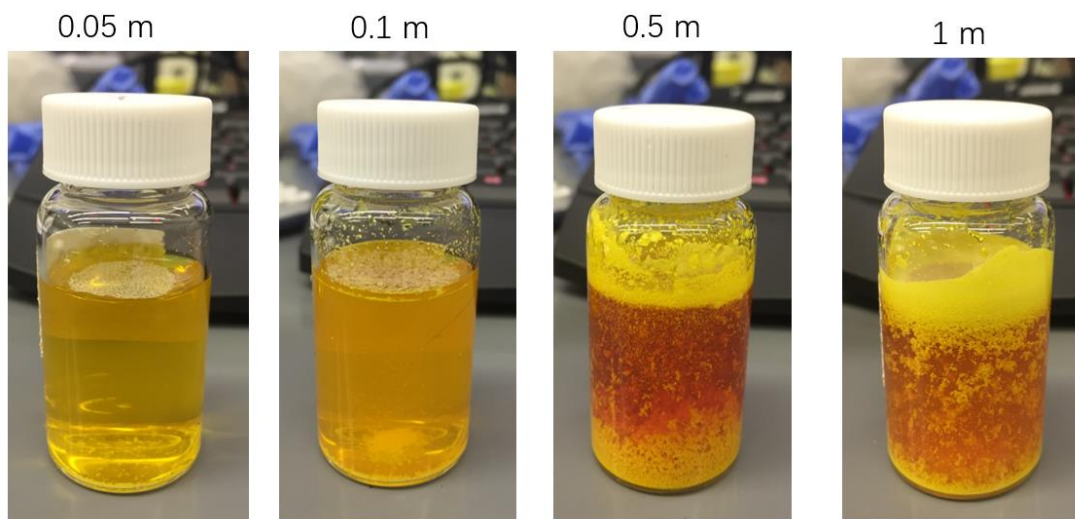


Figure 3.1. 8 Pictures of nominal Na_2S_5 solutions at 0.05 m, 0.1 m, 0.5 m, and 1 m concentrations.

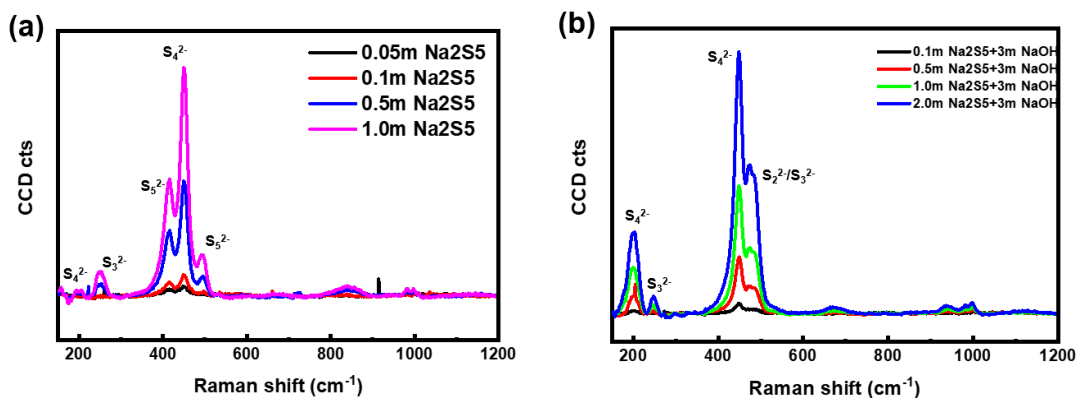
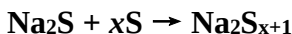


Figure 3.1. 9 Raman spectra of nominal Na₂S₅ solutions at 0.05 m, 0.1 m, 0.5 m, and 1 m concentrations.

The Na₂S_x aqueous solutions are prepared by mixing solid state Na₂S and elemental sulfur powder to NaOH solution. The following reaction happens during the mixing process:



The reaction completes after thorough stirring, and all the solids dissolves in the NaOH solution. For example, to prepare nominal Na₂S₄ solutions, Na₂S and S with nominal ratio of 1:3 are added to NaOH solution and stirred until dissolve.

For the above reaction, the amount of sulfur that can react with Na₂S has a limitation. The limit for x in the above reaction is around 3.8, which translates to a nominal Na₂S_{4.8} solution. In this section, the “solubility limit” is actually not referring to how much solid can be dissolved in NaOH solution, but referring to maximum molar ratio of S that can react with Na₂S. For Na₂S₅ solutions with different concentrations, they are “saturated” because the dissolved S and Na₂S have the same molar ratio (3.8:1) but the absolute concentration of sulfur is different.

It is clear that the nominal Na_2S_5 solutions contain undissolved sulfur solid as shown in Figure 3.1.8. For 0.05m Na_2S_5 solution, the color is light yellow. As the concentration increases to 0.1m, 0.5m, and 1m, the color of the solution turns yellow, orange, and dark orange.

The nominal Na_2S_5 solutions were transferred to a plastic vial and centrifuged at 2000 rpm for 5 min. The clear solution from the top layer was used for Raman spectroscopy. In Figure 3.1.9a, the 2 peaks at 200 cm^{-1} and 248 cm^{-1} are assigned to S_4^{2-} and S_3^{2-} . Another 3 peaks from $400\text{--}500\text{ cm}^{-1}$ are assigned to S_5^{2-} , S_4^{2-} and S_5^{2-} respectively. In general, the peak distribution for nominal Na_2S_5 solutions is similar to Na_2S_4 solutions (Figure 3.1.5).

3.1.5 Stability of polysulfide solutions in room temperature

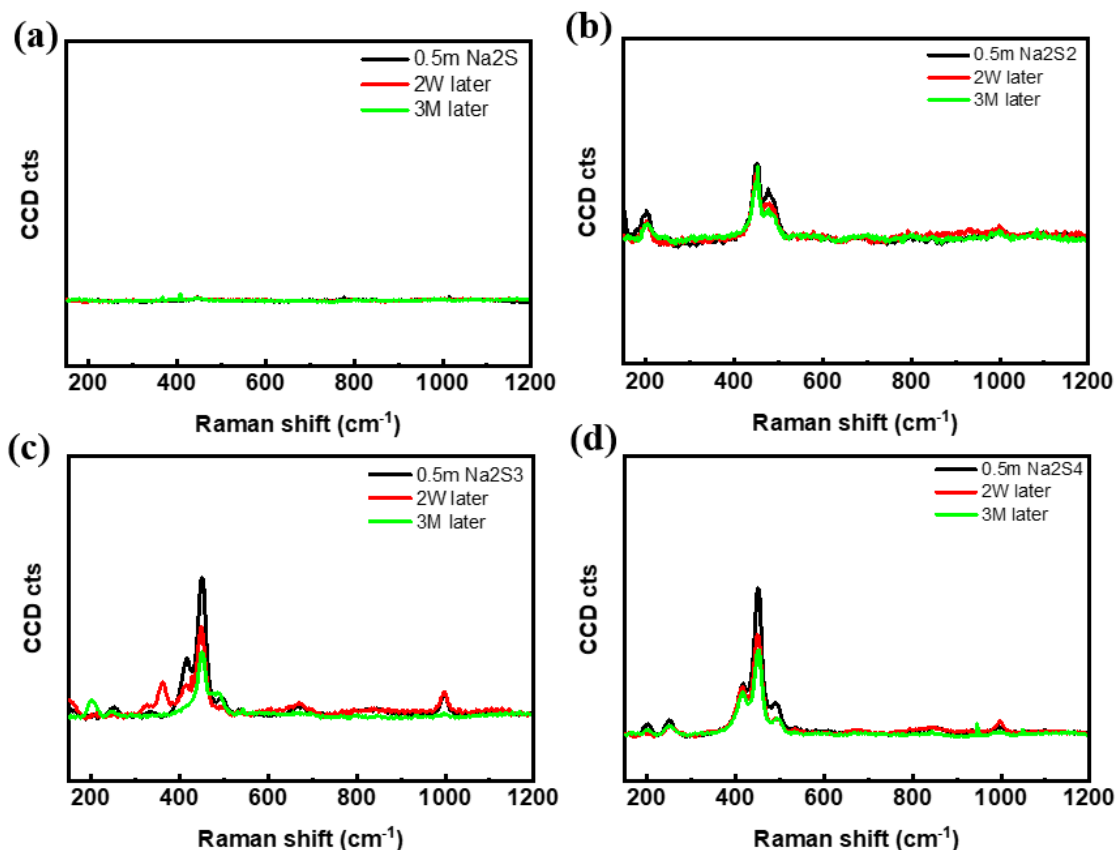


Figure 3.1. 10 Raman spectra 0.5 m sodium polysulfide solutions when prepared, after 2 weeks and after 3 months.

The stability of 4 different nominal polysulfide solutions was studied at room temperature (Figure 3.1.10). The Raman spectra of Na_2S , Na_2S_2 , Na_2S_3 , and Na_2S_4 solutions are taken at the time they were prepared, 2 weeks after they were prepared, and 3 months after they were prepared. Between the Raman analyses, the solutions were stored in a dry cabinet at 25°C. For Na_2S solution, no peaks are detected over the scan range of Raman spectroscopy. Also, no peaks appeared over the 3 months of storage time. For Na_2S_2 solution, 3 peaks are detected in the Raman spectrum and are assigned to S_4^{2-} , S_4^{2-} and S_3^{2-} . The Raman spectra obtained after 2 weeks and 3 months also show the same peaks, indicating the polysulfide species are relatively stable over the 3 months. For the Na_2S_3 solution, changes of Raman peaks are observed over the 3 months storage period. When the solution was first prepared, the S_3^{2-} peak at 249 cm^{-1} was detected. And another 3 peaks for S_5^{2-} , S_4^{2-} and S_5^{2-} also showed up. After 2 weeks, 2 new peaks at 323 cm^{-1} and 361 cm^{-1} appear. These 2 peaks are possibly related to intermediate sulfur species that are produced during the disproportionation or decomposition of polysulfide species. After 3 months, the peak at 416 cm^{-1} that was previously assigned to S_5^{2-} disappears. The S_4^{2-} peak at 450 cm^{-1} remains to be the strongest one. The S_5^{2-} peak at 495 cm^{-1} also disappears and a combined peak of $\text{S}_2^{2-}/\text{S}_3^{2-}$ appears at around 486 cm^{-1} . For Na_2S_4 nominal solution, the peaks identified for the freshly prepared solution remain unchanged after 3 months of storage.

3.1.6 Conclusions

The speciation of sodium polysulfide was investigated by Raman spectroscopy under various conditions: different hydroxide concentrations, different sulfur concentrations,

concentrations greater than the sulfur solubility limit, and different storage times. For Na₂S and Na₂S₂ solutions, the suppression of the HS⁻ peak is observed when the hydroxide concentration is above 10 m. Peaks for S₂²⁻, S₃²⁻ and S₄²⁻ are observed for Na₂S₂ solutions and the peak of S₄²⁻ gradually disappeared with increasing hydroxide concentration. Peaks of S₂²⁻, S₃²⁻, S₄²⁻ and S₅²⁻ are observed for Na₂S₃ and Na₂S₄ solutions. The concentration of sulfur does not affect the speciation of Na₂S₄ solutions and the speciation of nominal Na₂S₅ solution is very similar to that of Na₂S₄ solution. Except for Na₂S₃, the sodium polysulfide solutions remain stable and for 3 months and do not show any changes in Raman peaks.

3.2 Aqueous manganese solution as catholyte for redox flow batteries

3.2.1 Introduction

Redox flow batteries (RFBs) are receiving wide attention for large-scale energy storage due to the decoupling of energy storage and power output, high coulombic (CE) and energy (EE) efficiencies, and scalability. Currently, most of the RFBs are mainly based on metal ions dissolved in acidic solutions. There are several disadvantages including capacity losses due to membrane crossover, electrode corrosion, and the occurrence of undesired side reactions during battery operation. These will eventually result in high cell operational and maintenance costs. RFBs operating under alkaline environments have the advantages of low self-discharge and low hydrogen evolution rates. Alkaline solutions allow the use of materials that are cheaper and less susceptible to corrosion. Additionally, they can tolerate the use of more conductive metallic three-dimensional electrodes, allowing a higher energy efficiency. [97-101] The advantages and development of aqueous sulfur-based solutions as anolyte for RFBs have been discussed in Chapter 1. However, the cost for both the Br^-/Br_3^- and the I^-/I_3^- redox couple is still high. The conversion between permanganate/manganate (MnO_4^-/MnO_4^{2-}) is a potential to couple with polysulfide for a redox flow battery.[102-104] The MnO_4^-/MnO_4^{2-} redox couple has a positive redox potential, high electrochemical reversibility, and also high solubility, up to 3.62 M at room temperature.[102] And most importantly, manganese is more abundant and less expensive compared to elements like V and Br. Mn is the 12th most abundant element in the earth's crust.[105, 106]

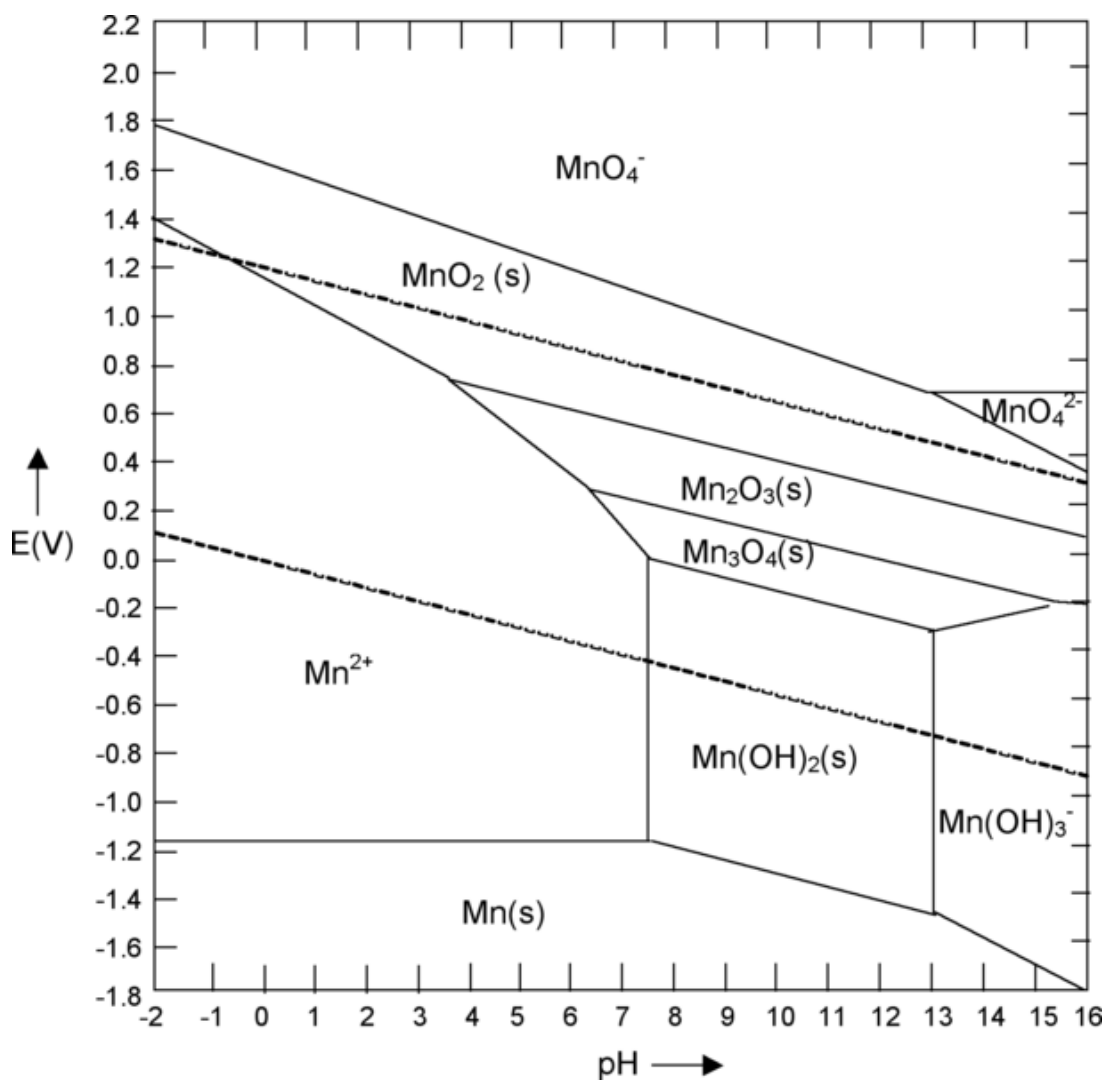
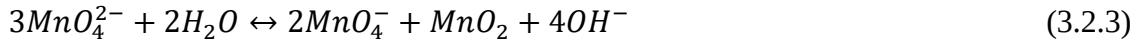
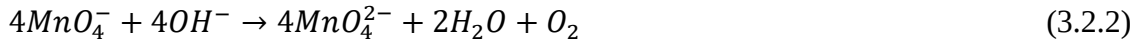


Figure 3.2. 1 Pourbaix diagram for manganese species in water at 25 °C.[107]

As shown in the Pourbaix diagram (Figure 3.2.1) for manganese species in aqueous solution, the operation of an $\text{MnO}_4^-/\text{MnO}_4^{2-}$ based redox flow battery requires a highly alkaline environment. At pH lower than 13, the permanganates are reduced to MnO_2 directly. At pH higher than 13, permanganates will first be reduced to manganates and then to MnO_2 .

Redox couple reaction for the aqueous manganese (AqMn) catholyte active material is shown in Equation 4.1.1. In addition, two decomposition reactions accompanied by the redox reaction are shown in Equation 3.2.2 and Equation 3.2.3:



In Equation 3.2.2, the AqMn species (permanganate), which are at the highest oxidation state (+7), are decomposed to manganate accompanied by the generation of oxygen gas. In terms of the battery cycling, this reaction will result in a decrease of state of charge (SoC) and therefore also defined as a self-discharge reaction. The reaction rate (self-discharge rate) increases with increasing pH. Equation 3.2.3 shows the disproportionation of manganate, where manganates become permanganates and manganese dioxides. The disproportionation of manganates irreversibly forms MnO_2 precipitates, which are electrochemically non-reactive. This will result in a decrease in the catholyte active material and lead to a decrease in catholyte capacity. Additionally, MnO_2 precipitation might also block the flow of AqMn catholyte and affect the transport of active materials. The reaction rate (precipitation rate) of Equation 3.2.3 increases with decrease in pH. In general, both reactions are related to the stability of AqMn solutions and are harmful to the electrochemical performance of the AqMn catholyte.

More studies to understand and improve the stability of AqMn catholyte will be crucial for the development of AqMn as catholyte for AqS redox flow batteries. In this chapter, the test protocols and quantitative metrics for the chemical and electrochemical stability of the AqMn solutions are developed. The performance of the AqMn catholyte is investigated via

in-situ and *ex-situ* experiments. A numerical model is also developed to simulate the performance of the AqMn – AqMn symmetric flow cell. The reaction pathway for the precipitation of catholyte is discussed and several mitigation strategies are proposed.

3.2.2 Test protocols and quantitative metrics for catholyte stability

The stability of the active materials is closely related to the reaction rate of Equation 3.2.2 and Equation 3.2.3. In the following part of this chapter, the SoC of the AqMn solution is defined as the concentration of permanganate over the concentration of total dissolved AqMn species (Permanganate + manganate). The reaction rate of Equation 3.2.2 (self-discharge rate) can be determined in 2 ways: by measuring and tracking the ratio of $\text{MnO}_4^- / \text{MnO}_4^{2-}$ (can be used to calculate the SoC) or the evolution rate of O_2 . The reaction rate of Equation 3.2.3 (precipitation rate) can be determined by measuring and tracking the total concentration of dissolved manganese. To study the stability of the AqMn solutions, test protocols and quantitative metrics that can accurately measure the reaction rate of the above two chemical reactions are developed. We particularly evaluated the use of Raman spectroscopy for permanganate/manganate species quantification, titration method for quantifying the AqMn concentration, open-circuit voltage (OCV) method for measuring the SoC, and gas chromatography for quantifying O_2 evolution in the self-discharge reaction.

Raman spectroscopy

Raman spectroscopy is widely used for the characterization of solid samples, but also presents features that permit its use for the analysis of aqueous media.[108, 109] The Raman spectrum of aqueous solutions will be influenced by several factors such as the ion

species in solution, solution concentration, laser power, and temperature. Therefore, the Raman spectrum of a set of solutions under controlled experimental conditions can provide concentration-related information. In this part, Raman spectrums were recorded using a confocal Raman microscope (WITec alpha 500R) equipped with a 10, 50, and 100 Olympus objective lens. Laser excitation (~ 5 mW at the sample) was provided by a 633 nm He-Ne laser.

