Evaluation of cost, materials, and safety of flow battery technologies for large scale energy storage

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เทคโนโลยีของโฟลว์แบตเตอรี่ได้มีการพัฒนามาอย่างต่อเนื่องแต่ว่าราคา วัสดุ และความปลอดภัยของเทคโนโลยีโฟลว์แบตเตอรี่ในแต่ละเทคโนโลยีนั้นยังขาดการประเมินราคา วัสดุ และความปลอดภัย ดังนั้นในงานวิจัยนี้จะประเมินราคา วัสดุ และความปลอดภัยของเทคโนโลยีโฟลว์แบตเตอรี่ฐานสังกะสี และ โฟลว์แบตเตอรี่วานาเดียม ประกอบไปด้วย โฟลว์แบตเตอรี่สังกะสีอากาศ โฟลว์แบตเตอรี่สังกะสีไอโอดีน โฟลว์แบตเตอรี่สังกะสีเหล็ก โฟลว์แบตเตอรี่สังกะสีแมงกานีสไดออกไซด์ และโฟลว์แบตเตอรี่วานาเดียม ประเมินสำหรับการใช้งานในการกักเก็บพลังงานในสเกลขนาดใหญ่ ทั้งหมด 12 การใช้งาน จากผลการวิจัยพบว่าโฟลว์แบตเตอรี่สังกะสีอากาศจะคุ้มค่ากับเงินลงทุนมากที่สุดเพราะว่ามีต้นทุนที่ต่ำที่สุดเมื่อเทียบกับทุกระบบที่ประเมินในทุกการใช้งาน เงินลงทุนของโฟลว์แบตเตอรี่สังกะสีอากาศอยู่ที่ 122.91 ถึง 194.17 $/kW และ 12.29 ถึง 194.17 $/kWh และมีต้นทุนปรับระดับอยู่ที่ 0.1-5 $/kWh และ 0.15-9.5 $/kW สำหรับโฟลว์แบตเตอรี่สังกะสีไอโอดีน โฟลว์แบตเตอรี่สังกะสีเหล็ก และโฟลว์แบตเตอรี่วานาเดียมจะมีการแข่งขันกันมากในเรื่องของต้นทุนปรับระดับทั้งนี้ขึ้นกับการใช้งาน การใช้งานแบตเตอรี่ที่กำลังและพลังงานสูงจะคุ้มค่ากว่าใช้งานแบตเตอรี่ที่กำลังและพลังงานต่ำเนื่องจากจะมีต้นทุนปรับระดับที่ต่ำกว่า และจากการประเมินวัสดุและความปลอดภัยพบว่า โฟลว์แบตเตอรี่ฐานสังกะสีทุกระบบปลอดภัยสำหรับใช้งานในการกักเก็บพลังงานในสเกลขนาดใหญ่เพราะว่าวัสดุและสารเคมีไม่เป็นพิษและปลอดภัย ยกเว้นระบบโฟลว์แบตเตอรี่วานาเดียมที่อิเล็กโทรไลต์นั้นเป็นพิษ สำหรับการจัดการอิเล็กโทรไลต์ในแต่ละระบบพบว่า ระบบโฟลว์แบตเตอรี่สังกะสีอากาศจะมีการจัดการอิเล็กโทรไลต์และนำกลับมาใช้ใหม่ง่ายกว่าทุกระบบ ดังนั้นระบบโฟลว์แบตเตอรี่สังกะสีอากาศจึงเหมาะสมที่สุดสำหรับใช้งานในการกักเก็บพลังงานในสเกลขนาดใหญ่

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New technologies of flow batteries have been developed but the cost, materials, and safety of each of the technologies are still lacking evaluation such as zinc-based flow batteries, so in this work, the cost, materials, and safety of zinc-based flow batteries including zinc air flow battery, zinc iodine flow battery, zinc iron flow battery, zinc manganese dioxide flow battery and vanadium flow batteries are examined for 12 large scale energy storage applications. This work demonstrated that zinc air flow battery is the most cost-effective because of the lowest cost of investment cost and Levelized cost of storage (LCOS) in all applications. The investment cost of zinc air flow battery is 122.91-194.17 $/kW and 12.29-194.17 $/kWh and the LCOS of zinc air is between 0.1-5 $/kWh and 0.15-9.5 $/kW. The Zinc iodine, Zinc iron, and Vanadium flow battery are very competitive in the LCOS. Using the flow battery at high power and energy is more cost-effective than using at low power and energy. For the materials and safety evaluation, all zinc-based flow batteries are safe for operating in large-scale energy storage because of non-toxic and not flammable materials and chemicals, but electrolyte for the vanadium flow battery is toxic. For electrolyte management, the zinc air flow battery is easier management than other systems, so zinc air flow battery is the best appropriate for use in large scale energy storage.