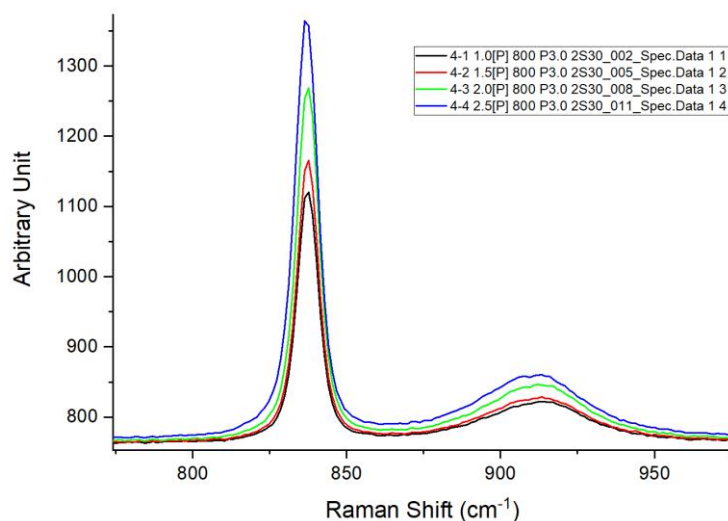


Figure 3.2. 2 Raman spectra of KMnO_4 solutions at concentrations of 1.0 M, 1.5 M, 2.0 M, and 2.5 M.

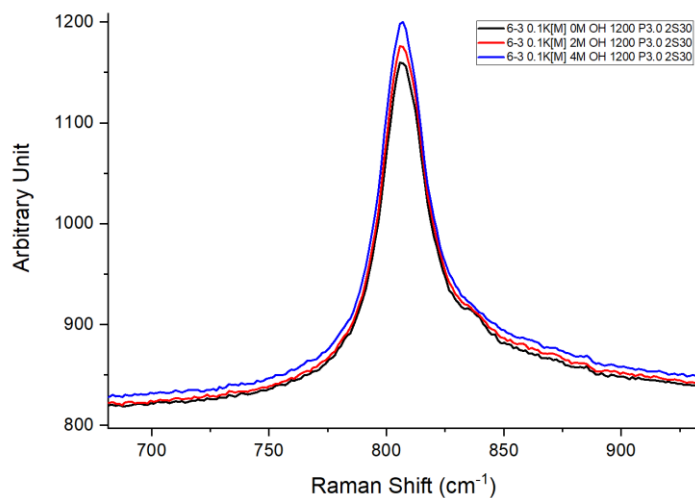


Figure 3.2. 3 Raman spectrum of 0.1M K_2MnO_4 solution with 0 M, 2 M, and 4 M of NaOH.

Different concentrations, 1 M, 1.5 M, 2.0 M, and 2.5 M, of permanganate solutions were analyzed by Raman spectroscopy. As shown in Figure 3.2.2, increased concentration of permanganate solutions results in increased peak area at 837 cm^{-1} and 912 cm^{-1} . This proved the feasibility of quantifying aqueous manganese species by Raman spectroscopy. The effect of pH on the Raman spectrum was investigated. Three 0.1M K_2MnO_4 solutions were prepared with 0 M, 2 M, and 4 M of NaOH. From Figure 3.2.3, the pH of the solution slightly affected the area of the peak at 807 cm^{-1} . The peak area difference among these three samples was up to 7%.

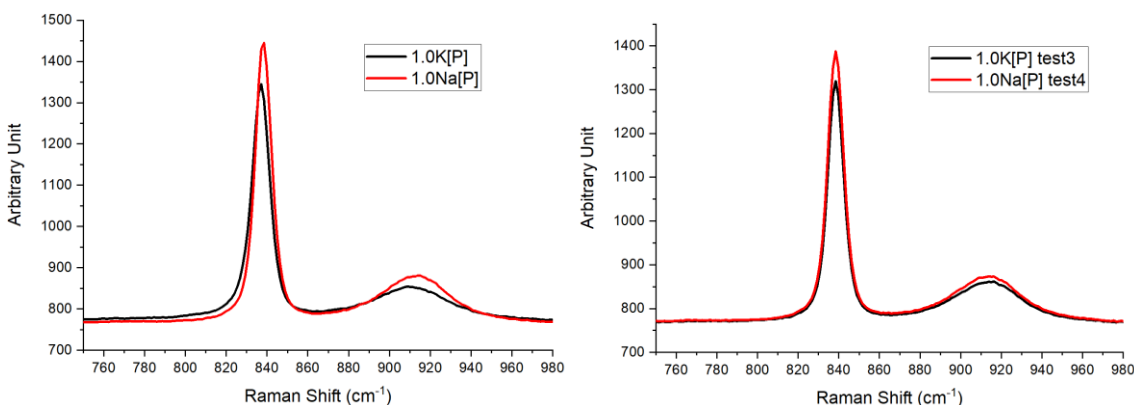


Figure 3.2. 4 Raman spectra of 0.1 M KMnO_4 and 0.1 M NaMnO_4 solution. The spectrum of the comparison was recorded twice (left and right) with the same experimental condition.

In Figure 3.2.4, the effect of Na/K ion on the Raman spectrum was studied. Two 1.0 M permanganate solutions were prepared with sodium and potassium salts. The comparison of these two samples was performed twice under the same experimental conditions. In both

comparisons, the sample with sodium salt showed ~7% larger peak area than the potassium salt sample. Note that for the same sample, we observed an peak are change by ~8% during two tests.

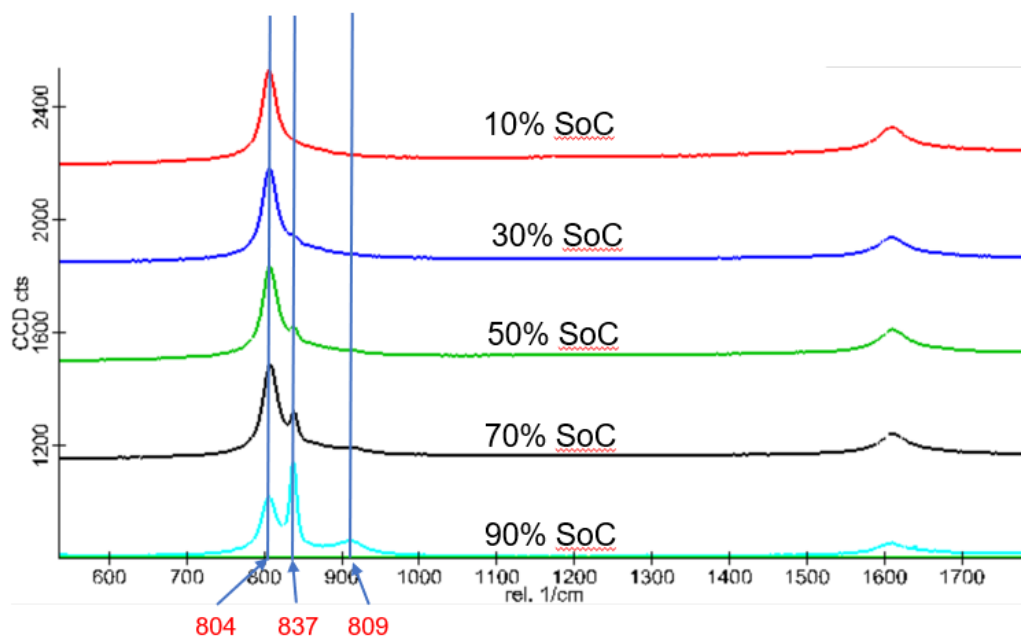


Figure 3.2. 5 Raman spectra of 5 AqMn solutions with different SoCs. The total dissolved manganese concentration for all 5 solutions is 0.5 M.

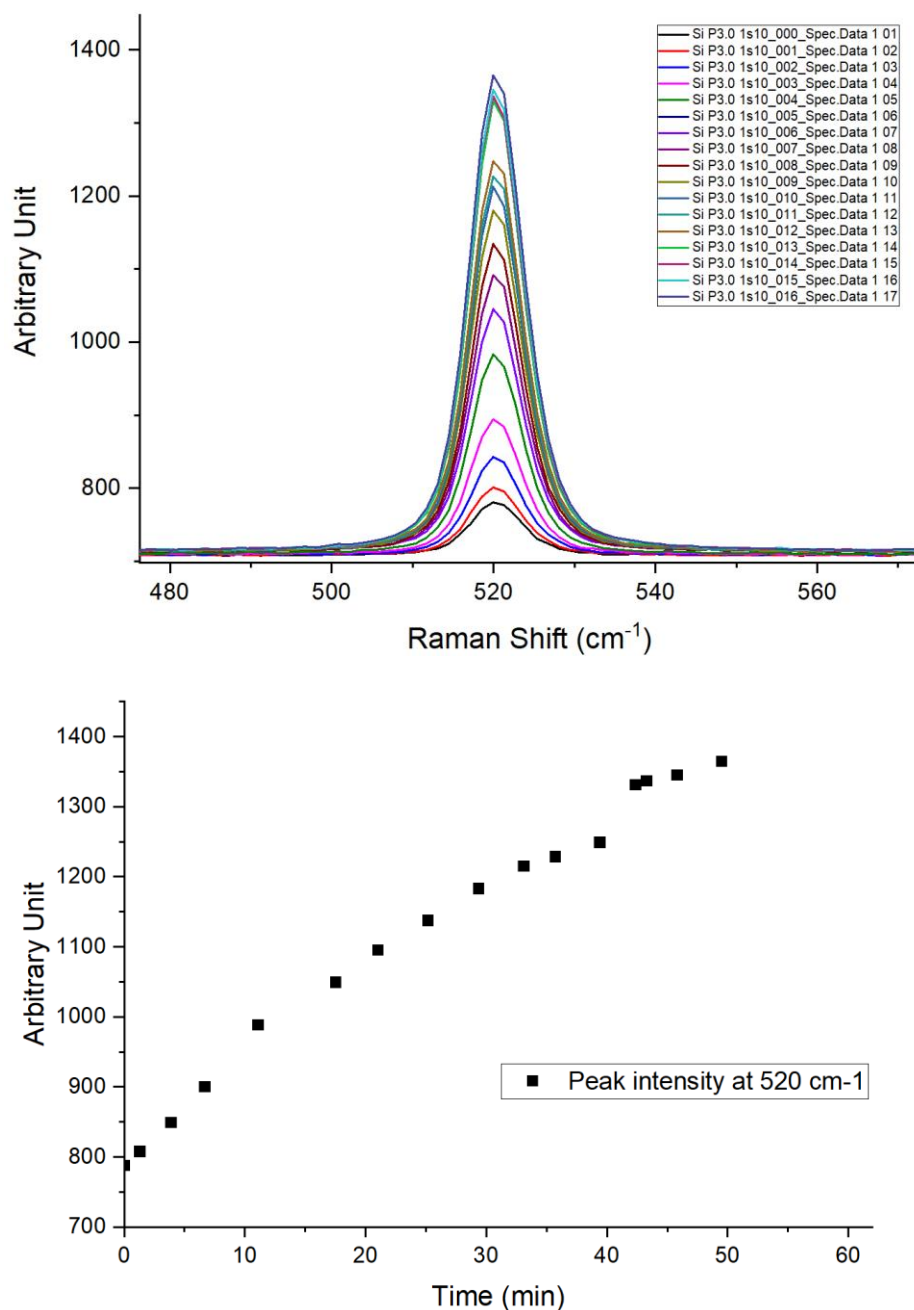


Figure 3.2. 6 (Top) Raman spectrum of Si wafer during laser warm-up. (Bottom) Si peak intensity vs time

To investigate the effect of different $\text{MnO}_4^-/\text{MnO}_4^{2-}$ ratios (SoCs) on the Raman spectrum, we prepared 0.5 M of KMnO_4 in DI water and 0.5M of K_2MnO_4 in 6 M NaOH. These two

solutions were mixed in 1:9, 3:7, 5:5, 7:3 and 9:1 by volume to get 10%, 30%, 50%, 70% and 90% SoC solution. Figure 3.2.5 shows that, as SoC increased, the peak at 837 cm^{-1} increased significantly while the peak at 804 cm^{-1} gradually decreased. The peak at 909 cm^{-1} was obvious when the SoC was higher than 70%. The ratio of the peak at 837 cm^{-1} to peak at 804 cm^{-1} was extrapolated to see how it is correlated to the SoC of the AqMn solution. As shown in Figure 3.2.7, the Raman spectrum from an experiment is fitted to 3 peaks. Then the peak ratio of 837 cm^{-1} to 804 cm^{-1} is plotted vs the SoC of the AqMn solution (Figure 3.2.8). The peak ratio maker doesn't change a lot when the SoC is below 60%. This indicates that the peak ratio from the Raman spectrum will only be able to quantify the SoC of the AqMn solution above 60% SoC.

This method will not be accurate when the SoC is below 60%. Higher SoC will bring more accuracy to this method.

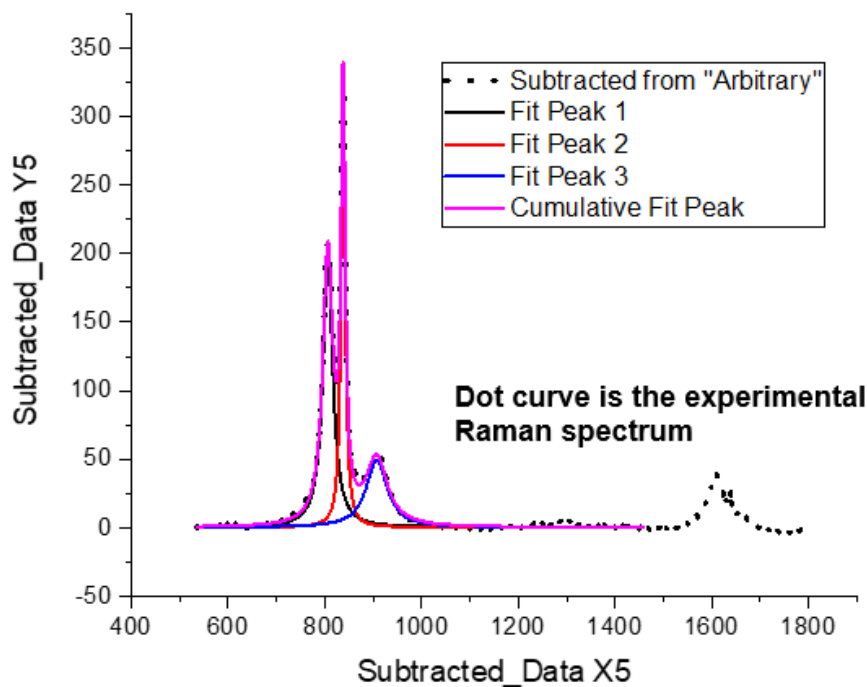


Figure 3.2. 7 Peak fitting for the 90% SoC AqMn sample

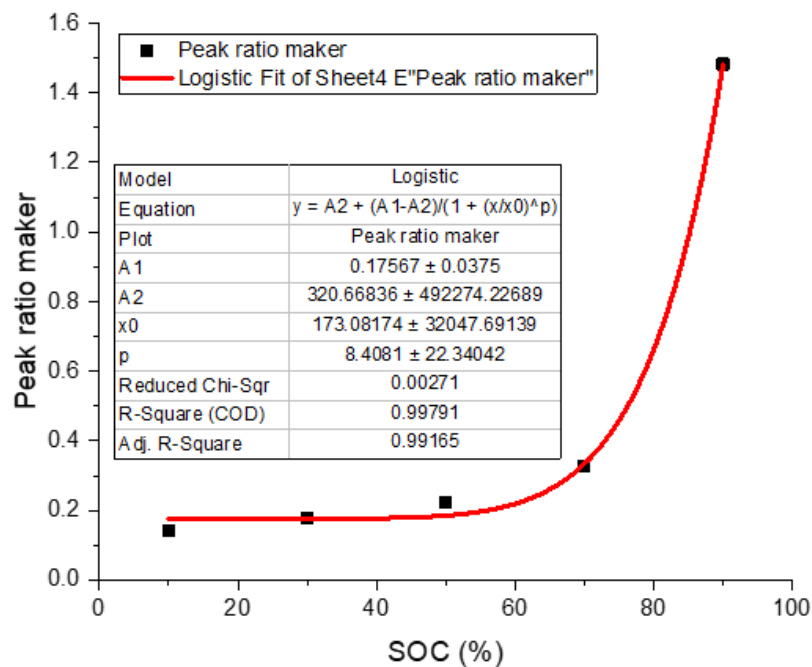


Figure 3.2. 8 Change of peak ratio for different SoC of AqMn solutions

It is also found that the laser generator seems to have a warm-up time. Raman spectrum of a Si slide at the same position was recorded every 2-3 minutes since the laser generator was turned on. Figure 3.2.6 plots the peak intensity at 520 cm^{-1} for Si vs time. The intensity of peak 520 cm^{-1} increased continuously for at least 60 minutes.

In summary, the pH and cation type of the permanganate/manganate solution will affect the Raman peak intensity by around 8%. Besides, for the same sample, there will be at least 8% of intensity variance from the instrument and/or test condition control. So, the intensity or integrated area of a single peak is not able to provide accurate concentration information. Based on these, we conclude that Raman spectroscopy cannot identify the precipitation rate and self-discharge rate of the active materials.

Gas chromatography for O₂ evolution quantification

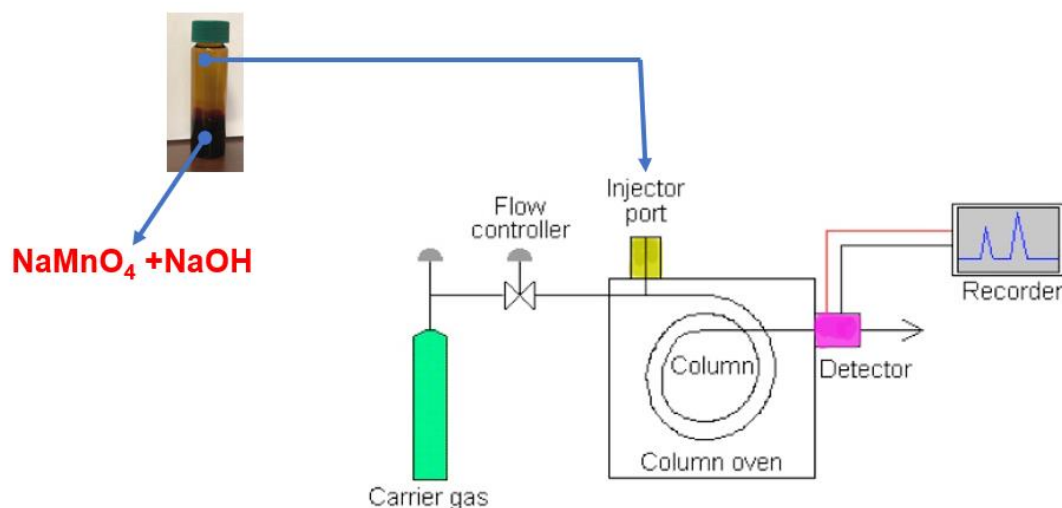


Figure 3.2. 9 Instrument diagram of gas chromatography for measuring the O₂ gas generated from AqMn samples.

Gas chromatography (GC) is a common type of chromatography used in analytical chemistry for analyzing compounds that can be vaporized without decomposition. The self-discharge reaction is accompanied by O₂ evolution. Gas chromatography can quantify the amount of O₂ injected[110, 111] to the instrument and therefore help determine the self-discharge rate of the catholyte. In this section, the gas chromatography was tested with a Shimadzu 2014 GC/TCD. The testing diagram is shown in Figure 3.2.9. A molecular sieve 1 mm x 2 m column was used. The carrier gas was helium and the flow rate is 20 ml/min. The detector temperature was 150 °C and the column oven temperature was 50 °C isothermal. Injection temperature was 150 °C. By selecting the right size of the syringe, the standard deviation of the results that comes from the manual injection can be controlled to 3.6%.

The calibration curve shown in Figure 3.2.10 describes the relationship between air (assume 20.95% O₂) injection volumes and O₂ peak areas. The O₂ peak areas present a linear relationship with the injected air (O₂) volumes. For each data point shown in the plot, at least 5 injections were done, and the %RSD are all lower than 4%. This calibration curve allows us to quantitatively measure the O₂ generated in a closed system and thus measure the self-discharge rate.