Field of Study:	Chemical Engineering	Student's Signature ....
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Chapter 1

Introduction

1.1 Introduction

Nowadays, electricity production from renewable energy sources such as wind and solar becomes more significant because of global warming and climate change issues. However, renewable energy sources are naturally intermittent and the electricity generated from these sources are unpredictable matching between demand and supply. Therefore, energy storage systems are significant for the effective utilization of renewable energy and prevent the unbalanced demand and supply of electricity generated. The need for large scale energy storage becomes priority to integrate renewable energy sources into the electricity grid. (Lao-atiman et al., 2019; Prifti et al., 2012)

There are many types of energy storage systems including pumped hydro, compressed air, flywheels, fuel cells, and flow batteries. (Prifti et al., 2012; Schmidt et al., 2019) Flow batteries are one of the energy storage systems that can be widely applied to storage of intermittent renewable energy sources that are suitable for large scale energy storage. (Prifti et al., 2012; Xie et al., 2018)

Flow batteries are the batteries that have electrolytes stored in the external tanks and circulated into the cell to produce electricity via electrochemical reactions. (Alotto et al., 2013)

Zinc based flow batteries are the new flow batteries that are low cost, high safety, high energy density, and environmentally friendly that are suitable for large scale energy storage because zinc is the metal that is abundant, low cost, non-toxic, and environmentally friendly. Zinc is stable and it doesn’t react violently with moisture and oxygen in the air so it doesn’t explode and safe. (Hosseini et al., 2019)

Flow batteries for large scale energy storage need to have long working times, easy maintenance, high cost performance, and high safety. (Huamin Zhang, 2018)

New technologies of flow batteries have been developed but the cost, materials, and safety of each of technologies are still lack of evaluation such as zinc-based flow batteries. (Abbasi et al., 2020; Li et al., 2020; Selverston et al., 2017; Xie et al., 2018)

In this work, the cost, materials, and safety of zinc-based flow batteries including zinc air flow battery, zinc iodine flow battery, zinc iron flow battery, zinc manganese dioxide flow battery, and vanadium flow battery are examined.

1.2 Objectives

1.2.1 Evaluate the cost, materials, and safety of flow battery technology including zinc air flow battery, zinc iodine flow battery, zinc iron flow battery, zinc manganese flow battery and vanadium flow battery.

1.2.2 Compare the commercial potential of cost of each flow battery technology at various power and energy.

1.3 Scope of research

1.3.1 The costs of chemicals and materials are industrial grade.

1.3.2 Evaluation of cost in term of the cost per energy ($/kWh) and power ($/kW)

1.3.3 The costs of electrolytes are the costs for 1 metric ton.

1.3.4 The evaluation of cost of flow batteries is calculated based on the literature review with possible range of capacity and power of flow batteries.

1.3.5 The costs of materials and chemicals are the costs in 2020.

1.3.6 Calculate the levelized cost of storage (LCOS) in each of application used in large scale energy storage from the LCOS model.

1.37 Sensitivity of input parameters that affect the LCOS in the model of LCOS including cycle life, round trip efficiency, depth of discharge, annual cycles, discount rate, and electricity price.

1.3.8 Toxicity and flammable of materials and chemicals are considered in materials and safety evaluation.

1.3.9 Recycle ability and electrolyte management in each flow battery system are considered in this work.

1.3.10 Method for recovery electrolyte are evaluated for large scale energy storage.

1.4 Schedule plan

Table 1 Working Plan

Activities	Month/Year 2020									Month/Year 2021				
	Apr	May	Jun	July	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May
Study about Literature review	▨	▨	▨	▨	▨	▨	▨							
Evaluation of cost of flow batteries			▨	▨	▨	▨	▨	▨	▨	▨	▨			
Evaluation of materials and safety of flow batteries												▨	▨	▨
Write the thesis										▨	▨	▨	▨	▨

Chapter 2

Theory and Literature review

2.1 Flow battery

Flow battery is the battery that have electrolytes stored in the external tanks and circulates in the systems of battery to produce electricity via electrochemical reactions. Flow battery consists of two electrolyte tanks. Electrolytes are circulated by pumps through electrodes located at each side in cell stack (Bin and Jun, 2017). There are two electrodes composed of anode (negative electrode) and cathode (positive electrode). Anode electrode performs the reduction half-reaction of electrolyte that release one electron and one ion while the cathode electrode performs an oxidation half reaction that recombines them into the other electrolyte. Ions can diffuse from anode to cathode through membrane, which are instead forced to pass through the external circuit thus exchanging electric energy (Alotto et al., 2013). The membrane acts as a separator to prevent cross-mixing of the positive and negative electrolytes, while still allowing the transport of ions to complete the circuit during the passage of current. (Prifti et al., 2012) Cathode and anode materials are made of electrolyte solutions in which the energy is stored. Typical flow battery must operate at room temperature in order to keep the solutions in the liquid phase. (Alotto et al., 2013)

The system of flow battery is mainly composed of electrode, electrolyte, tank, pump, bipolar plate, ion exchange membrane, and power source.

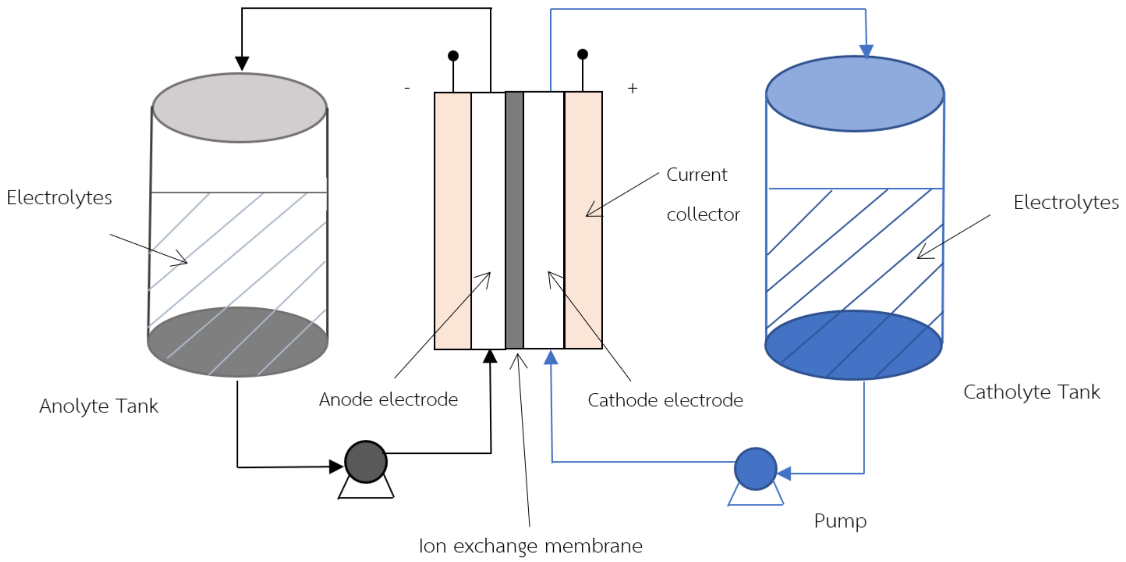

Figure 1 Flow battery system

2.2 Zinc-based flow battery

2.2.1 Zinc air flow battery

Zinc air flow battery consists of two electrodes including the Zn anode and the air cathode. The anode and cathode are separated by a separator allowing ions to transfer across the cell. Potassium hydroxide (KOH) aqueous solution is mostly used as an electrolyte. At the anode, Zn reacts with hydroxide ions (OH^-) and forms zincate ions ($Zn(OH)_4^{2-}$) in reaction (1). When the concentration of zincate ion reaches its solubility limit, zinc oxide (ZnO) precipitation reaction proceeds in reaction (2). Hydrogen evolution reaction (HER) is also considered as a parasitic reaction on the Zn electrode. Water receives electrons and converts to hydrogen and hydroxide ions in reaction (3), HER combined with reaction (1) and showed reaction (4). At the cathode, oxygen reduction reaction consumes oxygen and water and produces hydroxide ions. As the battery discharges, electrons are released from reaction (1) and received by reaction (5). Both reactions proceed and generate electricity (Lao-atiman et al., 2019).

Electrochemical reactions of zinc air flow battery

Zn electrode: $Zn + 4\ OH^- \leftrightarrow Zn(OH)_4^{2-} + 2e^-$ (1)

$Zn(OH)_4^{2-} \leftrightarrow ZnO + 2\ OH^- + H2O$ (2)

HER (Parasitic reaction): $2H2O + 2e^- \longrightarrow H2 + 2OH^-$ (3)

(1)+(3) $Zn + 2OH^- + 2H2O \longrightarrow Zn(OH)_4^{2-} + H_2$ (4)

Air electrode: $1/2O_2 + H_2O + 2e^- \leftrightarrow 2OH^-$ (5)

Overall reaction: $Zn + 1/2O_2 + \leftrightarrow ZnO + H_2$ (6)

2.2.2 Zinc iodine flow battery

Zinc iodine flow battery consists of two electrodes including Zn anode and the porous carbon material used as the cathode. Zinc chloride ($ZnCl_2$) and potassium iodine (KI) are use as the electrolyte. The electrolytes contain Zn^{2+} and I^-. At the anode, Zn transfer electron to produce Zn^{2+} and at the cathode, I^- will receive electron to produce I_2 Both (1) and (2) proceed and generate electricity. (Li et al., 2015)

Electrochemical reactions of zinc iodine flow battery

Anode: $Zn^{2+} + 2e^- \leftrightarrow Zn$ (1)

Cathode: $2I^- + 2e^- \leftrightarrow I_2$ (2)

Side reaction in cathode: $I_2 + I^- \longrightarrow I_3$ (3)

Overall reaction: $Zn^{2+} + I_2 \leftrightarrow Zn + 2I^-$ (4)

2.2.3 Zinc iron flow battery

Zinc iron flow battery consists of two electrodes including Zn anode and the porous carbon material used as the cathode. Zinc chloride ($ZnCl_2$), ferrous chloride ($FeCl_2$) and ferric chloride ($FeCl_3$) are use as the electrolyte. The electrolytes contain Zn^{2+},Fe^{2+} and Fe^{3+} At the anode, Zn transfer electron to produce Zn^{2+} and at the cathode, Fe^{3+} will receive electron to produce Fe^{2+} Both (1) and (2) proceed and generate electricity. (Selverston et al., 2017)