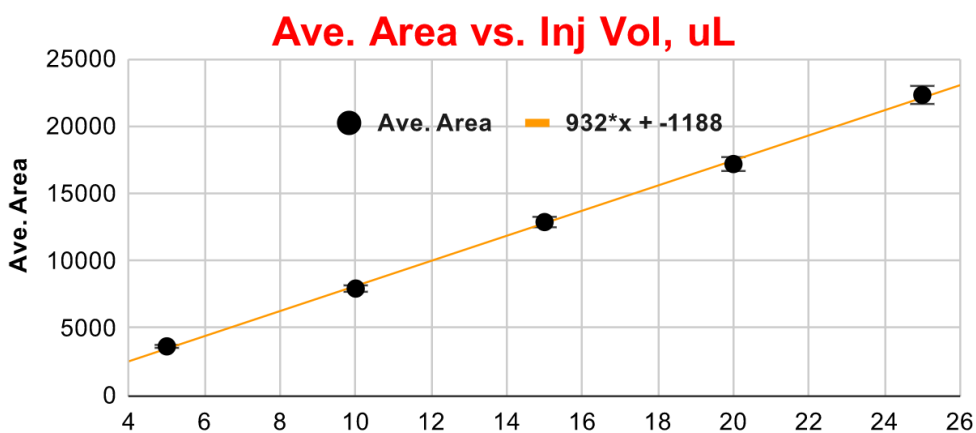


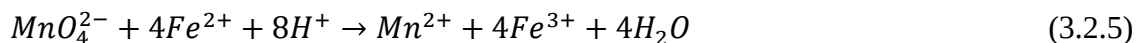
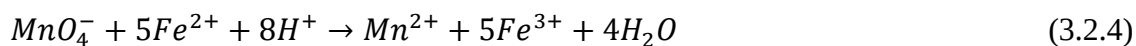
Figure 3.2. 10 Change of integrated O₂ peak area with injected gas volumes

Titration method for active material quantification

Titration is a quantitative chemical analysis method that can determine the concentration of an identified analyte. A reagent (titrant) is prepared as a standard solution of known concentration and volume. The titrant reacts with the analyte to determine the concentration of the analyte. The titration method is also used in some other RFB systems, for example, all-vanadium redox flow battery, to determine the concentration of the active species in the electrolyte.[112-115]

The analyte in this work will be aqueous manganese ($\text{MnO}_4^-/\text{MnO}_4^{2-}$) in an alkaline solution. The titrant used in this method is 0.1M $\text{FeSO}_4 + \text{H}_2\text{SO}_4$. During the titration,

aqueous manganese ($\text{MnO}_4^-/\text{MnO}_4^{2-}$) will react with Fe^{2+} in an acidic environment and be reduced to Mn^{2+} . The reactions are shown in Equation 3.2.4 and Equation 3.2.5.



During the reaction, a potentiometric sensor is immersed in the solution to monitor the voltage of the solution (Figure 3.2.11). The potentiometric sensor comprises a Pt wire working electrode and an Ag/AgCl reference electrode. The endpoint of the titration can be easily observed when a sudden increase in the voltage from $\sim 0.6\text{V}$ to $\sim 1.0\text{V}$ happens. Table 3.2.1 recorded the change of voltage with the volume of titrant added. The titration started when the titrant level was at 0.2 ml. The open-circuit voltage was close to 400 mV. As the titrant was gradually added to the AqMn sample, the stirring made sure the reaction can happen fast and thoroughly. When it came to an endpoint, 1-2 drops of titrant will increase the voltage significantly. Figure 3.2.12 shows a typical titration curve for manganate/permanganate titration. For an aqueous manganese (AqMn) sample with known SoC, the titration method can quantify the concentrations of permanganate and manganate of the analyte. The color change of the AqMn sample during the titration process is also obvious (Figure 3.2.13). Before the titration, permanganate with purple color exists in the beaker. With adding the reducing agent, permanganates and manganates gradually reduced to soluble Mn^{2+} ions and the color of the AqMn sample is less obvious. At the end-point, all the permanganates and manganates are reduced to Mn^{2+} and the solution becomes transparent.

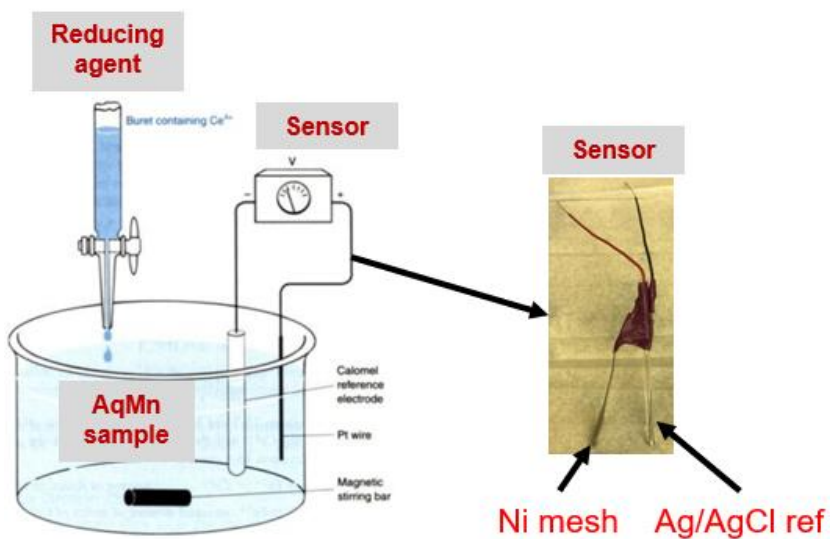


Figure 3.2. 11 Diagram for titration experiments

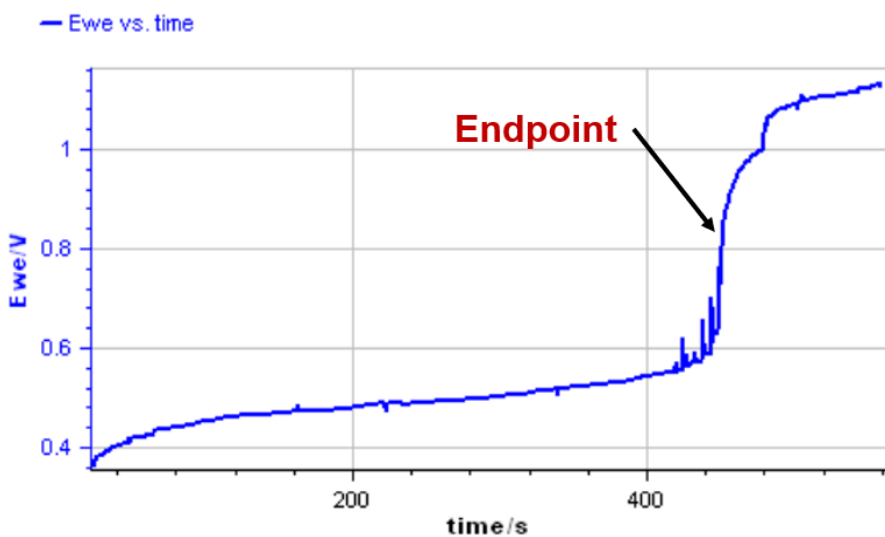


Figure 3.2. 12 Change of voltage during the potentiometric titration

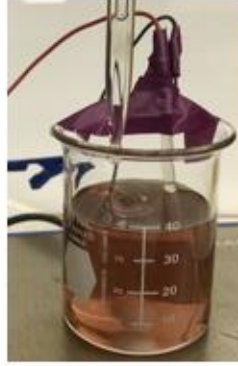
Table 3.2. 1 Change of voltage during the potentiometric titration

Titrant level	Voltage response
0.20 ml	Starting point

6.55 ml	-684 mV
6.60 ml	-495 mV
6.70 ml	-400 mV
6.75 ml	-390 mV



**Before
titration**



**Before
end-point**



End-point

Figure 3.2. 13 Color change of the AqMn samples during the titration process.

Open circuit voltage to track the SoC of the catholyte

The open-circuit voltage of the AqMn sample changes with the change of permanganate/manganate ratio according to the Nernst equation at 298 K:

$$E = E^0 + \frac{0.059V}{z} \log_{10} \frac{a_{Ox}}{a_{Red}} \quad (3.2.6)$$

Where E is the measured half-cell potential, E^0 is the standard potential for $\text{MnO}_4^-/\text{MnO}_4^{2-}$ redox couple. And $\frac{a_{Ox}}{a_{Red}}$ could be calculated using $\frac{[Ox]}{[Red]}$ since the activity coefficients tend to unity at low concentrations. Figure 3.2.14 shows how the open-circuit voltage is measured against a Hg/HgO (MMO) reference electrode in a blank solution. And the theoretical relationship between the measured half-cell voltage and the SoC of the AqMn

sample is shown in Figure 3.2.15. The slope of the plot is higher at the 2 ends of the SoC range and is lower at the middle part of the SoC range, which indicates that this method will be more accurate for SoC close to 100% and 0%.

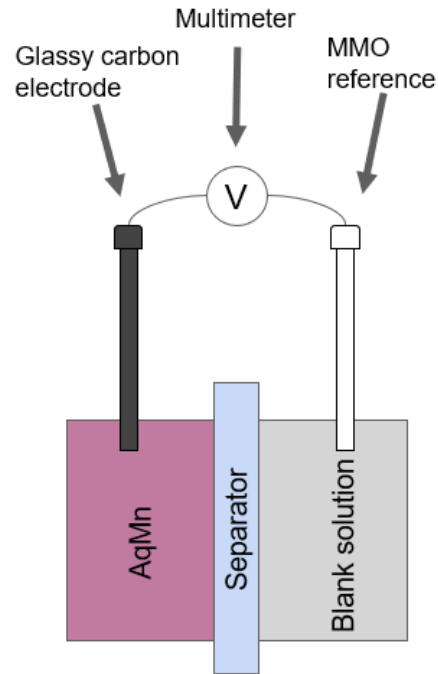


Figure 3.2. 14 Half-cell building to measure the open-circuit voltage of an AqMn sample

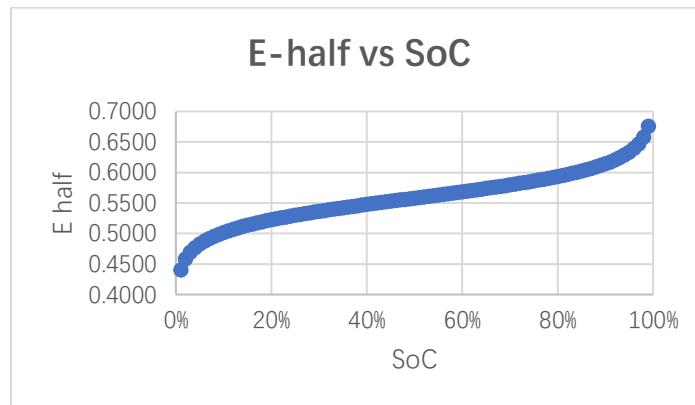


Figure 3.2. 15 Measure E-half for the AqMn solution versus the SoC of the AqMn solution

3.2.3 AqMn catholyte stability via *ex-situ* experiments

Self-discharge rate at different SoCs

Previous initial stability test has shown that the self-discharge rate increases at higher SoCs. In this section, more detailed studies have been done to investigate the self-discharge rate at different SoCs. 0.2 M aqueous manganese (AqMn) in 2 M NaOH solution are prepared at 5 different SoCs: 60%, 80%, 90%, 95% and 100%. All the samples are prepared with KMnO_4 and K_2MnO_4 . For example, an 80% SoC sample means an AqMn solution with 0.16 M KMnO_4 and 0.04 M K_2MnO_4 . Samples are prepared in a sealed vial. The gas chromatography method is used to quantify the O_2 evolution in the vial 48 hours after the sample preparation. Then the self-discharge rate is determined for each sample based on their O_2 evolution (Equation 3.2.2).

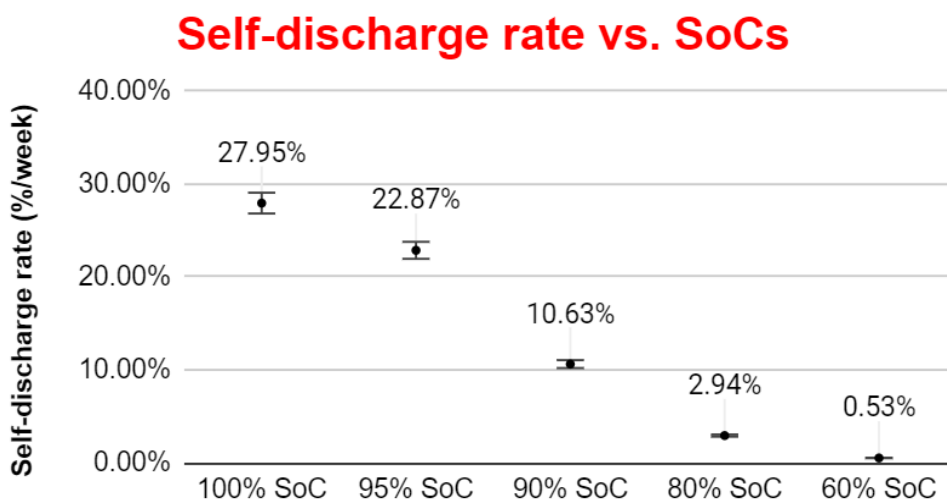


Figure 3.2. 16 Self-discharge rate of the AqMn sample at different SoCs

As shown in Figure 3.2.16, the self-discharge rate decreases when the SoC goes down. At above 95% SoC, the self-discharge rate is more than 20%/week. And it decreased drastically to less than 2%/week when the SoC goes below 80%/week. Note that the self-discharge rate/week is converted from the self-discharge rate in 2 days

Self-discharge rate at different concentrations

In this section, we studied how the self-discharge reaction goes at different active material concentrations. AqMn in 2M NaOH with different concentrations, 2 M, 1 M, 0.5 M, and 0.1M, are prepared at 100% SoC. All the samples are prepared with NaMnO₄ stock solution and the NaOH concentration remains the same at each sample. The gas chromatography method is used to quantify the O₂ evolution in the vial 48 hours after the sample preparation. Then the self-discharge rate is determined for each sample based on their O₂ evolution (Equation 3.2.2).

Figure 3.2.17 shows how the self-discharge rate changes with different concentrations. Generally speaking, the self-discharge rate increases when the AqMn concentration decreases. And we see a sharp increase in the self-discharge rate when the concentration decreased from 0.5 M to 0.1 M. We have known that higher OH⁻ concentration will accelerate the self-discharge rate. These results suggest that lower AqMn concentration or higher AqMn/OH⁻ the ratio will also increase the self-discharge rate.

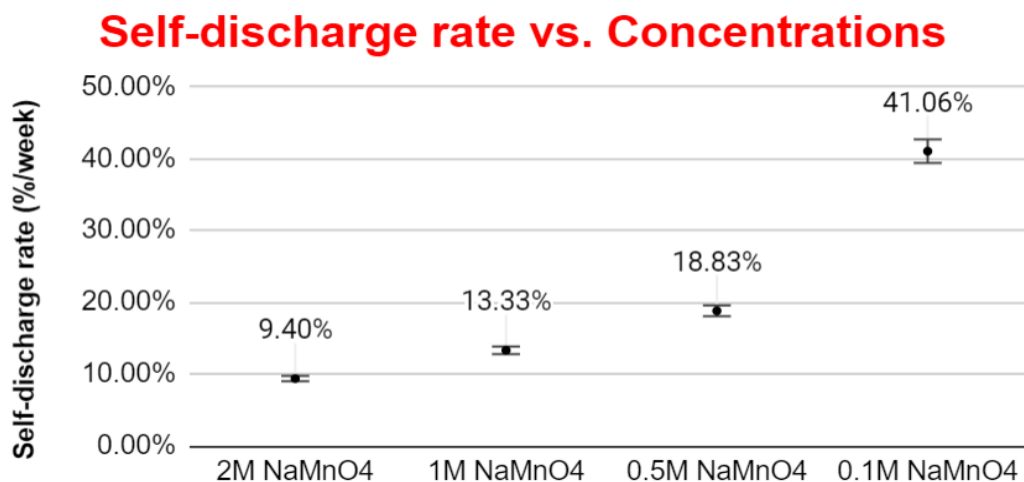


Figure 3.2. 17 Self-discharge rate of the AqMn sample at different concentrations

Decay rate at different SoCs

The decay of the active material refers to the decreased of dissolved manganese in the catholyte. This will result in an irreversible capacity loss. In this section, we studied the effect of SoC on the decay rate. 0.2 M AqMn in 2 M NaOH are prepared at 5 different SoCs: 0%, 5%, 10%, 20% and 50%. Samples are prepared with KMnO_4 and K_2MnO_4 . The total AqMn concentration of these samples is measured 7 days after the samples are prepared by using the OCV-SOC method and the titration method together.

As shown in Figure 3.2.18, a decay rate of 13.66%/week is measured for the 0% SoC sample. The decay rate gradually decreases to 9.07%/week when the SoC increases to 50%. In general, lower SoC will have a higher decay rate. However, the effect of SoC on the decay rate is much lower than on the self-discharge rate.

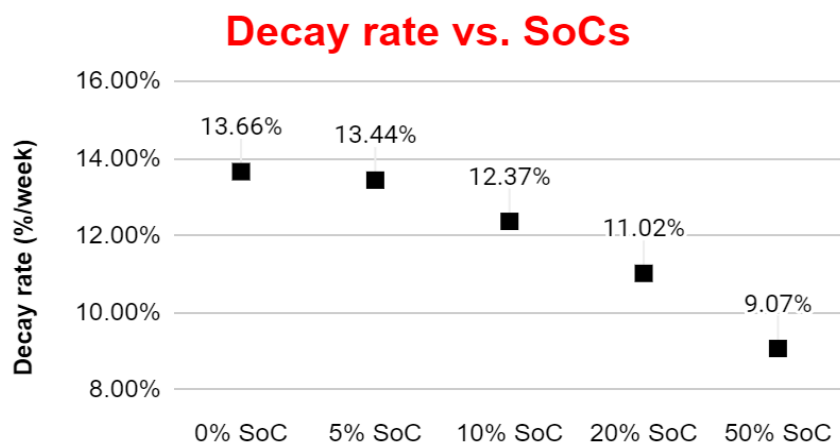


Figure 3.2. 18 Decay rate of the AqMn sample at different SoCs

Decay rate at different concentrations

The decay rate of the AqMn sample is studied at 4 concentrations: 2 M, 1 M, 0.5 M, and 0.1 M. Based on the background knowledge and previous studies, decay rate should be studied at low SoCs.

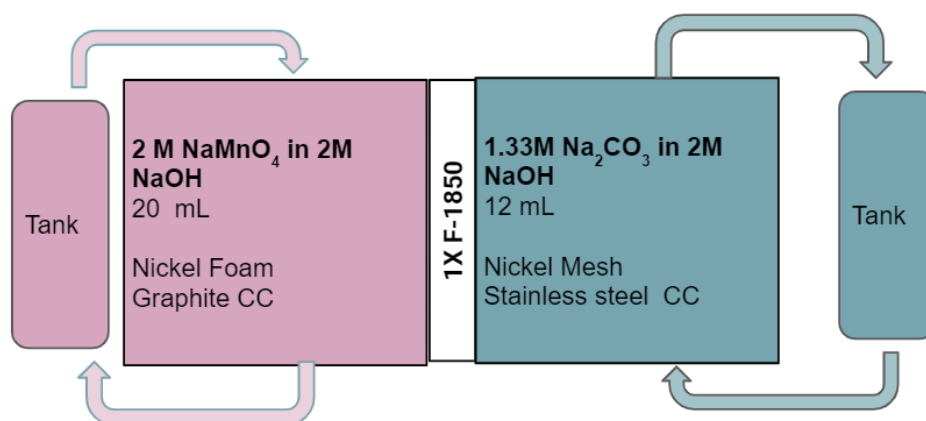


Figure 3.2. 19 Flow cell diagram for discharging the NaMnO₄ solution to Na₂MnO₄

Considering the solubility of the potassium manganate and sodium manganate, we prepared Na₂MnO₄ solutions, with the 4 concentrations mentioned above, in 2 M NaOH.

Na_2MnO_4 is not commercially available therefore we prepared the 2 M Na_2MnO_4 stock solution by electrochemically discharging a 2 M NaMnO_4 + 2 M NaOH solution in a flow cell. The flow cell setup is shown in Figure 3.2.19. The end of discharge is controlled by periodically measuring the SoC of the catholyte with the OCV-SOC method. The Na_2MnO_4 samples with 4 concentrations are all prepared from the 2 M Na_2MnO_4 stock solution. We used the titration method together with the OCV-SOC method to measure the total AqMn concentration of the 2 M Na_2MnO_4 stock solution. The results showed that the actual concentration of the stock solution is 1.834 M and the SoC is 5.7%. This indicates that the actual AqMn concentrations for the 4 AqMn sample that we prepared are: 1.834 M, 0.917 M, 0.458 M, and 0.0917 M. The total AqMn concentration of these 4 samples is measured again after 6 days. Figure 3.2.20 demonstrates how the concentrations affect the decay rates. The decay rate decreases a little from 12.72%/week to 8.65%/week when the concentration decreases from 2 M to 0.1 M. Comparing to the effect of concentrations on self-discharge rate, the effect on decay rate is much smaller.