Electrochemical reactions of zinc iron flow battery

Anode: $Zn^{2+} + 2e^- \leftrightarrow Zn$ (1)

Cathode: $Fe^{3+} + e^- \leftrightarrow Fe^{2+}$(2)

Overall reaction: $Zn^{2+} + 2Fe^{2+} \leftrightarrow Zn + 2Fe^{3+}$ (3)

2.2.4 Zinc manganese dioxide flow battery

Zinc manganese dioxide flow battery consists of two electrodes including Zn anode and the porous carbon material used as the cathode. Zinc sulphate ($ZnCl_2$) and manganese sulphate ($MnSO_4$) are use as the electrolyte. The electrolytes contain Zn^{2+} and Mn^{2+} At the anode, Zn transfer electron to produce Zn^{2+} and at the cathode, Mn^{2+}will receive electron to produce MnO_2 and H^+. Both (1) and (2) proceed and generate electricity. (Li et al., 2020)

Electrochemical reactions of zinc manganese dioxide flow battery

Anode: $Zn^{2+} + 2e^- \leftrightarrow Zn$ (1)

Cathode: $Mn^{2+} + 2H_2O \leftrightarrow MnO_2 + 4H^+ + 2e^-$ (2)

Overall reaction: $Zn^{2+} + Mn^{2+} + 2H_2O \leftrightarrow Zn + MnO_2 + 4H^+$ (3)

2.3 Energy storage

Energy storage is the technology that can be collect the energy produced to be used in need on the other period. The energy storage such as mechanical energy storage, thermal energy storage, chemical energy storage, electrochemical energy storage or electrical energy storage.

Energy storage have potential to be use in the electrical grid such as maintain the stability in power system, increase the efficiency of transmission electrical line, increase the efficiency in operation in power plant, electricity charge management and promoting the increase of renewable energy in the power system. (Institute, 2018)

Table 2 Energy storage technologies

Type of energy storage	Example of Technologies
Mechanical energy storage	Pumped-storage hydro Compressed Air Liquid Air Flywheels
Thermal energy storage	Thermo-chemical Sensible chemical Latent chemical
Chemical energy storage	Hydrogen Storage Substitute Natural Gas
Electrochemical energy storage	Lead-Acid Batteries Sodium-Sulfur Batteries Lithium-Ion Batteries Redox Flow Batteries
Electrical energy storage	Supercapacitors Superconducting magnetic

Table 2 showed the example of technologies in each type of energy storage. Flow batteries are the technologies in electrochemical energy storage that convert energy from chemical energy to electric energy.

The characteristics and selection of each energy storage technology are dependent on the application. First application, energy storage that store the large amounts of energy for a long time, they are suitable for transferring the energy produced for other periods especially using as load following instead of using power plant. Second, the energy storage that can release and accumulate energy quickly that is suitable for use to improve power quality and use it for uninterrupted supply, which requires the ability to meet the need for large amounts of energy quickly for a short period of time.

The differences in energy storage technologies depend on the ability of energy storage and discharge electricity, system performance, lifetime and cost. (Institute, 2018)

For the application of energy storage using in the large scale energy storage, There are many applications used in large scale energy storage including energy arbitrage, primary response, secondary response, tertiary response, peaker replacement, black start, seasonal storage, T&D investment deferral, congestion management, bill management, power quality, and power reliability applications.

The energy arbitrage application is the application that purchases power in a low price and sell in the high price periods on wholesale or retail market. The primary response application is correct continuous and sudden frequency and voltage changes across the network. The Secondary response application is the application that correct anticipated and unexpected imbalances between load and generation. The tertiary response application is application that replaces primary and secondary response during prolonged system stress. The Peaker replacement is application that ensures availability of sufficient generation capacity during peak demand periods. Black start is the application that restores power plant operations after a network outage without external power supply. The seasonal storage is the application that compensates long term supply disruption or seasonal variability in supply and demand. T&D investment deferral is the application that defers network infrastructure upgrades caused by peak power flow exceeding existing capacity. Congestion management is the application that avoid redispatch and local price differences due to the risk of overloading existing infrastructure. Bill management is the application that optimizes power purchase including minimize demand charges and maximize PV self-consumption. Power quality is the application that protects on site load against short duration power lose or variations in voltage or frequency and the power reliability is the application that covers temporal lack of variable supply and provide power during blackouts. (Schmidt et al., 2019)

2.4 Evaluation of cost of energy storage systems

For evaluation of cost of energy storage technologies are very significant for decide to buy or install the energy storage systems because of high cost performance of energy storage system. (Huamin Zhang, 2018)

However, comparison cost of energy storage systems cannot compare them directly because of the difference lifetime and size of each of technologies, so for comparing each of technologies, it needs to calculate the cost in term of levelized cost of storage or LCOS calculation because LCOS calculation is the constant value at all of the lifetime. (Institute, 2018)

LCOS is determined as the sum of all investments over the life time of energy storage system divided by the cumulative energy generated. (Melnikov et al., 2018)

$$\text{LCOS}\left(\frac{\$}{\text{kWh}}\right)=\frac{\text{Investment cost}+\sum_{n}^{N}\frac{\text{O\&M cost}}{(1+r)^{n}}+\sum_{n}^{N}\frac{\text{Charging cost}}{(1+r)^{n}}}{\sum_{n}^{N}\frac{\text{Elec}_{\text{discharged}}}{(1+r)^{n}}} \quad (1)$$

LCOS is the life cycle cost that calculated based on the lifetime of each technology for operating the energy storage system in each year of operation. The cost levelized to the present value of cost using a discount rate to adjust it as same as the NPV method. LCOS model including the investment cost, operating and maintenance cost, charging cost and electrical discharged as showed in equation (1).

2.5 Literature review

2.5.1 Evaluation of cost of energy storage system

Schmidt et al. (2019) evaluated and predicted the levelized cost of storage (LCOS) of electricity energy storage including 9 technologies and 12 applications by evaluate LCOS from 2015 to 2050 using monte carlo simulation by simulation 500 LCOS per technology at 80% confidence level and standard deviation of 1.285. LCOS is calculated based on investment, operating and maintenance cost, charging cost and end of life costs. They have calculated from the present parameters in year of 2015 and predicted the cost in the future. From the results, cost will be reduced by a third or half by 2030 and 2050, and from model application, lithium ion battery technology will be the most cost-effective investment from 2030 onwards. Other technologies were not worth the investment if it does not improve the efficiency of each technology Therefore, if the performance is improved, it might be more cost effective and competitive with lithium ion technology.

Melnikov et al. (2018) calculated the levelized cost of storage (LCOS) of electrical energy storage for short duration application and analyzed the LCOS sensitivity analysis to see the LCOS value changes when input parameter changes LCOS value. The input data for LCOS calculation including design life, energy storage capacity to power ratio, capital cost, operating cost, maintenance cost, electricity cost, cycles per day and energy storage efficiency. For the results, The LCOS calculation in the case of using energy storage system in a self-contained power system is 0.53 $/kWh. The capital cost of the system and the amount of energy delivered but the cost that calculated can't be determined very accurately because energy storage system is exposed to external such as climatic and internal factor including change in power consumption, disconnection of generating units.

2.5.2 Evaluation of cost of flow battery technologies

Ha and Gallagher (2015) evaluated the cost of vanadium flow battery and lithium polysulfide flow battery by fixed expense and manufacturing cost, and then compared the cost of each flow battery and with the lithium ion battery. Compared to lithium ion batteries, flow batteries use a lower cost of manufacture and have a lower material cost due to the cell design, less area, and easier manufacturing processes. Flow batteries provide a cost-effective at lower production volumes.

Minke and Dorantes Ledesma (2019) evaluated the price of novel vanadium flow battery with large area of bipolar plate with size 2.7 m^2 and a thickness of 7 mm. The power of vanadium flow battery is in a range of 1 MW-20MW. The energy capacities in a range of 4MWh to 160 MWh and energy to power ratio (E/P) at 4 h and 8 h. The objective is to find the system costs of vanadium flow battery from the economic model in term of energy and power related costs and to find the cost potentials. From the results, they showed a simple function for the calculation of system costs and the impact of cost reduction potentials for key components including membrane, electrode, bipolar plate and electrolyte is quantified and validated.

Ha and Gallagher (2015) reviewed the literature on techno-economic assessment of vanadium flow battery including materials, chemicals, system design and the future cost of materials, chemicals and system price from the model. The range of power and energy capacity are in the range of 2kW to 50MW with the energy to power ratio 0.25 h to 150 h. As the results, It showed that the electrolyte costs are 45-334 \$/kWh (30-60% of total system cost), the cost of ion-exchange is 300 Euro/m^2 for average (30% of total system cost), cost of bipolar plate is 19-418 Euro/m^2 (below 5% of total system cost), carbon felt electrode is 13-150 \$/m^2 (below 5% of total system cost). The system cost related to system power are in a range of 561-12,931 Euro/kW and the system cost related to energy capacity are in a range 89-1738 Euro/kWh and the results show the graphs between system cost to system power and cost of electrolyte, membrane, bipolar plate and carbon electrode and show the graph between energy to power ratio and system cost to system power.

Minke and Dorantes Ledesma (2019) evaluated the life cycle cost and profitability of vanadium flow battery and study the impact of cell design and maintenance strategy on life cycle cost and net present value (NPV) of vanadium flow battery for residential, industrial small cell and industrial large cell. From the results, it is showed that LCOS are highly sensitive to energy to power ratio or discharge duration and at 8% discount rate a profitability of vanadium flow battery at LCOS below of 0.3 Euro/kWh was highly probable.

2.5.3 Evaluation of cost of zinc-based batteries

Knehr et al. (2018) optimized the minimal architecture zinc bromine battery by using levelized cost of storage (LCOS) model. Charge and discharge times ranging from 4 to 48 hours and capacity ranging from 320 to 4000 mAh. LCOS model used to demonstrate how the energy efficiency or discharge energy trade-off within the system can be minimized the LCOS. The results showed that the LCOS of unoptimized cell was 0.08\$/kWh and electricity purchase prices was 0.02 \$/kWh. At all purchase prices, greater than 60% of the LCOS come from the capital cost including carbon foam electrode and zinc bromide electrolytes. LCOS model can be used to determine the optimal electrode spacing. Finally, they will compare the LCOS of zinc bromine battery with other technologies indicating that the zinc bromine battery was competitive with lithium ion, lead-acid, vanadium redox flow batteries and zinc bromine flow batteries.