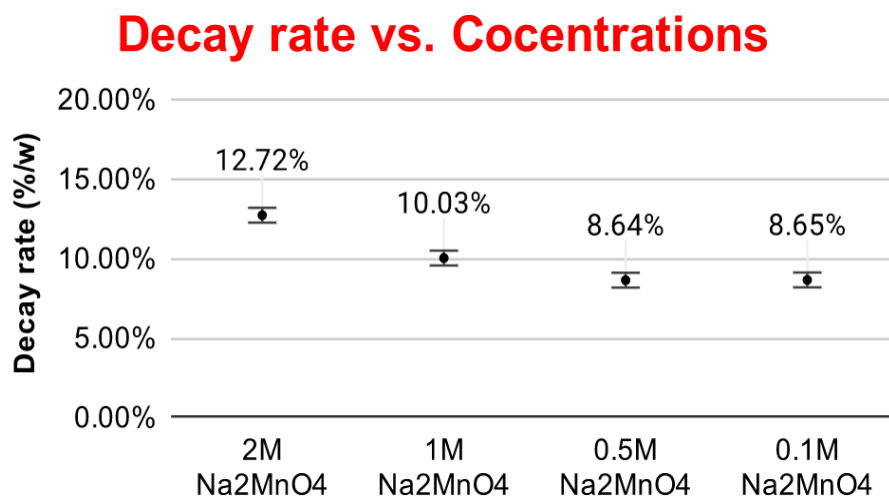


Figure 3.2. 20 Decay rate of the AqMn sample at different concentrations

3.2.4 Catholyte performances via *in-situ* experiments

Preliminary electrochemical testing

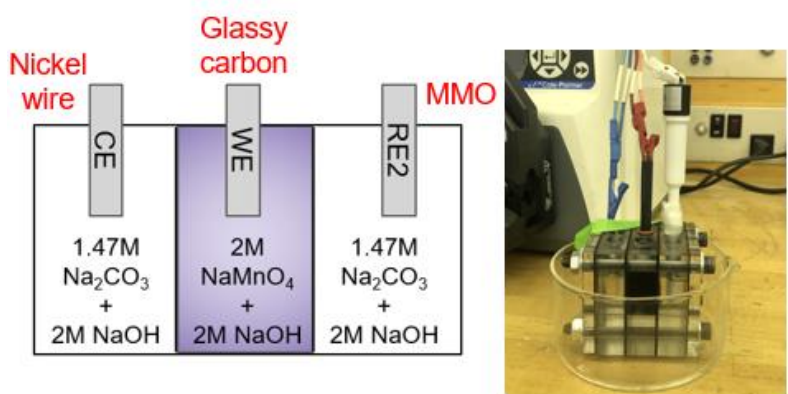


Figure 3.2. 21 Three-electrode setup for cyclic voltammetry tests

The electrochemical performance of the AqMn solution was tested through cyclic voltammetry (CV). A 3-electrode cell was built to conduct the CV scans (Figure 3.2.21). The cell is composed of a glassy carbon working electrode immersed in 2 M NaMnO₄ + 2 M NaOH solution, a nickel wire counter electrode immersed in 1.47 M Na₂CO₃ + 2M NaOH solution, and a Hg/HgO reference electrode immersed in 1.47 M Na₂CO₃ + 2M NaOH solution. The working electrolyte was separated from the counter electrolyte and reference electrolyte to avoid the contamination of permanganate and manganate to the reference electrode. The electrolytes were separated by a layer of Fumasep F-1850 perfluorinated sulfonic acid membrane. The membrane was clamped by a rubber gasket in between each chamber. The CV scan was taken in two voltage windows: an extended window, which is 0.2 V – 1.0 V vs MMO at a scan rate of 20 mV/s; and a limited window, which is 0.425 V – 0.65 V vs MMO at a scan rate of 20 mV/s. For the CV scans at the extended window, two strong reduction peaks show up at 0.47 V vs MMO and 0.25 V vs

MMO. The 1st reduction peak represents the reduction from permanganate to manganate, and the 2nd reduction peak represents the further reduction of manganate to Mn (+5) species. Only one weak oxidation peak shows up at around 0.56 V vs MMO, corresponding to the oxidation of a small amount of manganate to permanganate. At the 2nd reduction peak, the reduction from manganate to Mn species at a lower oxidation state is irreversible, and therefore only one weak oxidation peak shows up during the back scan. However, for the CV scans at the limited window, a reversible CV plot shows up with an obvious reduction peak at 0.47 V vs MMO and oxidation peak at 0.56 V vs MMO, which represents the reversible conversion between permanganates and manganates. The results also align well with that reported in the literature.

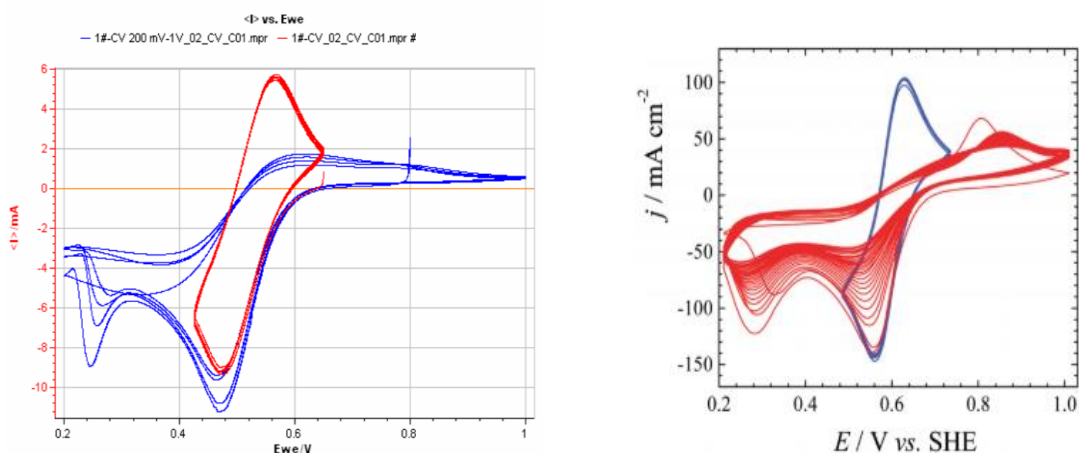


Figure 3.2. 22 Cyclic voltammetry of 2 M NaMnO₄ in 2 M NaOH solution at 2 voltage windows: (Left) experiment results and (right) literature results[102]

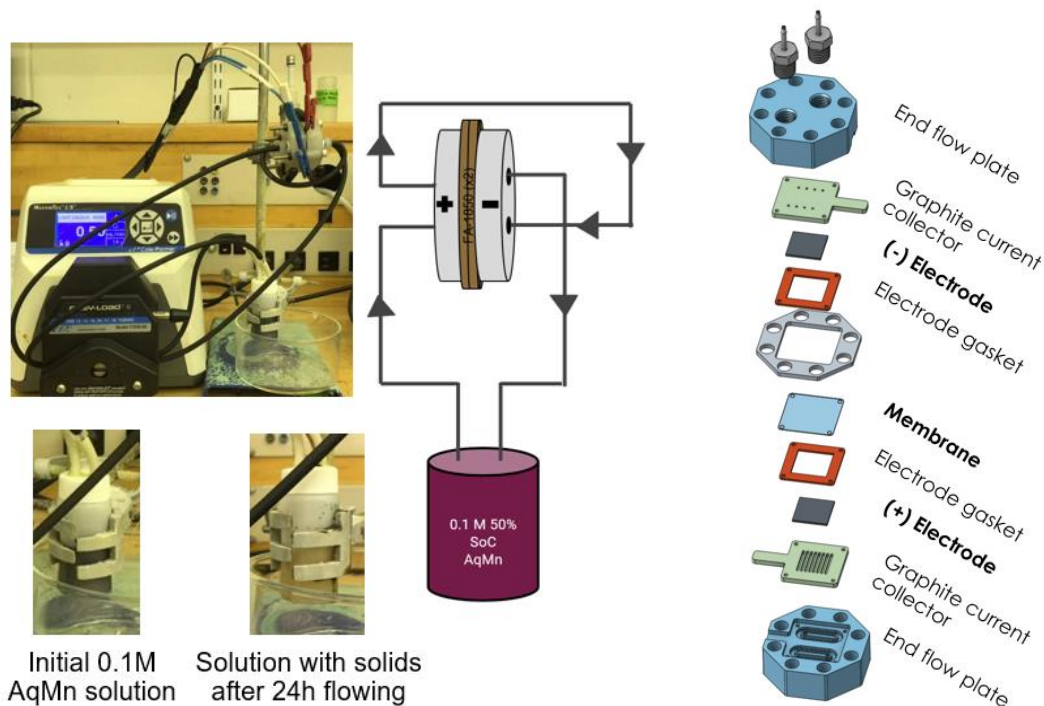


Figure 3.2. 23 (Left) Flow cell set up to study the electrochemical decay of the AqMn catholyte and (right) the structure of the flow cell body.

Next, the AqMn catholyte was tested in the flow cell with a self-cycling design. The flow cell body is a multilayer design that includes 2 end flow plates, 2 current collectors, 2 porous electrodes, 2 gaskets, and a membrane in between the positive and negative sides (Figure 3.2.23). The 0.1 M 50% SoC AqMn catholyte solution was prepared and stored in a plastic bottle. The AqMn solution was pumped following the protocols: 1) into the positive bottom side of the reactor, 2) out from the positive upper side of the reactor, 3) into the negative bottom side of the reactor and 4) out from the negative upper side of the reactor. A constant voltage of 1.0 V was applied to the cell. The flow rate was set to 0.5 ml/min. During the testing, the manganates on the positive side were oxidized to permanganates. While the permanganates on the negative side were reduced to manganates. The AqMn

kept an overall balanced SoC theoretically. However, the current decreased gradually after an initial decrease. The decrease of the current is due to the decrease of active materials, which is caused by the precipitation of MnO_2 . The self-discharge of the AqMn is much slower at this SoC and concentration. After 24 h of cycling, the color of the AqMn solution turned from deep purple to faint yellow. Also, solids were observed at the bottom of the bottle. These observations also indicate the decrease of active materials and the precipitation of MnO_2 .

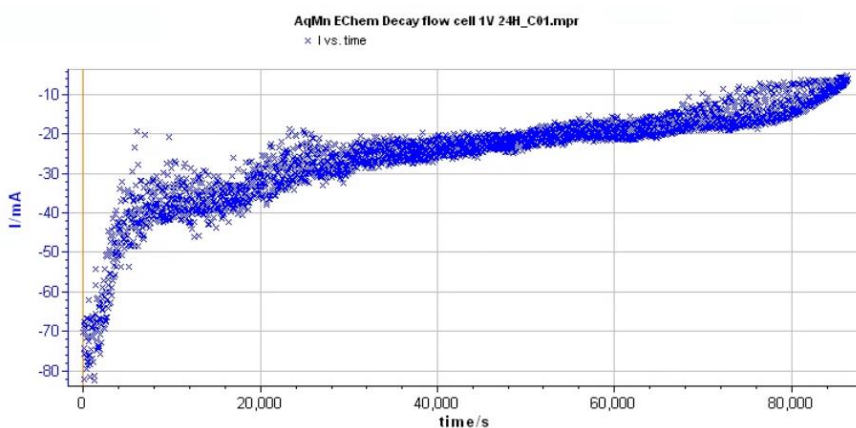


Figure 3.2. 24 Cell current versus time for the electrochemical decay experiment

Capacity decay of AqMn in flow cell testing: effect of internal resistance and effort to decrease the resistance

The work in this section is based on a symmetric flow cell test platform. This design has 0.15 M potassium permanganate and 0.15 M potassium manganate in 2 M sodium hydroxide solution (50% SoC AqMn) as both catholyte and anolyte in the flow cell. Cell components used in the symmetric flow cell include Flexelene tubing, graphite current collectors, Viton gaskets/O-rings. Two layers of Fumasep F-1850 perfluorinated sulfonic acid membranes and the 0.5mm thick Nickle foam are used as separators and electrodes

unless otherwise noted. A diagram of the symmetric cell test platform is shown in Figure 3.2.25.

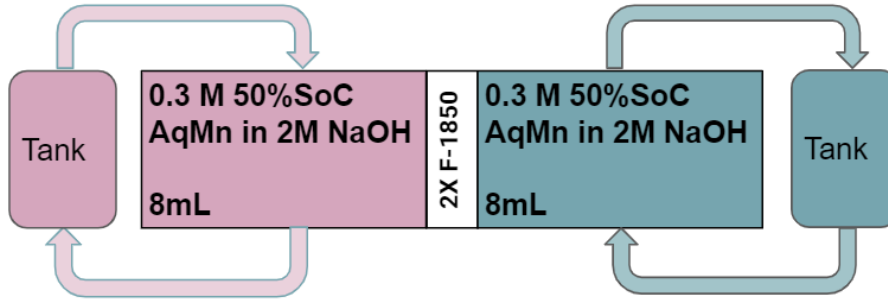


Figure 3.2. 25 Symmetric flow cell diagram

The symmetric cell is electrochemically cycled at a constant voltage of ± 0.2 V and cut off at 0.5 mA/cm^2 . At the end of each cycle, the applied voltage can be written as:

$$V_{appl} = E_{oc} + \eta_{act} + \eta_{ohm} + \eta_{con} \quad (3.2.7)$$

Where

E_{oc} is the open-circuit voltage that can be calculated from the Nernst equation

η_{act} is the activation overpotential

η_{ohm} is the ohmic overpotential

η_{con} is the concentration overpotential

Ohmic overpotential is given by Ohm's law in Equation 3.2.9 where i_{cut} is the cutoff current and R_{ohm} is the ohmic resistance of the cell. When the current is sufficiently small, the activation overpotential can be expressed as Equation 3.2.8, where R_{ct} is the charge transfer resistance.

$$\eta_{act} = i_{cut} \cdot R_{ct} \quad (3.2.8)$$

$$\eta_{ohm} = i_{cut} \cdot R_{ohm} \quad (3.2.9)$$

Therefore, the open-circuit voltage at the end of each cycle can be expressed as

$$E_{oc} = V_{appl} - i_{cut} \cdot (R_{ct} + R_{ohm}) - \eta_{con} \quad (3.2.10)$$

Electrochemical impedance spectroscopy (EIS) measurements were performed on the symmetric flow cell with a 200 mV AC perturbation in the frequency range from 100 kHz to 100 MHz at the end of each cycle. Figure 3.2.26a shows the EIS of the symmetric flow cell at the end of each cycle and the change of $R_{ct} + R_{ohm}$ over time is plotted in Figure 3.2.26b. After 5 cycles, the internal resistance increased from 21.6 Ω to 44 Ω (the 1st data point in Figure 3.2.26b is measured at the beginning of the cycle). Assuming the change of concentration overpotential η_{con} can be ignored, the decrease of open-circuit voltage E_{oc} would be ~17 mV according to Equation 3.2.10. Based on the calibrated OCV-SOC relationship, this OCV decreased corresponds to ~2.5% SoC decrease. This means 2.5% of the catholyte capacity will not be cycled due to the internal resistance increase and can be converted to ~11%/month capacity decay rate. Note that the overall capacity decay rate at 150 h is around 52%/month.

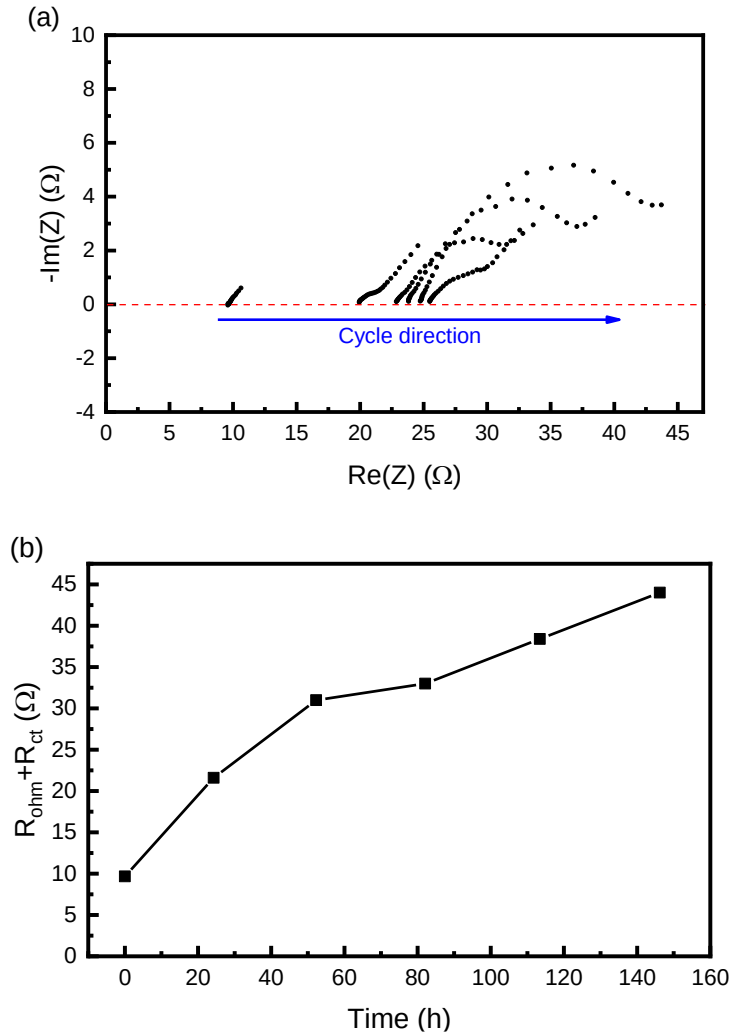
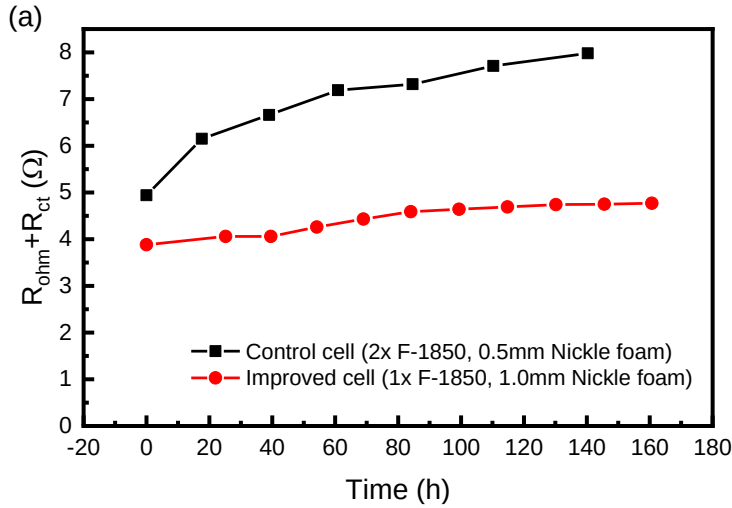


Figure 3.2. 26 (a)Electrochemical impedance spectroscopy of the symmetric flow cell over 6 cycles. (b)Internal resistance change over time.

To slow down the ohmic resistance increase, we replaced the 2-layer membranes with just a 1-layer membrane because the precipitants formed at the membrane surface can cause the ohmic resistance increase. And we used a Nickle foam electrode with 1mm thickness instead of 0.5mm trying to increase the charge transfer kinetics and thus slow down the increase of charge transfer resistance. Besides, a thicker electrode should also help decrease the ohmic resistance of the cell. Figure 3.2.27 compares the internal resistance change and

capacity retention of two symmetric cells. These two symmetric cells have the same build-up and cycling conditions except the improved cell have a 1-layer membrane and 1mm thick Nickle foam electrode. In Figure 3.2.27a, the improved cell showed only a 0.89 Ω internal resistance increase after ~150 hours cycling compared with a 3.04 Ω internal resistance increase for the control cell. The improved cell also showed better capacity retention as shown in Figure 3.2.27b. Capacity fade rate is 24%/month for the control cell after 150h cycling while the fade rate is 4.3%/month for the improved cell. The theoretical capacity of the control cell and improved cell is 35mAh. Because we observed variance of capacity decay rate between cells with the same build-up, so the absolute value of the improvement on capacity decay needs further verification. However, we are confident at the positive performance of the change on membrane layer and electrode thickness.



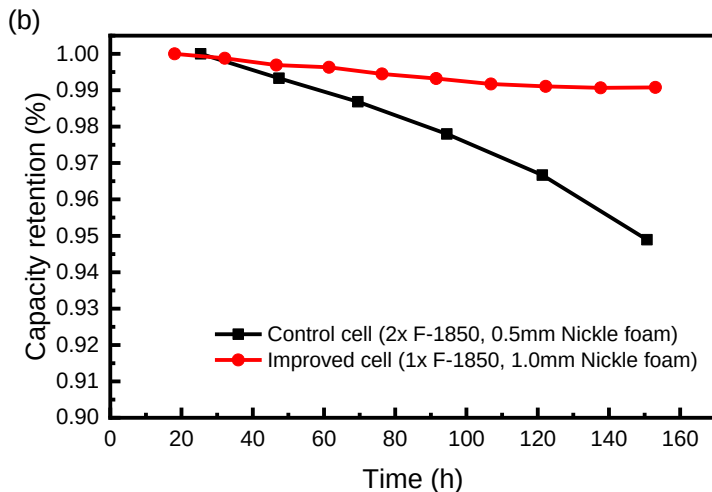


Figure 3.2. 27 (a)Comparison of internal resistance change for the control cell and improved cell. (b)Comparison of capacity retention for the control cell and improved cell.