2.5.4 Developing the zinc-based flow batteries

Lao-atiman et al. (2019) developed a mathematics model of a zinc-air flow battery with zinc electrolyzer system by using MATLAB and validate against experiment results. The operating parameters that studied including the flow rate of the electrolyte, the initial concentration of potassium hydroxide (KOH) and the initial concentration of zincate ion. They study the influence of these parameters on the performance of the system. From the results, optimal KOH concentration was found to be about 6–7 M which give a highest discharge energy. Whilst increased KOH concentration enhanced the discharge energy of the battery, it also increased HER of both the battery and the electrolyzer. However, higher initial concentration of zincate ion reduced HER and improved the coulombic efficiency of the system. Besides, a higher flow rate of electrolyte enhanced the performance of the system especially at a high charge/discharge current by maintaining the concentration of active species in the cell but the battery suffered from a higher rate of HER at a high flow rate. They conclude that the model-based analysis provided better insight into the behavioral characteristics of the system leading to an improved design and operation of the integrated system of zinc-air flow battery with the zinc electrolyzer.

Abbasi et al. (2020) studied about zinc air flow battery that provided the experimental data including discharge profiles at various discharge currents and electrolyte flow rates with discharge current in the range of 100–200mA, and electrolyte flow rates in the range of 0–140ml/min. From the results, it showed the discharge profile of each of experiments.

Hosseini et al. (2019) studied about effects of dimethyl sulfoxide with 0-20 % dimethyl sulfoxide in 7 M KOH aqueous electrolyte on the performance of zinc air flow battery. Dimethyl sulfoxide reveals a critical role of dimethyl sulfoxide on the dissolution and deposition of zinc. The presence of DMSO showed improved zinc dissolution performance with the highest peak of zinc dissolution being the electrolyte containing 5% v/v DMSO. When using DMSO, it will decrease in polarization resistance and an increase in corrosion rate due This suggests that DMSO has the ability to suspend zinc oxide in the electrolyte, thus preventing passivation of the zinc surface. When adding DMSO to the electrolyte, charge transfer resistance increased. Maximum power densities of 130 mW/cm2 (5% v/v DMSO) and 125 mW/cm2 (20% v/v DMSO) were obtained and were observed to be about 43% and 28% higher than that of the DMSO-free electrolyte. Results indicated that when 20% v/v DMSO was added to KOH solution, there was 67% zinc utilization efficiency which provided 20% improvement in discharge capacity. Further, the battery with 20% v/v DMSO demonstrated excellent cyclability. Overall, DMSO shows great promise for enhancement of zinc dissolution/deposition in zinc-air batteries.

Xie et al. (2018) developed zinc-iodine flow battery that achieves very long cycle life and high power and energy density by using cyclic voltammogram and cycling performance measurement. From the results, The zinc-iodine flow battery was very stable for more than 1000 cycles over 3 months with energy density 80 Wh/L and can operate at high current density at 180 mA/cm^2 and the cell stack with 700 W output can operate at 80 mA/cm^2 for more than 300 cycles so they conclude that zinc iodine flow battery could be an excellent option for large scale energy storage.

Selverston et al. (2017) studied about zinc iron flow battery with electrolytes $ZnCl_2$, $FeCl_2$ and $FeCl_3$ and using Daramic 175 as a microporous separator membrane. First, they studied about effect of deposition and dissolution onto titanium substrate at three Zn/Fe ratios; and at different pH electrolyte solutions Second, they studied the effect of rotation rate and negative scan limit on deposition and stripping on carbon electrodes. And third, they estimated the cost of the system of zinc iron flow battery. From the results showed that anomalous deposition of zinc from mixed $ZnCl_2$ $FeCl_2$ and $FeCl_3$ electrolytes can be used to enable zinc-iron chloride batteries that are crossover-tolerant and can use microporous separator. The system cost was estimated using a model developed by PNNL. At 1.2 V and 50mA/cm^2, the system cost was about 100 $/kWh, so they concluded that zinc-iron chloride flow batteries could achieve an excellent balance between cost, safety, and performance for grid-scale energy storage applications.

Li et al. (2020) studied about the zinc manganese flow battery without using membrane at 0.5 to 2 mAh/cm^2 and different discharge rate between 0.5C to 10C. From the results, this flow battery exhibits a high discharge voltage of 1.78 V, good rate capability (10C discharge), and excellent cycling stability with 1000 cycles without decay at the capacity 0.5 to 2 mAh/cm^2. More importantly, this battery can be readily to scale-up flow cell of 1.2 Ah with good capacity retention of 89.7% at the 500 cycle, displaying great potential for large-scale energy storage.