Capacity decay of AqMn in flow cell testing: effect of electrolyte self-discharge

The 2 diagrams in Figure 3.2.28 demonstrate how the self-discharge in the electrolyte will cause an unbalanced capacity and thus results in a reversible capacity loss in the full cell cycling. In these diagrams, we assume a fast self-discharge rate (10% at each half-cycle) for the AqMn solution so the effect can be better demonstrated. Figure 3.2.28 further compares the effect of self-discharge in a symmetric cell and an asymmetric cell. In the symmetric cell, both catholyte and anolyte are AqMn and will have self-discharge during cycling. In the asymmetric cell, AqMn is used only as the catholyte and we assume there's no self-discharge in the anolyte. The comparison of the 2 diagrams shows that the symmetric cell test platform which introduces the AqMn as the anolyte will have accelerated capacity unbalance and therefore faster capacity loss

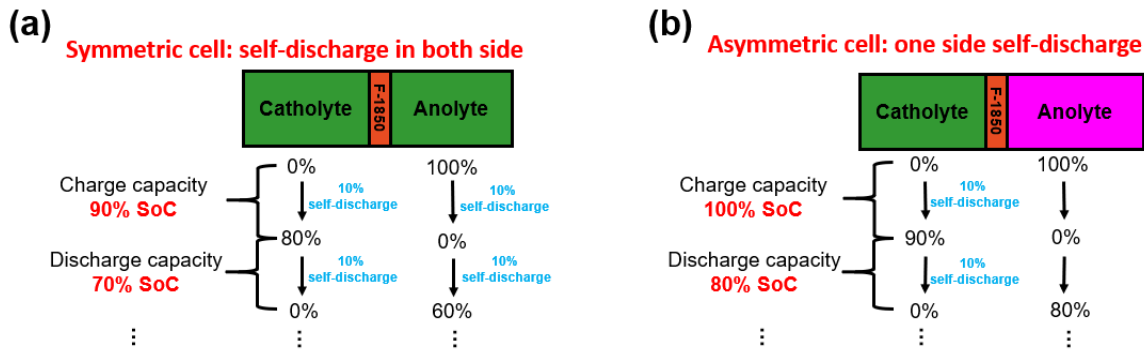


Figure 3.2. 28 The effect of self-discharge in a (a)Symmetric cell, and an (b)asymmetric cell.

In symmetric cell testing, the SoC of the catholyte and anolyte was measured at the end of the cycle at 28h and 100h. The results are shown in Table 3.2.2. The SoC window decreased from 86.5% at 28h to 69.1% at 100h due to the self-discharge of AqMn. The theoretical capacity is close, which suggests that in symmetric cell testing, the precipitation contributes much less to the capacity decay comparing with the self-discharge. This confirmed the effect of self-discharge demonstrated in Figure 3.2.28.

Table 3.2. 2 SoC of electrolytes at the end of the cycle

Time	Catholyte SoC	Anolyte SoC	Cycle capacity	Theoretical capacity
28h	3.01%	89.53%	55.42 mAh	64.05 mAh
100h	5.08%	74.15%	45.86 mAh	66.40 mAh

Next, we tried to use a solid electrode coupling with the AqMn catholyte and build an asymmetric cell. Comparing with the symmetric cell, a stable solid electrode can reduce the capacity loss due to the self-discharge of AqMn on the anolyte. We first tried $\text{Na}_{0.44}\text{MnO}_2$ (NMO), which is a Na ion intercalation material that has been used in aqueous

Na ion batteries. Figure 3.2.29a shows the X-ray diffraction (XRD) pattern for the synthesized and it agrees well with the pattern reported in the literature[116] as shown in Figure 3.2.29b.

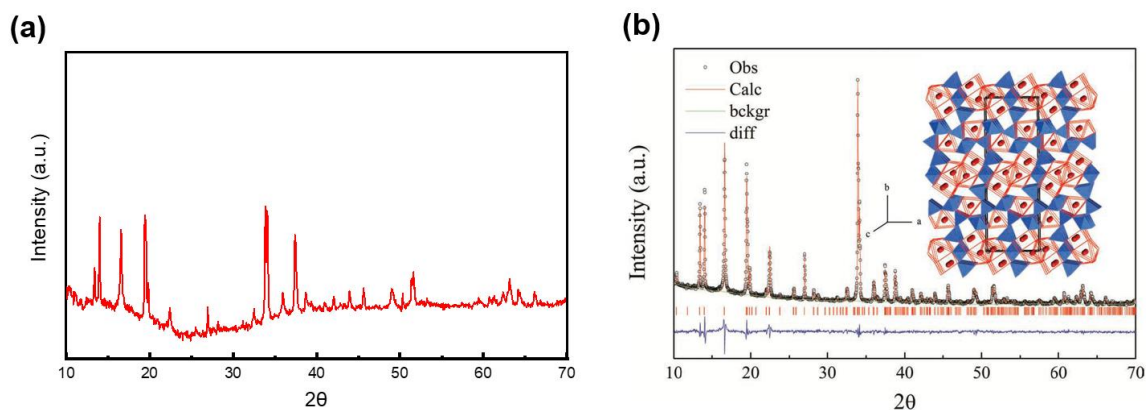


Figure 3.2. 29 X-ray diffraction pattern of (a)synthesized $\text{Na}_{0.44}\text{MnO}_2$ and (b) $\text{Na}_{0.44}\text{MnO}_2$ reported in literature.[116]

The electrodes were prepared by mixing 80 wt% $\text{Na}_{0.44}\text{MnO}_2$ powder with 16 wt% conductive carbon and 4 wt% Polytetrafluoroethylene (PTFE). The initial electrochemical test of the NMO electrode was performed in a symmetric H cell. NMO electrode was immersed in 1M Na_2SO_4 solution on both sides and an Ag/AgCl reference electrode is also immersed on the working electrode side. The diagram and cell setup are shown in Figure 3.2.30a. The voltage profile of NMO (Figure 3.2.30b) shows three separate plateaus due to the phase transitions upon Na ion extraction/insertion. This accords well with the relative potentials published in literature except the polarization is larger than that in literature, which is possibly due to the higher ohmic resistance of the H cell.

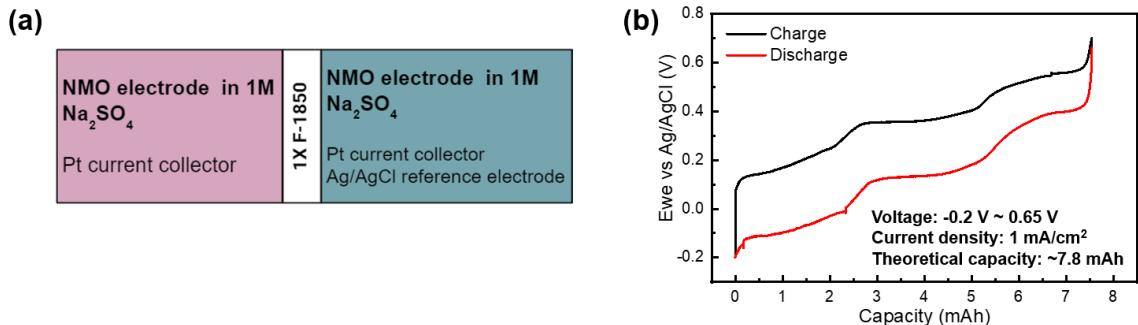


Figure 3.2. 30 (a)Diagram of an NMO symmetric cell and (b) Voltage profile of $\text{Na}_{0.44}\text{MnO}_2$ in the NMO symmetric cell.

Then the AqMn-NMO full cell was build and tested (diagram shown in Figure 3.2.31). In this cell, the NMO working electrode in 1M Na_2SO_4 solution was coupled with the AqMn counter electrolyte by an F-1850 membrane. Graphite current collector and Nickle foam electrode were used in the AqMn side and Pt current collector was used on the NMO side. Note that the AqMn solution used in this cell is sodium-based.

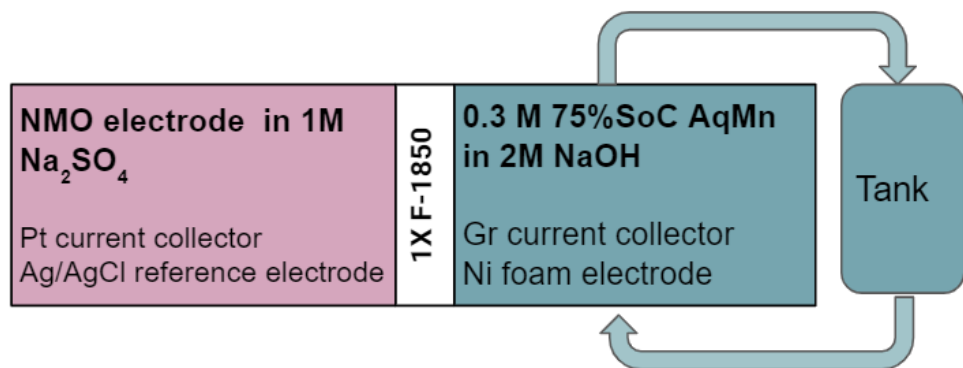


Figure 3.2. 31 AqMn-NMO full cell diagram

The full cell was electrochemically cycled at a current density of 1.5mA/cm². Cutoff voltage for the NMO working electrode was set to -0.1V~0.7V vs Ag/AgCl reference electrode. Figure 3.2.32 shows the voltage profile of the NMO electrode and AqMn

electrolyte. During the 1st cycle, the 3 plateaus of the NMO electrode were well presented. However, starting from the 3rd cycle, capacity decay of the NMO electrode was severe. After cycling, no color change was observed on the NMO side. This suggests that the AqMn crossover to the NMO chamber is very limited. The electrolyte in the NMO chamber showed a pH>13 measured by a pH test strip. The decreased chemical/electrochemical stability of the NMO electrode at a highly alkaline solution is probably the reason for the capacity decay.

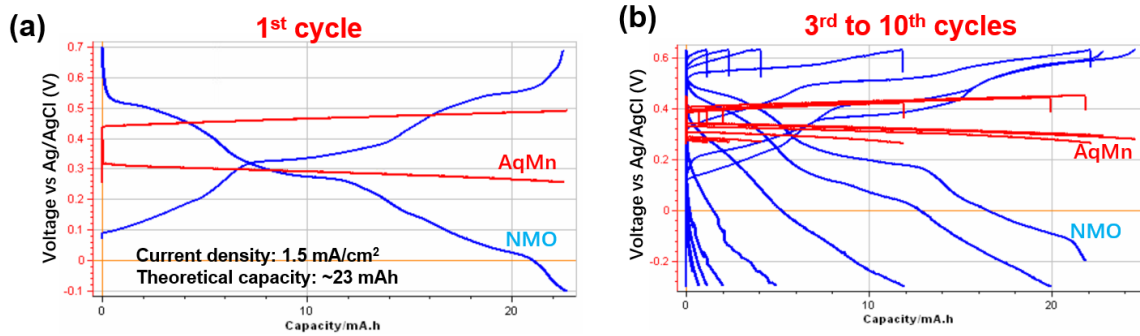


Figure 3.2. 32 Voltage profile of NMO electrode and AqMn electrolyte in the full cell for the (a)1st cycle and (b) 3rd to 10th cycle.

3.2.5 Numerical simulation of the AqMn-AqMn flow cell

In this part, a numerical model is built to simulate the cycling of an AqMn-AqMn flow cell. In experiments, the cells are cycling under constant voltage and cut off at a certain current. The purpose of this model is to estimate how the self-discharge rate of the AqMn solution will affect the electrochemical performance of the AqMn solution, including the capacity decay, current profile, discharge time...

The key relationship during the electrochemical cycling of the AqMn solutions is:

$$OCV_t + i_t \cdot R_{int} + \eta_0 = V_{appl} \quad (3.2.11)$$

Where the OCV_t is the open-circuit voltage of the flow cell at time t . i_t is this current of the cell at time t . R_{int} is the internal resistance of the flow cell. η_0 is the activation overpotential for the cell and V_{appl} is the applied voltage on the flow cell. The relationship stands during the whole cycling process. Discretize the problem in the time dimension with a short time step $\Delta_t = t_{x+1} - t_x$:

$$SoC_t = SoC_{t-1} + \frac{i_t \cdot \Delta_t}{Cap_{theoretical}} - selfdischarge_rate \cdot \Delta_t \quad (3.2.12)$$

$$OCV_t = E_0 - 0.0591 \cdot \log_{10} \frac{1 - SoC_t}{SoC_t} \quad (3.2.13)$$

$$i_{t+1} = \frac{V_{appl} - (WE_OCV_t - CE_OCV_t) - \eta_0}{R_{int}} \quad (3.2.14)$$

In Equation 3.2.12, the SoC of the catholyte at the time t is expressed as the SoC at time $t-1$ plus the increased SoC during the time step due to the current charging and minus the SoC change due to the self-discharge of the catholyte. In Equation 3.2.13, the open-circuit voltage at time t is calculated by the Nernst equation using the open-circuit voltage at time t . And Equation 3.2.14 is another form of Equation 3.2.11.

The equations are solved with Python using a “while” loop. Figure 3.2.33 shows the code of main loops to solve the current during the charging and discharging process.

```

while current > 0.5e-3:
    we[0] = we[0] + current*1000*timestep/total_cap - hour_rate*timestep
    we[1] = E0 - 0.0591* np.log10((1-we[0])/we[0])
    ce[0] = ce[0] - current*1000*timestep/total_cap - hour_rate*timestep
    ce[1] = E0-0.0591* np.log10((1-ce[0])/ce[0])
    current = (E_app-(we[1]-ce[1])-overp)/int_res
    t +=timestep
    t_abs +=timestep
    time.append(t_abs)
    i_t.append(current)

```

Charge

```

while current < -0.5e-3:
    we[0] = we[0] + current*1000*timestep/total_cap - hour_rate*timestep
    we[1] = E0 - 0.0591* np.log10((1-we[0])/we[0])
    ce[0] = ce[0] - current*1000*timestep/total_cap - hour_rate*timestep
    ce[1] = E0-0.0591* np.log10((1-ce[0])/ce[0])
    current = (E_app-(we[1]-ce[1])+overp)/int_res
    t +=timestep
    t_abs +=timestep
    time.append(t_abs)
    i_t.append(current)

```

Discharge

Figure 3.2. 33 Code of main loops to solve the current change of an AqMn-AqMn flow cell

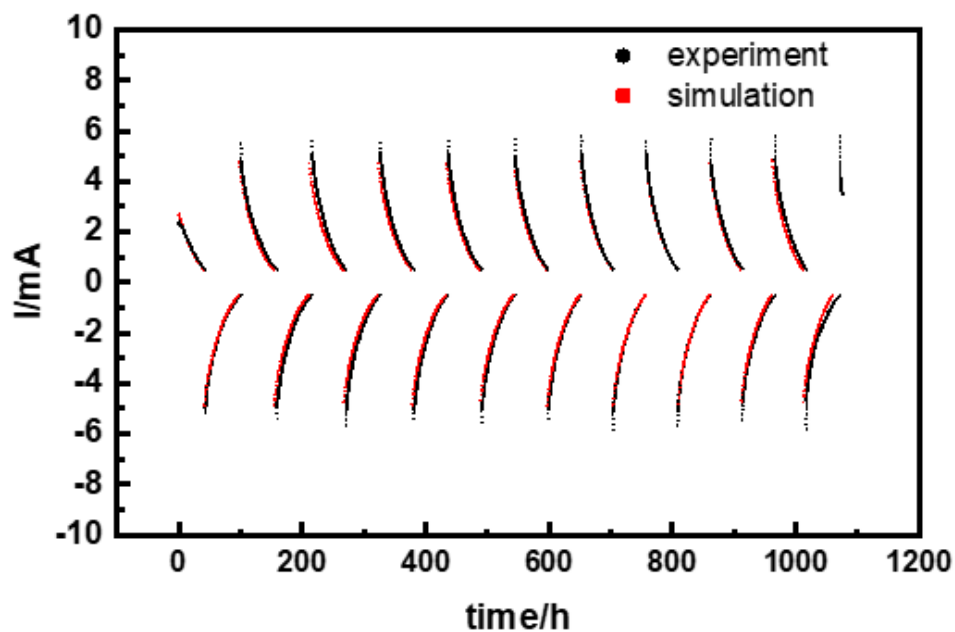


Figure 3.2. 34 Cycling performance of an AqMn-AqMn symmetric flow cell. Comparison of experiment results and simulation results.

To validate the numerical model, the simulation results are compared with an experiment result. In the experiment, the working and counter electrolyte are both 25 ml of 0.2M 50% SoC AqMn solution. The theoretical capacity of the catholyte is 200 mAh based on the full conversion between permanganates and manganates. The activation overpotential in the numerical model is determined to match the cycling capacity, which is not affected by self-discharge. The self-discharge rate is chosen so the simulation results match the capacity fade trend in the experiments. Internal resistance is from the EIS of the flow cell. A detailed parameter list is shown in Table 3.2.3.

Table 3.2. 3 Parameters used in the numerical model for the AqMn-AqMn flow cell

Parameter	Value
Self-discharge rate	10 %/month
Activation overpotential (η_0)	10 mV
Theoretical capacity	200 mAh
Internal resistance (R_{int})	30 ohms
Timestep	0.02 h
Applied voltage (V_{appl})	90 mV
Cutoff current	0.5 mA

In Figure 3.2.34, the current response from the simulation matches well with the recorded current from the experiment. Figure 3.2.35 shows the cycling capacity versus cycle number for both experiment and simulation. The simulation results matched well with the experiment results. For experiment results, the capacity goes up at the first 3 cycles and then starts to decrease while the simulation results show a decrease in capacity from the 1st

cycle. This is possible because of the gradual optimization of the catholyte flow and wetting of the cell components. Table 3.2.4 shows the change of SoC at the end of each cycle for the working and counter side from the simulation. The accessible SoC window decreases as the cycling goes, which is the main reason for the capacity decay.

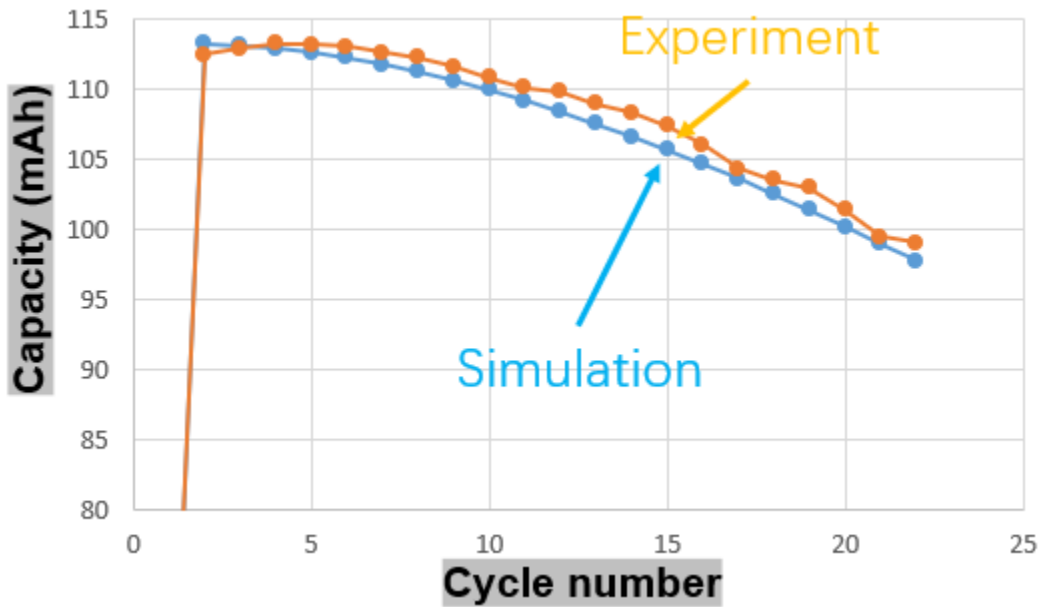


Figure 3.2. 35 Change of capacity versus cycle number

Table 3.2. 4 SoC of electrolyte versus cycle number from simulation

Cycle #	WE_end_SoC	CE_end_SoC
1	0.7777	0.2109
2	0.2033	0.7696
3	0.7612	0.1959
4	0.1887	0.7528
5	0.7441	0.1818
6	0.1751	0.7353
7	0.7263	0.1686
8	0.1623	0.7172
9	0.7080	0.1563
10	0.1505	0.6986
11	0.6892	0.1449
12	0.1395	0.6796
13	0.6700	0.1343

3.2.6 Reaction pathway of precipitation and solutions for mitigation

The disproportionation of manganate ions leads to the precipitation of colloidal MnO₂ and finally results in an irreversible decrease of the active materials.

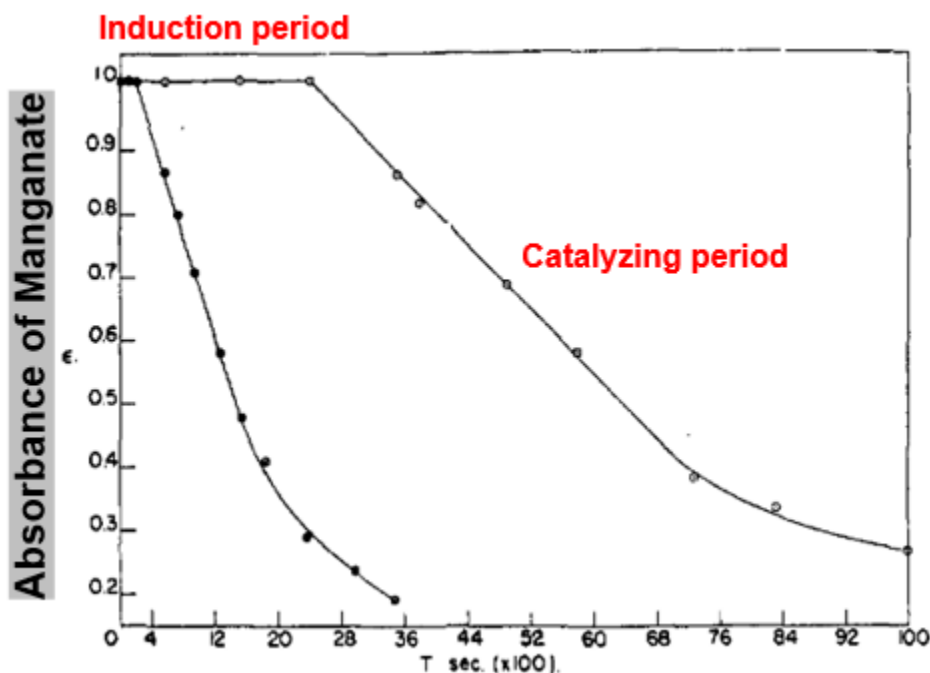
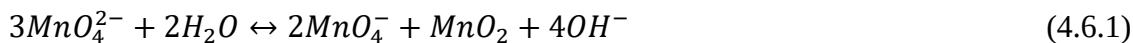


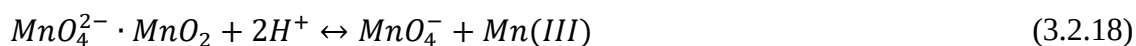
Figure 3.2. 36 Absorbance of manganate versus reaction time. The left line for 0.1 M OH⁻, right line for 0.2 M OH⁻. [117]

It was believed that the reaction, when starting species only include the reactants, first enters an induction period and then proceeds in a much faster way.[117] Figure 3.2.36 shows the change of manganate species with the reaction time. The reaction during the induction period is homogenous. The reaction rate is slow, and the induction period is increased with increasing pH. The reaction pathway during the induction period could be described as:





Both reactions are far to the left. After the induction period, the reaction enters a heterogenous catalyst period, where the MnO_2 acts as a heterogeneous catalyst and the reaction proceeds in a much faster way. The catalyzing period shows a zero-order dependency on manganate ions and a second-order dependency on hydrogen ions. The reaction pathway could be described as:



Reaction (4.6.4) is the adsorption on MnO_2 and is far to the right. The reaction rate of reaction (4.6.5) is the measured reaction rate.[117]

The equilibrium constant of the precipitation reaction (Equation 3.2.1) can be expressed as:

$$K_{eq} = \frac{[MnO_4^-]^2 [OH^-]^4}{[MnO_4^{2-}]^3} \quad (3.2.20)$$

Literature has reported that $K_{eq} = 53$ at a temperature of 45 °C.[118] And $K_{eq} = 16 \pm 7$ at temperature of 25 °C.[119]

Table 3.2. 5 Composition of the equilibrium mixtures and the equilibrium constants at 45 °C [118]

Expt.	Millimols per 1000 g. of water.			Equil. const.	Density at 45°.
	KMnO ₄	K ₂ MnO ₄	KOH.		
1.....	11.48	3.29	375.4	73.5	1.013
2.....	7.04	4.17	584.8	79.7	1.024
3.....	7.71	4.95	474.0	25.0	1.019
4.....	13.60	4.34	389.5	52.2	1.014
5.....	8.13	4.34	380.5	16.9	1.014
6.....	11.26	10.13	606.0	16.1	1.027
7.....	7.53	4.37	582.5	78.6	1.024
8.....	7.07	3.22	484.0	81.9	1.019
9.....	16.14	4.94	452.8	82.0*	1.018
10.....	15.67	4.08	446.5	90.4*	1.017
11.....	13.38	7.38	559.0	43.5*	1.023
12.....	13.65	6.77	534.1	48.8*	1.022
13.....	15.11	4.78	444.0	81.0*	1.017
14.....	14.84	5.16	446.0	63.4*	1.017
15.....	11.47	5.27	472.0	44.5*	1.019
16.....	12.07	8.69	604.0	29.5*	1.030
17.....	6.51	7.39	802.3	43.8	1.034
18.....	8.88	11.27	809.0	23.5*	1.038
19.....	5.30	6.26	804.4	48.1	1.038
20.....	9.56	9.94	805.0	39.3*	1.037
Means				{ 51.6 54.6*	

Table 3.2. 6 Equilibrium constant of the reaction between manganate, permanganate and hydroxide ions at 25 °C[119]

[OH ⁻] $\times 10^3$	[MnO ₄ ⁻] $\times 10^3$	[Ba ⁺⁺] $\times 10^3$	[MnO ₄ ⁻⁻] $\times 10^7$	Days in thermostat	K _{eq.}
4.131	0.0331	1.06	2.32	9	25.5
2.715	.0709	1.11	2.22	7	24.6
1.957	.1848	0.69	3.56	6	11.1
2.077	.3466	.43	5.72	31	12.0
1.297	.3839	.72	3.42	36	10.5
0.957	.4613	1.03	2.39	9	13.8
1.082	.8714	0.69	3.57	6	22.9
0.848	.8742	.71	3.46	17	9.5
Mean					16.2

Given the reaction pathway, several possible strategies are proposed to mitigate the precipitation of MnO₂. First, extending the induction period could be helpful. The reaction rate is much slower during the initial induction period. The length of the induction period is strongly dependent on the pH of the solution. Higher pH would increase the induction period. However, the self-discharge rate will also increase. A detailed study on pH's effect

on self-discharge rate and precipitation rate will be necessary to determine the best pH for the AqMn solution. Besides, Mn(V) is an intermediate product during the induction period. The use of agents to form a complex with Mn(V), could also prevent the precipitation of MnO₂ and extend the induction period. Secondly, deactivate/destabilize the MnO₂ during the catalyzing period can also mitigate the precipitation rate. The use of agents to form a complex with Mn(III) can decrease the reaction rate of reaction (4.6.2) and (4.6.3).[120]

The adsorption of multivalent ions on MnO₂ will destabilize the MnO₂. [121-124] This will decrease the catalytic effect of MnO₂. However, the inactive MnO₂ will favor the forward reaction of the precipitation. The tradeoff between these 2 effects needs to be further investigated. Possible additive for metal ions sorption on the MnO₂ includes: Mn²⁺, Mg²⁺, Ca²⁺, Ba²⁺, Sr²⁺, Zn²⁺, Ag⁺, Pb²⁺, and Cd²⁺. Besides, the adsorption of some organic compounds on MnO₂ will also destabilize the MnO₂. Some neutral and cationic molecules show a good adsorption level on MnO₂. [125]

Chapter 4 - A semi-solid Sodium-sulfur flow

battery

Disclosure:

A major part of this chapter has been published by Wiley-VCH: Yang, Fengchang, Seyed Mohammad Ali Mousavi, Tae K. Oh, Tairan Yang, Yingqi Lu, Charles Farley, Robert J. Bodnar, Li Niu, Rui Qiao, and Zheng Li. "Sodium–sulfur flow battery for low-cost electrical storage." *Advanced Energy Materials* 8, no. 11 (2018): 1701991.

4.1 Introduction

Rechargeable batteries are promising solutions to provide energy storage services for renewable energy generation which is inherently intermittent. Lithium-ion batteries, flow batteries, and high-temperature Na–S batteries are currently three of the most deployed technologies for grid-scale energy storage.[126-128] For conventional redox flow batteries, the redox-active chemicals are dissolved in solutions and stored in external tanks. The catholyte and anolyte are pumped into a power stack where a redox reaction happens, and the chemical energy is converted to electrical energy. The energy density of an aqueous solution-based redox flow battery is limited by the solubility of the redox-active materials. For example, vanadium redox flow [46, 47, 51, 112] batteries normally have a concentration of 1-2 M. Besides, the operation voltage window for aqueous-based redox flow batteries will be limited by the electrolysis voltage of water. This will finally result in

a low energy density. Semi-solid flow batteries utilize the suspension of redox-active materials.

The suspension is composed of nano-scale carbon, which forms a continuous conductive network, and densely packed larger solid active materials particles suspended in electrolytes.[66, 69, 129-131] The suspension form of active material can significantly increase the energy density by storing energy in the solid phase instead of the liquid phase that increases the nominal molar concentration of redox-active species. Besides, the use of organic solvent instead of water can expand the electrochemical window of the flow battery and therefore increase the energy density.

For conventional high-temperature (HT) sodium-sulfur batteries used in large-scale energy storage, the theoretical specific energy is 760 Wh/kg and the discharge current density can go up to 200-300 mA/cm². A typical tubular design of an HT Na-S battery is shown in Fig.5.1.1. In a sealed system, molten sodium anode is contained in a sodium β -alumina (β -NaAl₁₁O₁₇) tube which is surrounded by the sulfur cathode. The high ionic conductivity and good insulating property of the solid electrolyte at 300°C allow fast Na ion transportation transport between anode and cathode and also prevent self-discharging. During discharge, liquid sodium is oxidized and forming Na⁺ ions. These Na⁺ ions migrate through the sodium β -alumina solid electrolyte and form sodium polysulfide with the reduced sulfur species. The high operating temperature leads to increased thermal management and also many safety and reliability-related issues. Room-temperature sodium-sulfur batteries have been studied intensively to address these issues but still facing several challenges so far: the low chemical reactivity, the polysulfide shuttle effect, and the dendrite growth of Na metal. Besides the conventional high-temperature Na-S battery and

the room-temperature battery, the intermediate temperature Na-S battery offers an alternative strategy. The concept was first introduced in the 1980s[132]. Lu et.al. [133] demonstrated a static Na-S battery working at intermediate temperature (150°C). The Na-S battery used the dense β'' -Al₂O₃ solid membrane as separator and tetraglyme as catholyte solvent. The shuttling effect of polysulfides is suppressed by the solid electrolyte separator. The cell shows an initial discharge capacity of 473 mAh/g and 70% of the capacity retained after 60 cycles.

In this chapter, a semi-solid sodium-sulfur flow battery is developed. This cell utilizes flowable sulfur-based suspension and molten sodium as catholyte and anolyte. The power stack of the flow battery works at intermediate temperature (150°C) while the storage tank of the battery is near room temperature. A static Na-S semi-solid battery was assembled and tested first. Then a Na-S semi-solid flow cell was assembled. The flow cell was cycled with a two-aliquots and three-aliquots intermittent flow

4.2 Battery design

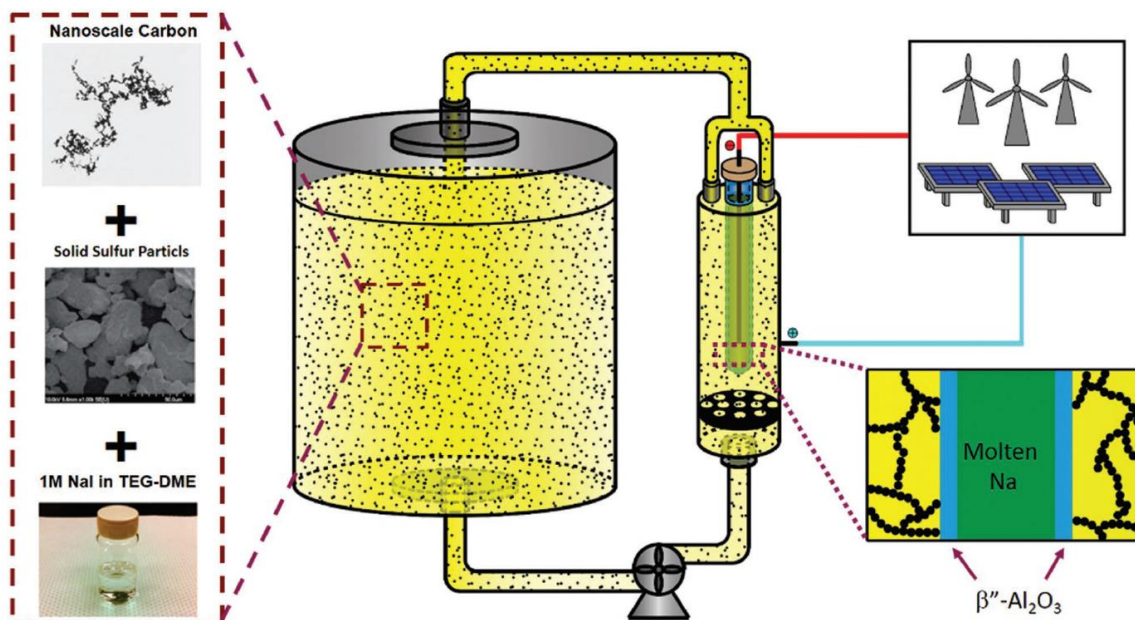


Figure 4.2. 1 A schematic of the semi-solid Na-S flow battery. Nanoscale carbon picture is reproduced with permission.[129] Copyright 2011, Wiley-VCH. Solid sulfur particles picture is reproduced with permission.[134] Copyright 2015, Royal Society of Chemistry.

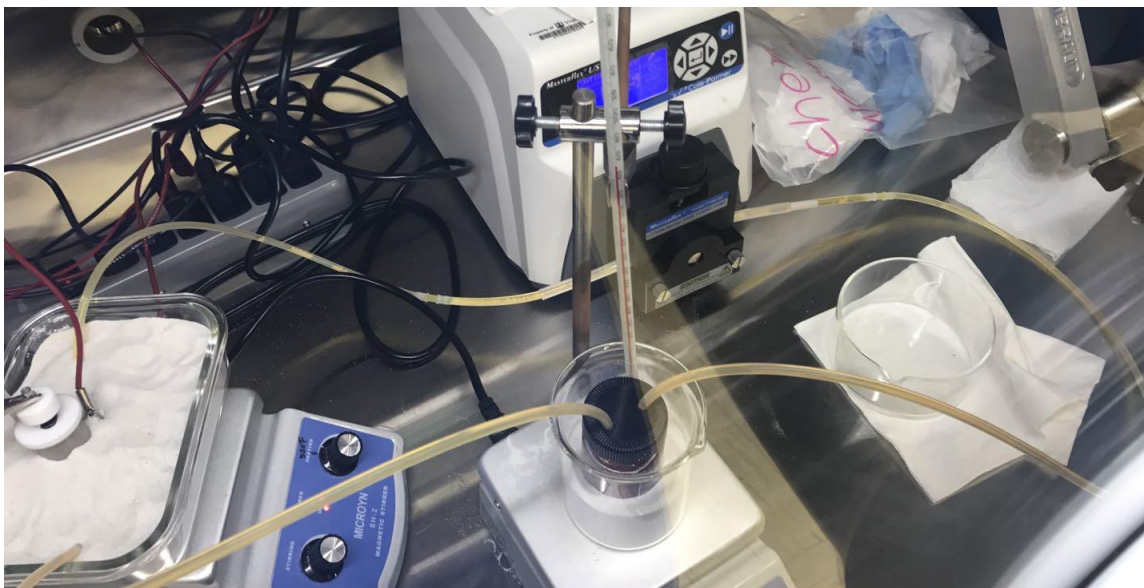


Figure 4.2. 2 The experiment setup of the semi-solid Na-S flow cell in an argon-filled glovebox.

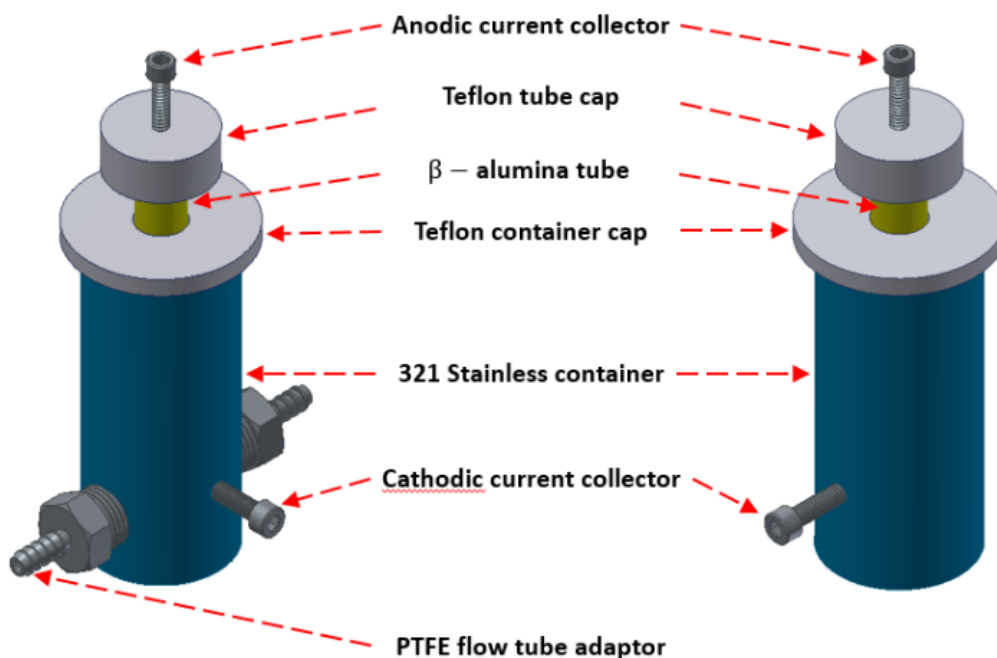


Figure 4.2. 3 Schematic drawings of Na-S flow battery cell assembly (left) and static battery cell assembly (right). [68]

Figure 4.2.1 shows a schematic drawing of the proposed semi-solid Na-S flow battery. The flowable semi-solid sulfur suspension is used as a catholyte and stored in an external storage tank. A solution pump can pump the sulfur suspension into the current-extracting reactor. The semi-solid suspension contains nanoscale carbon particles and solid sulfur particles dispersed in NaI tetraglyme solution. The design of the reactor (power stack) is shown in Figure 4.2.1. On the left is the reactor used in the flow battery setup and on the right is the reactor used in the static battery setup. In general, the reactor has a stainless steel metal casing to house the semi-solid sulfur suspension. A β'' - Al_2O_3 (abbreviated as

BASE) tube with metal sodium filled inside is inserted into the SS casing and serves as the separator of the cell. The β -alumina, with a composition of $\text{Na}_2\text{O} \cdot (5 \sim 11)\text{Al}_2\text{O}_3$, is a non-stoichiometric compound of Na_2O and Al_2O_3 with a layered crystalline structure. β -alumina typically includes $\beta\text{-Al}_2\text{O}_3$ ($\text{Na}_2\text{O} \cdot (9 \sim 11)\text{Al}_2\text{O}_3$) and $\beta''\text{-Al}_2\text{O}_3$ ($\text{Na}_2\text{O} \cdot (5 \sim 7)\text{Al}_2\text{O}_3$). [135] The $\beta''\text{-Al}_2\text{O}_3$ has higher sodium ionic conductivity due to its higher sodium ratio and is typically used in the HT Na-S battery system. However, the β'' phase is not stable near the sintering temperature. Some divalent or monovalent cations such as magnesium or lithium are added to replace a fraction of Al^{3+} ions and increase the stability of $\beta''\text{-Al}_2\text{O}_3$. The composition for magnesium-replaced $\beta''\text{-Al}_2\text{O}_3$ is represented by $\text{Na}_{1+x}\text{Mg}_x\text{Al}_{10-x}\text{O}_{17}$, where the value of x is typically 0.67.