Chang et al. (2019) developed the membrane that used in zinc-iron flow battery by prepared a low cost K^+ formed sulfonated poly(ether ether ketone) or called SPEEK-K membrane. The cost of membrane was also evaluated compared to commercial membrane (Naffion 117). The results were showed the good performance with coloumbic and energy efficiency of 95 % and 78% at high current density 40 mA/cm^2. SPEEK-K membrane was cheaper than Naffion 117 and have the good performance as well as Naffion 117 membrane.

Zhou et al. (2020) developed the Ni-Zn battery with energy densities of 165 Wh/kg and 506 Wh/L. They used a low cost and ultra-dense Co-free for the cathode of cell. The enhanced in proton-diffusion kinetics with capacity 41.3 mAh/cm^2 and fast power response of 715 mW/cm^2, with 80,000 cycles. They demonstrate a commercial-grade 3.5 Ah Ni-Zn pouch battery, which concomitantly presents record-high energy densities and estimated the cost of Ni-Zn battery. The cost was 32.8$/kWh. This result opened a new opportunity to advance high-energy Ni-Zn batteries, and should be of immediate benefit toward low cost, practical energy storage and grid-scale applications.

Li et al. (2015) developed the zinc poly-iodine electrolyte for zinc iodine flow battery possesses the desired ambipolar and bifunctional characteristics with high solubility, benign nature and high energy density. The results were shown that the discharge energy at 5M ZnI_2 was 166.7 Wh/L and it is proved experimentally and theoretically that adding alcohols into electrolytes could effectively stabilize the cathode electrolyte at lower temperature and ameliorate zinc dendite growth at the anode because of ligand formation between oxygen on hydroxyl group and zinc ions. When compare with commercial lithium ion batteries and zinc ion batteries, zinc iodine batteries provide much more design latitude in the choice and development of membranes and additives because of not have the highly oxidative of V^{5+} and Br_2.

Yuan et al. (2018) developed the membranes and electrode used in zinc-iron flow battery. They used polybenzimidazole membrane and 3D porous carbon felt electrode which give the coulombic efficiency 99.5% and energy efficiency 82.8% at 160 mA/cm^2 that is the highest value among recently that reported for flow battery systems. The battery can run for more than 500 cycles and show good stability and the cost of the system is under 90 $/kWh

2.5.5 Review paper of zinc-based flow batteries

Khor et al. (2018) reviewed and discussed the zinc-based flow batteries. This review provided fundamental information on zinc electrodeposition and showed how to improve zinc electrodeposit morphology that are essential for long term charge-discharge cycling and summarized the recent developments of flow batteries in the relevant flow battery chemistries, along with recent application. The future challenges and opportunities for this technology for development are discussed.

Li and Liu (2017) reviewed the progress and directions in low-cost redox flow batteries for large scale energy storage. The review focused on current and future direction to address one of the most significant challenges in energy storage that is reducing the cost of redox flow battery systems. A high priority is developing aqueous systems with low cost materials and high solubility redox chemistries and highly water solubility inorganic redox couples are important for developing technologies that can provide high energy densities and low-cost storage. Developing membranes and separators and in controlling side reaction on electrode surface also are needed.

Alotto et al. (2013) reviewed the main features of the redox flow battery technology and presented the current state-of-the-art of both industrial and research systems and to highlight the main research challenges based on an extensive survey of recent literature as well as on the experience of the authors in the modeling of redox flow batteries.

From the literature reviews of evaluation of cost of flow batteries have evaluated the cost in term of LCOS only the vanadium flow batteries, so it can conclude that it doesn’t have the literature reviews that evaluate the LCOS for the zinc-based flow batteries. Most of literatures about zinc-based flow batteries focused on developed the zinc-based flow batteries system but the costs of the zinc-based flow batteries are still lack of evaluation. The materials and chemicals that used in the flow batteries have many and difference of materials and chemicals that used in batteries and it doesn’t have literatures that evaluated about material and safety of the system of flow batteries, so in this work, cost, materials, and safety of zinc-based flow battery are examined for large scale energy storage.

Chapter 3

Methodology

3.1 Evaluation of cost of flow batteries

The system of flow battery that evaluated cost composed of zinc air flow battery, zinc iodine flow battery, zinc iron flow battery, zinc manganese dioxide flow battery and vanadium flow battery.

This work will evaluate the cost of flow batteries in term of cost per power and energy from the literature related. The first step of evaluation of flow batteries, it needs to know what materials and chemicals that they used in the cell. Second is finding the cost of all material and chemicals in the unit of cost per mass or cost per area and then see in the literature review that how much of chemicals used and area of materials is it and the third step is to converts the unit of cost of material and chemical in term of cost per mass and cost per area to cost per energy and cost per power by using power, capacity, energy density or power density of the battery to convert the unit.

The data of cost are collected from the internet, asking vendors, and from literature review related. The grade of chemicals and materials are industrial grade and the cost is the cost in 2020.

The literature reviews that evaluate the cost of flow batteries are related from literature review of (Abbasi et al., 2020; Li et al., 2020; Selverston et al., 2017; Xie et al., 2018).

This work calculated cost per power ($/kW) and cost per energy ($/kWh) from the literature review related and calculated the levelized cost of storage (LCOS) from the model of LCOS for each application used in large scale energy storage. The model including the investment cost, operating and maintenance cost, charging cost and electrical discharged.