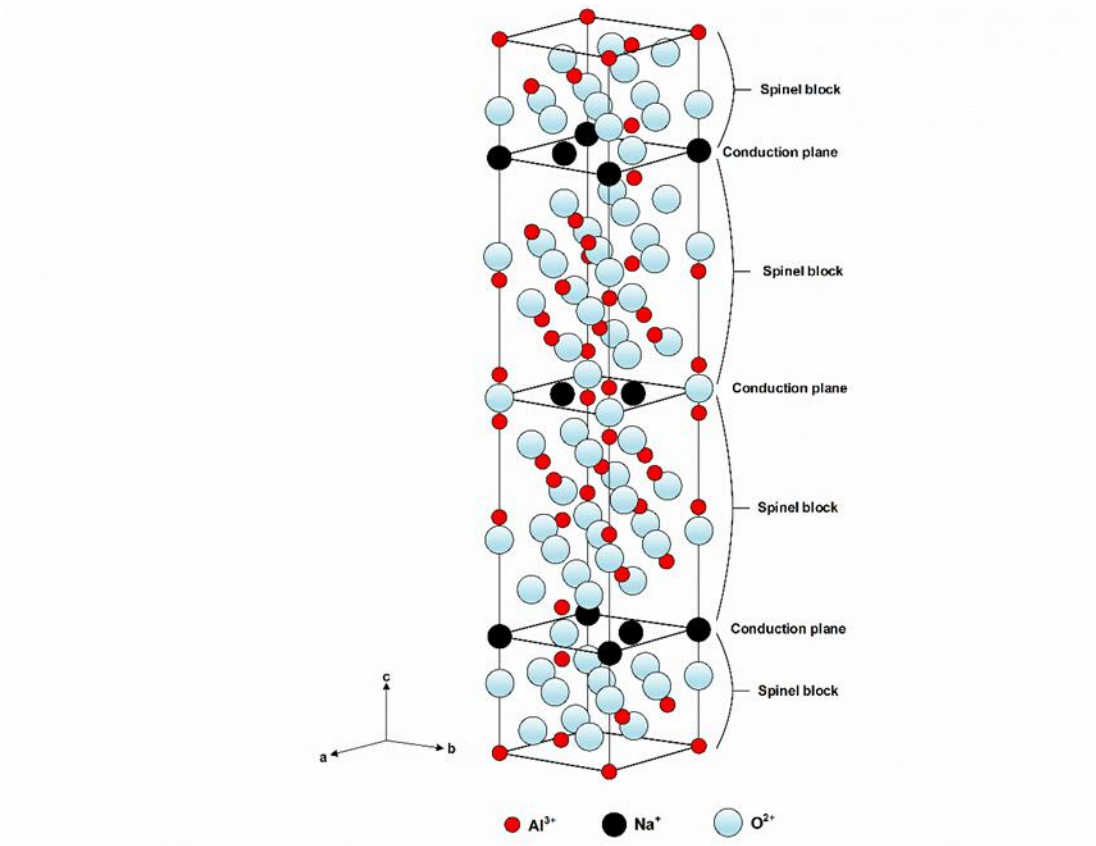


Figure 4.2. 4 Schematic structure of $\beta''\text{-Al}_2\text{O}_3$ [136]

Fig.5.2.1 presents the ideal structure of β'' - Al_2O_3 . The structure consists of densely packed spinel-type blocks, separated by loosely packed Na ion-containing layers (conduction plane) where the Na ions can move freely under the electric field. The Al^{3+} ions occupy both octahedral and tetrahedral interstices formed by the oxygen ions. This layered structure of β'' - Al_2O_3 indicates the conductivity of Na ions is two-dimensional. The Na ion's mobility is high within the conduction plane (perpendicular along the c axis) while the mobility is zero parallel to the c axis. The ionic conductivity of β'' - Al_2O_3 can reach ~ 0.4 S/cm at 300°C . For the production of β'' - Al_2O_3 electrolyte, composition design and synthesis process control are critical to avoid the defects of β'' - Al_2O_3 (e.g. composition deviation, impurity phase, and grain boundary). [136]

As shown in Figure 4.2.1, the cell is buried in a thermostated sand bath to 3/4 of the body and is maintained at 150°C (controlled by a hot plate, Microyn Technologies Inc., USA, for electrochemical tests) to keep the sodium at the molten state during operation. For intermittent flow mode, each suspension aliquot is pumped into the reactor and then gets pumped out after charge or discharge. For the operation of a static cell, a fixed amount of sulfur suspension is sealed inside the reactor cell and the cycling test is performed. The static and flow cell body was machined using Stainless Steel 321 and Teflon as shown in Figure 4.2.3. For the static cell assembly, 1 ml of cathode suspension was injected into the cell case using a syringe. Then the prepared sodium-filled BASE tube with anode current collector assembly was inserted into the cell case. For the flow cell assembly, two PTFE tubes connect the outlet and inlet of the cell to a glass bottle that serves as a suspension reservoir. The tubes are connected by a peristaltic pump (MasterFlex®, Cole-Palmer, USA)

which can pump the suspension forward and backward. Then the sodium-filled BASE tube with anode current collector assembly was inserted into the cell case leaving about 1 ml vacant space for suspension flow. The glass bottle reservoir will be filled with sulfur suspension at room temperature which is pumped into the cell case through the Teflon tube. For the flow cell case, the suspension reservoir maintains at ambient temperature without heating. The cell assembly and electrochemical measurements were done in the Argon-filled glove box. All electrochemical tests were performed using a Biologic SP-150 single channel potentiostat

The materials used in the experiments and cell assembly include: 1,2-Dimethoxyethane (DME, 99+%), tetraethylene glycol dimethyl ether (TEGDME, 98+%), sulfur powder (precipitated, 99.5%), sodium sticks (99%), sodium iodide (metals basis, 99.9%) and sodium sulfide (anhydrous) were purchased from Alfa Aesar. β'' -Al₂O₃ solid electrolyte (BASE) tubes were used as received from Ionotec Ltd, UK. The conductive carbon additives (Ketjen Black EC-600JD) were provided by Azko Nobel Polymer Chemicals LLC, USA. The cathode sulfur suspension is composed of sulfur and 1~2 vol% Ketjen in 1M NaI TEGDME solution. The calculated amount of sulfur powder and Ketjen Black was first homogeneously mixed in a 20 ml glass vial and then 1 M NaI in TEGDME electrolyte was added to the mixture to form a suspension. The suspension was sonicated (MTIEQ-VGT, USA) for 30 minutes before using. For the anode preparation, the BASE tube was inserted in the stainless-steel cell case buried in a thermostated sand-bath at 150 ± 5 °C in an Argon-filled glovebox (MBRAUN, USA) with oxygen and water levels below 10 and 0.1 ppm, respectively. The sodium metal stick was cut into chunks to fill 3/4 of the BASE tube. The stainless-steel rod was inserted into the molten sodium through a Teflon cap as

shown in Figure 4.2.3 to serve as the anode current collector. Teflon tape was used between the BASE tube and the Teflon container cap to decrease the evaporation of sulfur suspension during the battery operation.

4.3 Battery testing results

To evaluate the electrochemical performance of the semi-solid Na–S battery, we first tested the charge/discharge of this battery with 1 m sulfur nominal concentration under nonflow conditions at 150 °C (Static cell). Since the nominal concentration of elemental sulfur is below the solubility of sulfur in tetraglyme (2.3 M)[133], the elemental sulfur should exist as a dissolved state at the beginning of the discharge.

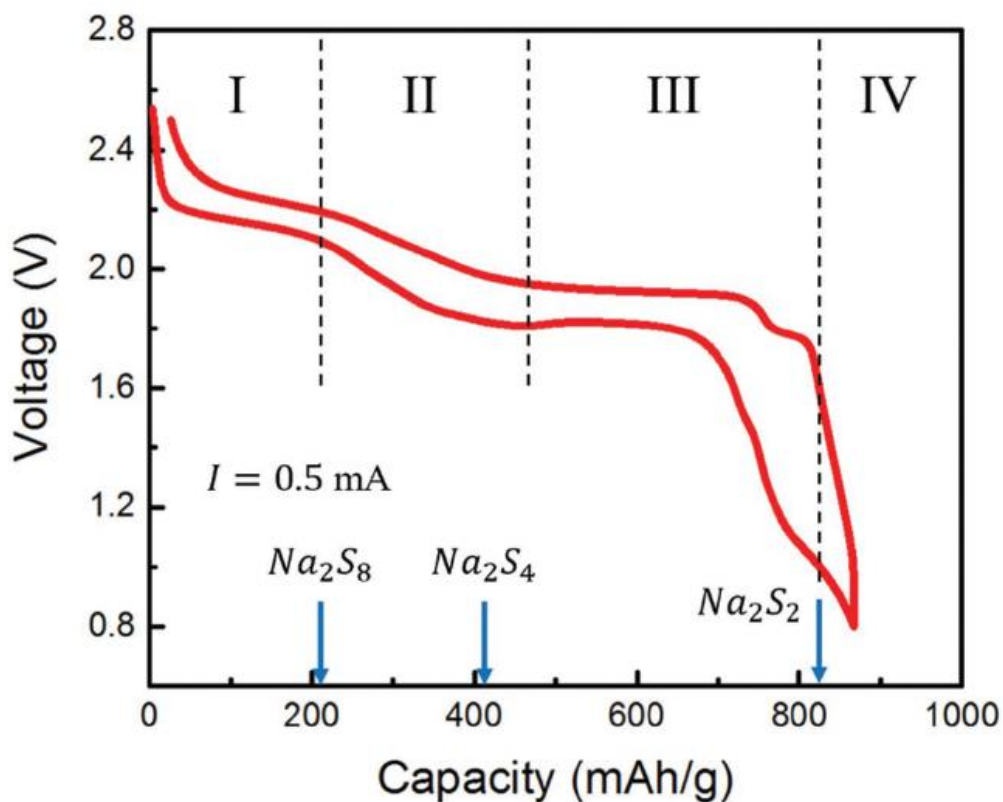


Figure 4.3. 1 Initial discharge and charge profile of semi-solid Na–S battery.

Nominal 1 M sulfur concentration.

The static Na-S cell is discharged to 0.8 V at a constant current of 0.5 mA. The suspension-covered membrane area is around 1.2 cm² (translate to a current density of 0.42 mA/cm²). The blue arrows on the capacity axis indicate the theoretical capacities of different polysulfides as the final discharge product. The sulfur suspension catholyte is composed of 1 m sulfur and 1 vol% Ketjen in 1 m NaI TEGDME solution. The discharge capacity is calculated based on the mass of sulfur, both dissolved and undissolved, in the initial catholyte.

The cell shows an initial discharge capacity of 864 mAh/g. This capacity is higher than that of the intermediate temperature Na–S batteries reported previously (e.g., 473 mAh/g was reported by Lu et al.) and close to the theoretical capacity of the cell when Na₂S₂ is considered as the final discharge product (836 mAh/g). The high discharge capacity indicates a high sulfur utilization in the semi-solid Na–S cell. Elemental sulfur, instead of using elemental sulfur mixed with polysulfides, is used in the present cell to prepare the starting catholyte. This helps with the high discharge capacity of the proposed Na-S cell.

The discharge process can be divided into 4 regions based on the voltage profile, similar to the room-temperature Na–S batteries.[137-139] Region I begins from the start of the discharge and ends at the 1st plateau, corresponding to a capacity of ≈ 200 mAh/g. This region features a sharp drop of the cell voltage at the beginning of discharging and a subsequent weak plateau between 2.2 and 2.1 V. Similar weak plateau has been observed in room-temperature Na–S and Li–S batteries and is often attributed to the reaction $S_8 +$

$2e^- \rightarrow S_8^{2-}$. [138, 139] Besides, the discharge capacity of this region also supports this reaction mechanism. Region II starts from ≈ 200 mAh/g and ends at the theoretical capacity for Na_2S_4 . In this slope region, the voltage decreases from 2.1 to 1.82 V. The electrochemical reaction at this region can be attributed to the gradual degradation of S_8^{2-} to S_n^{2-} ($4 \leq n < 8$) . [133, 138, 139] The electrochemical formation of lower order polysulfides and the chemical equilibrium between polysulfides are the main factors that determine the voltage profile in this region. Previous studies indicated that the reaction product for this discharge region is dominated by Na_2S_4 . [133] The discharge capacity in our cell also supports such a conclusion.

Region III starts with a plateau at 1.82 V and then is followed by a sudden drop of the cell voltage toward 1.6 V. The plateau in region III closely resembles that reported in prior studies of intermediate and room temperature Na–S batteries. [133, 138] The dominant electrochemical reaction in this plateau is the reduction of S_4^{2-} to S_2^{2-} . Short chain polysulfides have low solubility. Once the metal polysulfide species exceed their solubility, they precipitate in the solution and can reach chemical equilibrium with the dissolved polysulfide and thus maintains the cell voltage at a constant value. [140, 141] At the end of region III, a sharp drop of voltage to 1.6 V appears. This voltage drop is possibly attributed to the solid-solid reaction between Na_2S_2 and Na_2S or the passivation of the active surface area caused by the precipitation of Na_2S_n ($n \leq 2$) precipitating. [133]

Region IV shows a further drop of the cell voltage to around 0.8 V. The discharge capacity has exceeded the theoretical capacity for Na_2S_2 , which suggested that the reduction of Na_2S_2 to Na_2S happened. The charging voltage profile also shows similar regions which indicate that the cell has good reversibility.

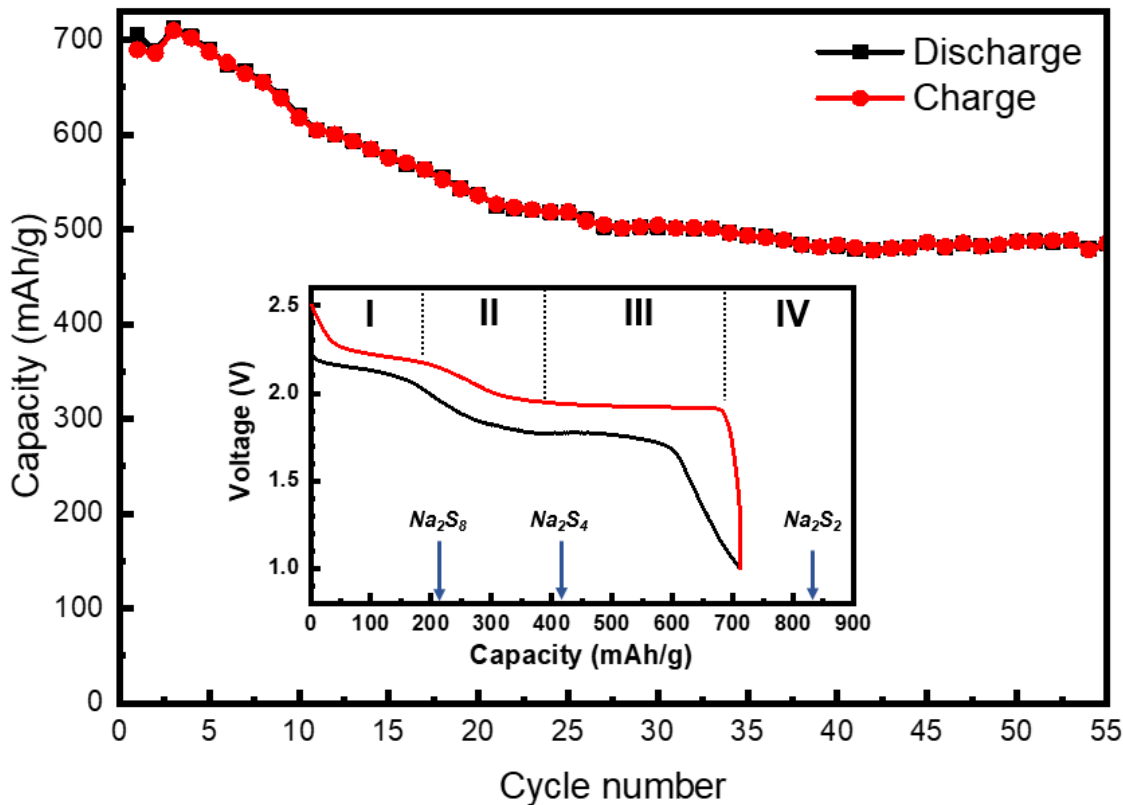


Figure 4.3. 2 The cycling performance of semi-solid Na-S static cell. The cell was cycled at 0.5 mA ($\approx C/4$) between 1 V and 2.5 V. The sulfur suspension catholyte is composed of 0.5 M sulfur and 2.5vol% Ketjen in 1M NaI TEGDME solution. The suspension-covered membrane area is around 2 cm². The charge and discharge voltage profile of the 3rd cycle is shown in the inset.

The electrochemical cycling performance of the Na-S cell was also tested using the static cell design. The sulfur suspension is composed of 0.5 M sulfur and 2.5 vol% Ketjen in a 1 m NaI tetraglyme (TEGDME) solution. Figure 4.3.1 shows the cycling performance of a semi-solid Na-S battery at 150 °C. The cell is cycled at a constant current of 0.5 mA ($\approx C/4$) between 1 and 2.5 V and the inset figure shows the voltage profile of the 3rd cycle. The cell shows a discharge capacity of 705 mAh/g for the 1st cycle and the capacity retention

is around 484 mAh/g after 55 cycles. The capacity fading mechanism is not clear at this stage and needs further characterization on the cycled electrode.

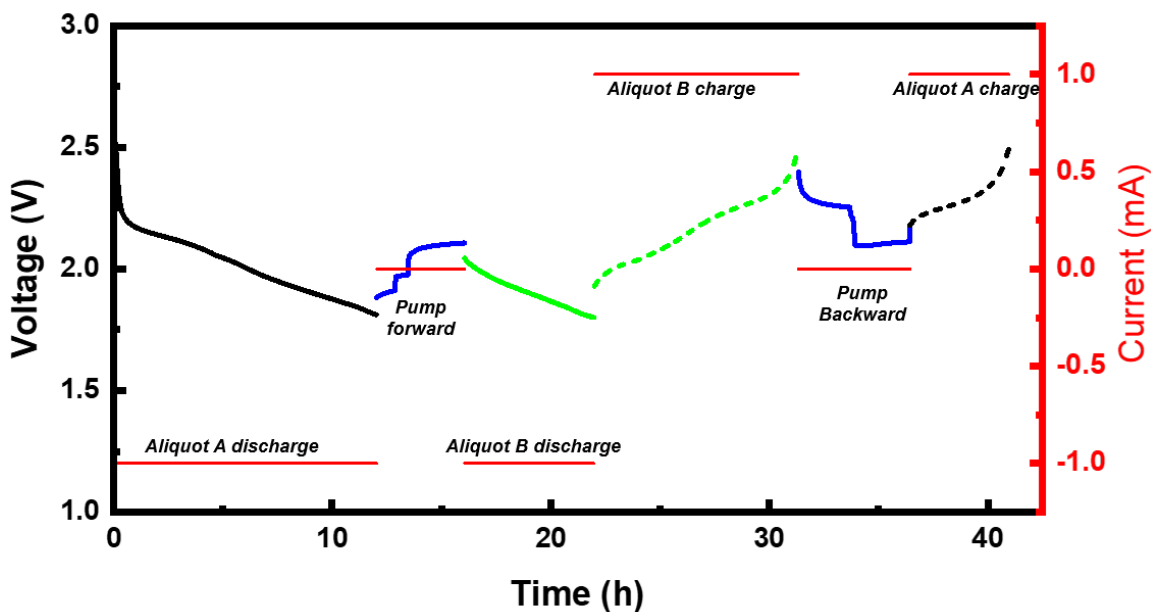


Figure 4.3. 3 Discharge–charge voltage profiles for Na-S flow cell setup with three aliquots intermittent flow. The cell is cycled between 1.8 and 2.5 V. The sulfur suspension catholyte is composed of 1 m sulfur and 1 vol% Ketjen in 1 m NaI TEGDME solution. The suspension-covered membrane area is around 1.2 cm². The aliquot A discharge capacity is around 420 mAh/g sulfur.

After testing the Na-S battery in the static cell and gaining insights into the reaction mechanism, the Na-S battery was then tested in the flow cell design. The electrode composition remains the same as used in a static cell. The suspension form of catholyte has a relatively high viscosity and mechanical energy dissipation happens if using continuous flow for battery operation.[131, 142] Therefore, an intermittent flow model was used for the semi-solid Na–S flow battery tests. In the following tests, a unit aliquot of the

suspension is equal to the volume in the SS cell body that can house the catholyte suspension.

Figure 4.3.3 shows the change of voltage and cell current as a function of time. for Na–S flow battery cycling between 1.8 and 2.5 V. The flowable sulfur suspension is composed of 1 m sulfur and 1 vol% Ketjen in 1 m NaI TEGDME solution. The cell is operated in a two-aliquots intermittent flow mode: (I) discharging aliquot A which is already replenished the electroactive region of the power stack; (II) pumping forward the catholyte forward so aliquot A is replaced by aliquot B; (III) discharging aliquot B; (IV) charging aliquot B; (V) pumping backward the catholyte so aliquot B is replaced by aliquot A; (VI) charging aliquot A. Black solid lines and dashed lines are discharge and charge voltage curves, respectively, for aliquot A. Green solid lines and dashed lines are discharge and charge voltage curves, respectively, for aliquot B. Blue lines indicate the voltage relaxations after each discharge or charge and the onset of the suspension flow.

The discharging time for aliquot A is longer than that of aliquot B, indicating a larger discharge capacity of aliquot A. Two underlying reasons might cause this phenomenon: 1) The replacement of aliquot A with aliquot B during the pumping is incomplete. Some of the suspension from aliquot A still stays inside the electroactive region of the power stack due to geometrical hindrances (e.g., sharp edges at inlet and outlet); 2) The charge redistribution by diffusion. Since aliquot A and B are still electrically connected by the small tubing, charged suspension of aliquot B in the power stack region could equilibrate with the discharged suspension of aliquot A outside of the electroactive zone slowly. During step IV of the two-aliquot intermittent flow, the charging time of aliquot B is longer than its discharging time. Possibly because of charge redistribution with the discharged

suspension of aliquot A as described above. The lower charge capacity of aliquot A in step VI also aligns well with this interpretation.

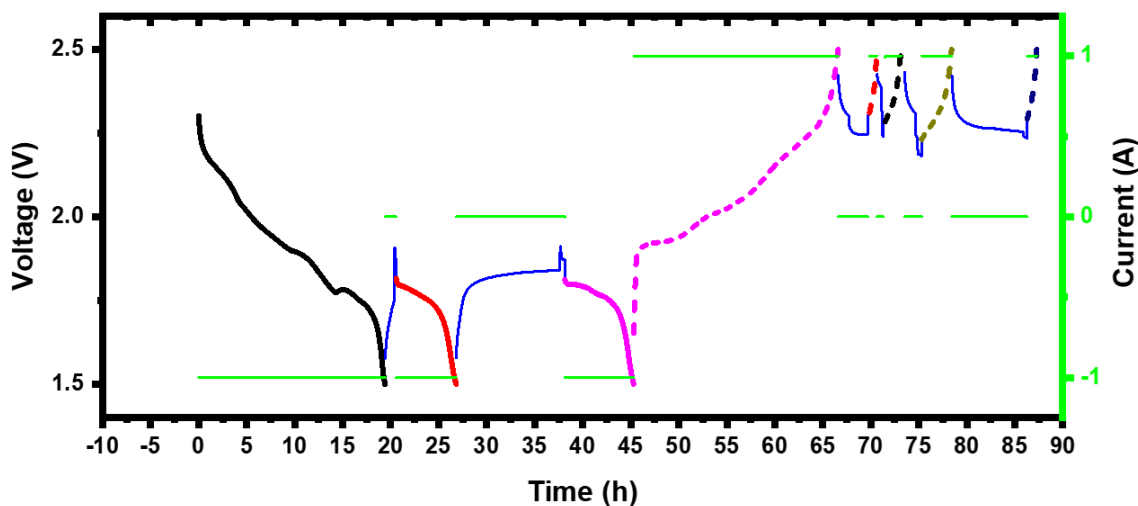


Figure 4.3. 4 Discharge-Charge voltage profiles of three-aliquots intermittent flow cell cycled between 1.5 V and 2.5 V.

The cutoff voltage for the two-aliquot intermittent flow test is 1.8 V, which is higher than the voltage that leads to the sulfur precipitation region.

To increase the sulfur utilization, a 1.5 V discharge cutoff voltage is also tested. Figure 4.3.1 demonstrates the discharge and charge profile of a three-aliquots intermittent flow test. The cell is cycled between 1.5 and 2.5 V at a constant current of 1 mA. The suspension-covered membrane area is around 1.2 cm². The discharge capacity for Aliquot A is around 700 mAh/g sulfur. The coulombic efficiency for the two-aliquot and three-aliquot intermittent flow tests are 77% and 85%, respectively. The coulombic efficiency and discharge capacity could be further optimized by a better mechanical design of the flow cell body and more precise volume control of the pumping system.

4.4 Tech-economics analysis

In this section, a system-level model is developed for the performance and cost of the proposed Na-S flow battery. The key inputs of the cost model are experimentally verifiable performance parameters of the power stack and semi-solid sulfur suspensions based on the work presented in previous sections of this chapter.

System model

The system cost of the Na-S battery is made up of the following three parts in \$/kWh:

$$c_{system} = c_{reactor} + c_{chemicals} + c_{others}$$

where $c_{reactor}$ includes the cost of the casing, current collectors, and the solid electrolyte membrane in \$/kWh, $c_{chemicals}$ includes the cost of the catholyte and anolyte in \$/kWh and c_{others} is the cost of balance of plant and additional cost in \$/kWh.

Reactor cost

The reactor cost is calculated as follow:

$$c_{reactor} = \frac{c_a}{p \cdot t_d}$$

where c_a is the reactor cost per unit area in \$/m², p is the peak density of the Na-S battery in kW/m² and t_d is the discharge time in hours. The reactor cost c_a includes the cost of stainless steel casing, stainless steel current collectors, and the solid electrolyte membrane as tabulated in Table 4.4.1 For the peak power density, we investigated 5 different power densities: 8W/m², 66 W/m², 125 W/m², 1000 W/m², and 2500 W/m².

Table 4.4. 1 Semi-solid Na-S flow battery reactor components cost.

Component	Cost (\$/m ²)	Source
Stainless steel case	12.00	[143]

Seals, current collectors, and fittings	2.00	[144]
Separator (BASE)	100.00	[145]

Chemical cost

The chemical cost includes the cost of catholyte and anolyte. The catholyte sulfur suspension is composed of 1M/20M/15M sulfur and 1 vol% Ketjen in 1M NaI TEGDME solution. Table 4.4.2 shows the unit price of each component. The chemical cost was calculated by the following equation:

$$C_{\text{chemicals}} = \left(\frac{c_{\text{anode}} \left(\frac{\$}{\text{L}} \right) \cdot \frac{1 \text{ Ah}}{SC_{\text{anode}} \left(\frac{\text{Ah}}{\text{L}} \right)} + (c_{\text{catholyte}} \left(\frac{\$}{\text{L}} \right) + c_{\text{tank}} \left(\frac{\$}{\text{L}} \right)) \cdot \frac{1 \text{ Ah}}{SC_{\text{catholyte}} \left(\frac{\text{Ah}}{\text{L}} \right)}}{E_d} \right) \frac{1}{\varepsilon_{q,rt} \varepsilon_{v,d} \varepsilon_{\text{sys},d}}$$

Where SC_{anode} and SC_{cathode} are the specific capacity of anode sodium metal and the catholyte suspension in Ah/L respectively. E_d is the discharged energy in kWh and is calculated for a 1Ah

Battery. The cost of the tank C_{tank} is taken into account as 0.15\$/L[146] for the flowing catholyte. $\varepsilon_{\text{sys},d}$ is the energy efficiency of system which is assumed to have constant value of 0.94 based on literature.[147] The discharge voltage efficiency is defined as $\varepsilon_{v,d} = V_d/V_{OCV}$ where V_d is the discharge voltage and V_{OCV} is the open circuit voltage. $\varepsilon_{v,d}$ was taken as a constant 0.75. $\varepsilon_{q,rt}$ is the round-trip columbic efficiency and was assumed to be 1. Table 4.4.3 tabulates the chemical cost breakdown for nominal sulfur concentration of 1M, 10M and 20M in the catholyte.

Table 4.4. 2 Na-S flow battery catholyte and anolyte chemical components unit cost.[143]

Component	Unit Price (\$/Kg)
KetjenBlack	30.00
Sodium metal	2.80
Sodium iodide	25.00
Sulfur powder	0.30
TEGDME	2.50

Table 4.4. 3 Chemical cost breakdown for Na-S flow batteries with 1M, 10M, and 20 M sulfur nominal concentration of catholyte suspension.

Catholyte suspension, 1 M S, 1vol% Ketjen in 1M NaI TEGDME solution, $S^{2-} \leftrightarrow S^0$			
	Unit Price (\$/Kg)	Concentration	Cost breakdown (\$/kWh)
KetjenBlack	30.00	1%vol.	0.65
Sulfur powder	0.30	1 M	0.19
Sodium iodide	25.00	0.97 M	71.70
TEGDME	2.50		46.29
$c_{catholyte}$ (\$/kWh)			118.83
Tank	0.15 \$/L		2.95
Sodium metal anolyte			
$c_{anolyte}$ (\$/kWh)			1.26
$c_{chemicals} = 123.04$ (\$/kWh)			

Catholyte suspension, 10 M S, 1vol% Ketjen in 1M NaI TEGDME solution, $S^{2-} \leftrightarrow S^0$			
	Unit Price (\$/Kg)	Concentration	Cost breakdown (\$/kWh)
KetjenBlack	30.00	1%vol.	0.06
Sulfur powder	0.30	15 M	0.19
Sodium iodide	25.00	0.97 M	6.14
TEGDME	2.50		3.97
$c_{catholyte}$ (\$/kWh)			10.36
Tank	0.15 \$/L		0.29
Sodium metal anolyte			
$c_{anolyte}$ (\$/kWh)			1.26
$c_{chemicals} = 11.92$ \$/kWh			

Catholyte suspension, 20 M S, 1vol% Ketjen in 1M NaI TEGDME solution, $S^{2-} \leftrightarrow S^0$			
	Unit Price (\$/Kg)	Concentration	Cost breakdown (\$/kWh)
KetjenBlack	30.00	1%vol.	0.03
Sulfur powder	0.30	15 M	0.19
Sodium iodide	25.00	0.97 M	2.50
TEGDME	2.50		1.62
$c_{catholyte}$ (\$/kWh)			4.34
Tank	0.15 \$/L		0.15
Sodium metal anolyte			
$c_{anolyte}$ (\$/kWh)			1.26
$c_{chemicals} = 5.75$ \$/kWh			

Other cost

Other cost is calculated as follows:

$$c_{others} = \frac{c_{bop} + c_{add}}{t_d}$$

where c_{bop} is the balance of plant cost in \$/kW, c_{add} is the additional cost in \$/kW and t_d is the discharge time in hours. The balance of plant costs includes but is not limited to inverters, transformers, and control electronics for controlling temperature and actively

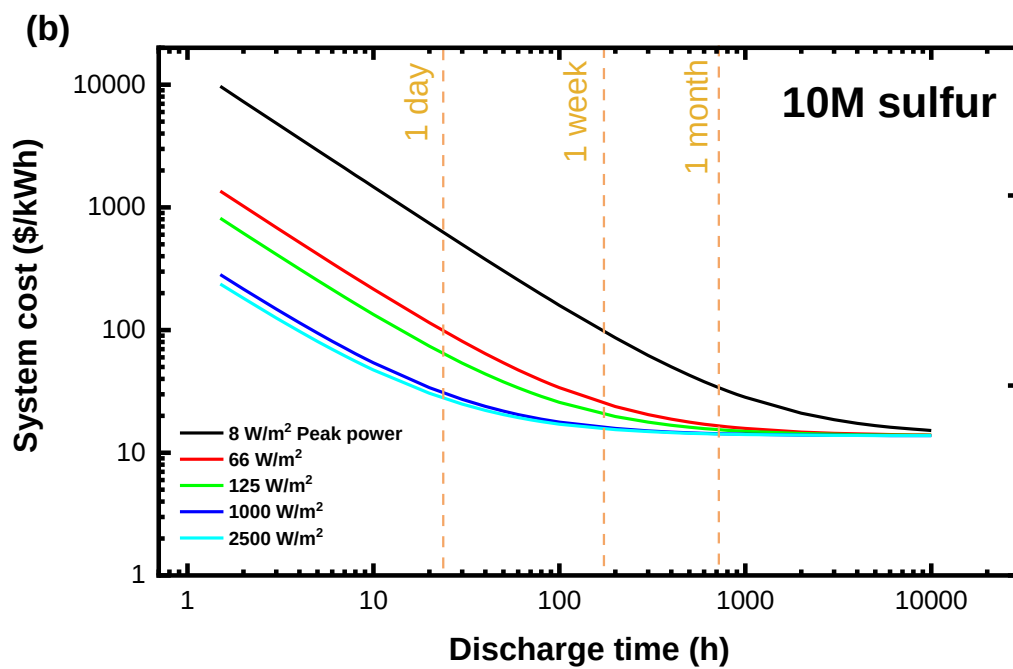
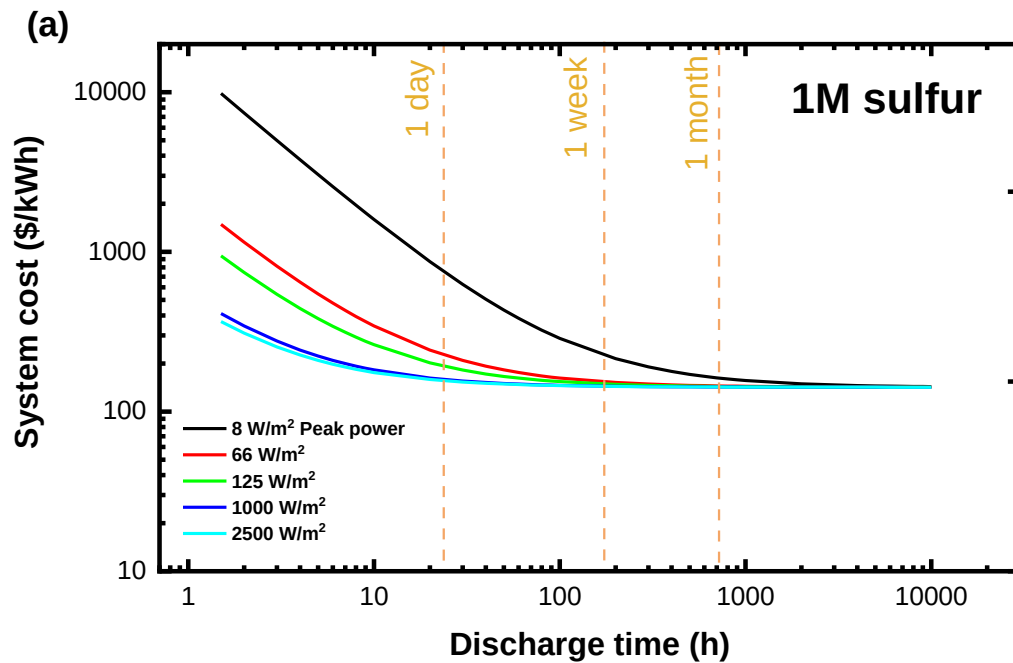
monitoring the condition of the Na-S battery. The balance of plant cost is calculated by the following equation:

$$c_{bop} = c_{pcs} + c_{controls} + N_{flow} \cdot c_{pump}$$

where c_{pcs} is the cost of power electronics in \$/kW, $c_{controls}$ is the cost of controllers in \$/kW, c_{pump} is the cost of one pump system for flow parts in \$/kW and N_{flow} is the number of the flow pump system. For our model calculation, the balance of plant cost of \$202.5/kW is used based on average upper and lower bound values at a 95% confidence interval suggested by Viswanathan et al.[147] and Darling et al.[144] for flow batteries. Additional costs cover surges over the material, production, maintenance, etc. This includes the cost of manufacturing and assembly labor, maintenance, materials and devices depreciation, costs of administration, profits, research, and development. The additional costs were determined to be 112.5 \$/kW based on average upper and lower bound values at a 95% confidence interval suggested by Darling et. al.[144].

System-level performance and cost output

Figure 4.5.1 shows the system cost for the catholyte with 1M, 10M, and 20M nominal sulfur concentrations. For each sulfur concentration plot, system performance and cost with five different power densities are compared.



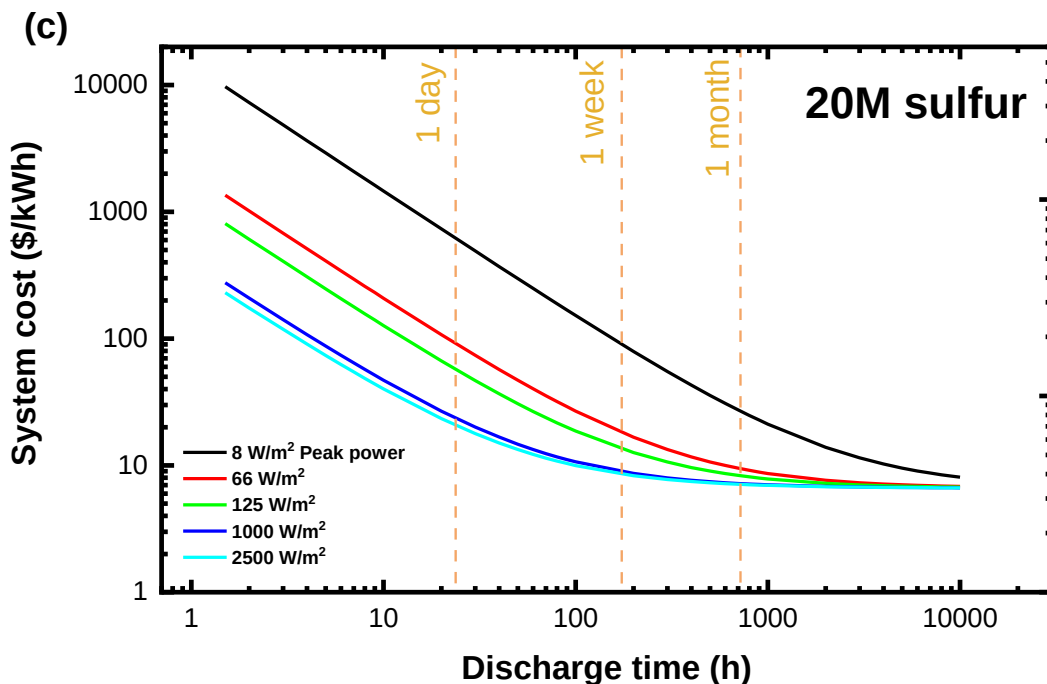


Figure 4.5. 1 System-level performance and cost projection for the Na-S flow battery with the catholyte sulfur nominal concentration of (a)1M, (b)10M, and (c)20M at different power densities.

4.5 Conclusions

An intermediate temperature Na-S flow battery is demonstrated using semi-solid sulfur-based suspension as catholyte. The electrochemical performance and reaction mechanism of the Na-S battery is studied first in a static cell design.

The discharge process of the static cell shows 2 clear plateaus at 2.2 V and 1.8V with 1M nominal sulfur catholyte. The static cell shows an initial discharge capacity of 864 mAh/g, which far exceeds some of the capacity of existing Na-S batteries. This indicates a deep discharge into short-chain polysulfides and a high sulfur utilization. The cycling

performance of the Na-S cell is also tested using a static cell design. The cell shows an initial discharge capacity of around 700 mAh/g and maintains a discharge capacity of 484 mAh/g after 55 cycles. The Na-S battery is also demonstrated with a flow cell design. A discharge capacity of 420 mAh/g is achieved for a two-aliquot intermittent flow test. The discharge capacity and coulombic efficiency still need to be improved. Overall, the demonstrated Na-S battery offers high energy density, efficient utilization of sulfur, and high tolerance of volume change for the cathode. In terms of cost, the semi-solid flow battery has low materials cost due to the high abundance of sodium and sulfur, the low manufacturing cost of the catholyte, and the low operating cost due to the reduced requirements for thermal management of the system. The Na-S system is competitive comparing to other grid storage technologies in terms of both cost and electrochemical performance. With further development, this will be a promising energy storage solution for future grid-scale energy storage.

Chapter 5 - Summary and future work

In chapter 2, an electrochemical flow system is designed to restore the lithium concentration in the end-of-life Li_xCoO_2 cathode materials by reacting with lithium-ion-containing aqueous solutions. The proposed mechanism is demonstrated in a static configuration for both loose cathode materials and cathode electrode sheets. Followed by heat treatment, the relithiated cathode materials show comparable electrochemical performances to the virgin battery-grade cathode materials. The layered structure and morphology of the cathode materials are maintained throughout the recycling process. The life cycle analysis of the recycling process indicates that the energy consumption of producing 1kg LiCoO_2 can be reduced to 4-32% with recycling. Direct recycling consumes the least energy comparing to pyrometallurgical and hydrometallurgical methods. Next, the proposed direct recycling process needs to be demonstrated on a flow configuration. The performance of the membrane, the formulation of the li-ion-containing electrolyte, the choice of the current collector, and the design of the flow field are the most important aspects to be considered in the design of the flow configuration. The performance of the membrane determines the transportation of lithium ions and the level of cross-contamination of other soluble species. The formulation of the electrolyte can affect the reaction kinetics and also the choice of cell materials. A good design of the flow field will have a homogeneous distribution of the electrolyte over the electrode. Besides, making the flow configuration scalable for large-scale production is also an important principle to be considered during the design.

Research work on aqueous sulfur flow battery systems is presented in chapter 3. In section

3.1, polysulfide speciation in aqueous sulfur solutions is characterized. The results are meaningful to understand the performance of aqueous sulfur electrolytes in redox flow battery systems. In section 3.2, aqueous manganese solutions are studied as promising catholyte to pair with aqueous sulfur anolyte for a redox flow battery. Several test protocols and quantification metrics are developed to measure the self-discharge rate and precipitation rate of the aqueous manganese catholyte. The chemical and electrochemical stability of the catholyte is investigated via *ex-situ* and *in-situ* experiments. A numerical model is developed to simulate the cycling performance of the AqMn-AqMn symmetric flow cell. The model shows high accuracy and helps predict the cycling performance from the basic stability-related parameters of the catholyte. The mitigation of AqMn precipitation should be the main focus for future study. The precipitation process results in the loss of active materials irreversibly and can lead to the blocking of flow fields or tubing. Using agents to form a complex with intermediate products of the precipitation reaction seems a promising way to suppress the precipitation reaction. Metal ions or organic compounds that can deactivate the MnO_2 are also a good alternative way. Besides, a detailed study on pH's effect on self-discharge rate and precipitation rate will be necessary to determine the best pH for the AqMn solution.

In chapter 4, a semi-solid sodium-sulfur flow battery is proposed. The flow battery employs flowable sulfur suspension as a catholyte and molten sodium as an anolyte. The Na-S battery is first tested under nonflow configuration and shows an initial discharge capacity of 864 mAh/g. With 0.5 mA cycling, the static configuration shows an initial discharge capacity of around 700 mAh/g and maintains a discharge capacity of 484 mAh/g after 55 cycles. A discharge capacity of 420 mAh/g is achieved for a two-aliquot intermittent flow

configuration. Tech-economics analysis of the proposed Na-S system is performed. A cost model based on the system-level performance is developed. System-level performance and cost projection for the Na-S flow battery with 3 catholyte sulfur nominal concentrations are presented. Next, improving the electrochemical performance of the Na-S cell under flowing conditions will be the main focus. Currently, the cell shows less than 60% coulombic efficiency and less than 500 mAh/g of discharge capacity in the flowing configuration. The flow field design of the cell needs to be improved to avoid the dead-room, where the sulfur suspension is isolated from the flowing suspension, in the flow cell. In addition, the precipitation of sulfur at regions with lower temperatures could possibly affect the flow of the suspension. Further development is needed to push the proposed Na-S battery towards a promising energy storage solution for future grid-scale energy storage.

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