The investment cost is the cost that paid at first time before operating the flow batteries including anode, cathode, ion exchange membrane, bipolar plate, electrolytes, pump, heat exchanger, tanks, pipeline and fitting and cell frames, gasket and seals. The operation cost is the cost that paid when operating the flow batteries including the electricity cost of operating the pumps. The charging cost is the cost of the electricity when operating the flow batteries.

The input parameters including investment cost, operation cost, electricity price, round trip efficiency, depth of discharge, annual cycle, cycle life, time degradation, cycle degradation, construction time, discount rate, self-discharge and power of each application used in large scale energy storage.

The model of the Levelized cost of storage (LCOS) showed in equation (1) to equation (5).

$$\mathrm{LCOS}\left(\frac{\$}{\mathrm{kWh}}\right)=\frac{\text{Investment cost}+\sum_{n}^{N}\frac{\text{O\&M cost}}{(1+r)^{n}}+\sum_{n}^{N}\frac{\text{Charging cost}}{(1+r)^{n}}}{\sum_{n}^{N}\frac{\mathrm{Elec}_{\mathrm{discharged}}}{(1+r)^{n}}} \quad (1)$$

$$\text{Investment cost}=C_{P}\mathrm{Cap}_{\mathrm{nom},p}+C_{E}\mathrm{Cap}_{\mathrm{nom},E} \quad (2)$$

$$\sum_{n}^{N}\frac{\text{O\&M cost}}{(1+r)^{n}}=\sum_{n=1}^{N}\frac{C_{P\text{-}OM}\mathrm{Cap}_{\mathrm{nom},P}+C_{E\text{-}OM}\left(\mathrm{Cyc}_{\mathrm{pa}}*\mathrm{DOD}*\mathrm{Cap}_{\mathrm{nom},E}\right)*\left(1-\mathrm{Cyc}_{\mathrm{Deg}}\right)^{(n-1)\mathrm{Cyc}_{\mathrm{pa}}}*(1-T_{\mathrm{Deg}})^{(n-1)}}{(1+r)^{n+T_{c}}} \quad (3)$$

$$\frac{\sum_{n}^{N}\frac{\text{Charging cost}}{(1+r)^{n}}}{\sum_{n}^{N}\frac{\mathrm{Elec}_{\mathrm{Discharged}}}{(1+r)^{n}}}=\frac{P_{el}}{n_{RT}} \quad (4)$$

$$\sum_{n}^{N}\frac{\mathrm{Elec}_{\mathrm{Discharged}}}{(1+r)^{n}}=\mathrm{Cyc}_{\mathrm{pa}}*\mathrm{DOD}*\mathrm{Cap}_{\mathrm{nom},E}*n_{RT}*(1-n_{\mathrm{self}})*\sum_{n=1}^{N}\frac{(1-\mathrm{Cyc}_{\mathrm{Deg}})^{(n-1)\mathrm{Cyc}_{\mathrm{pa}}}*(1-T_{\mathrm{Deg}})^{(n-1)}}{(1+r)^{n+T_{C}}} \quad (5)$$

Where Cp is the investment cost in power term

C_E is the investment cost in energy term

$C_{p\text{-}OM}$ is the operation cost in power term

$C_{E\text{-}OM}$ is the operation cost in energy term

$Cap_{nom,P}$ is the nominal power in each application

$Cap_{nom,E}$ is the nominal energy in each application

DOD is the depth of discharge

Cyc_{pa} is the annual cycle

Cyc_{Deg} is the cycle degradation

T_{Deg} is the time degradation

n_{RT} is the round-trip efficiency

n_{self} is the self-discharge

n is the year of operation

N is the life time of each technology

r is the discount rate

T_c is the construction time

P_{el} is the electricity price

The model of LCOS are based from the literature review of Schmidt et.al. (2019)

Table 3 Application used in large scale energy storage

Application	Power (MW)	Discharge time (h)	Annual cycle (cycles/year)
Energy arbitrage	0.02-2000	1-10	50-400
Primary response	1-2000	0.02-1	4000
Secondary response	10-2000	0.25-10	1000
Tertiary response	5-1000	4	20-50
Peaker replacement	1-500	2-6	5-100
Black start	0.1-400	0.25-4	1-20
Seasonal storage	500-2000	24-2000	1-5
T&D upgrade deferral	1-500	2-8	10-500
Congestion management	1-500	1-4	50-500
Bill management	0.02-10	1-6	50-500
Power quality	0.05-10	0.017-0.5	10-200
Power reliability	0.02-10	2-10	50-400

Reference: Schmidt et.al. (2019)

Table 4 Input parameters in the LCOS model

Input parameters	Zinc air	Zinc iodine	Zinc iron	Zinc manganese	Vanadium
Investment cost-Power ($/kW)	122.91-194.17	613.97-858.63	616.17-667.58	193.9-483.81	512.21-551.47
Investment cost-Energy ($/kWh)	7.198	422.23	1.8	2.16	199.6
Operation cost-Power ($/kW)	6	12	12	12	12

Operation cost-Energy ($/kWh)	0.0005	0.001	0.001	0.001	0.001
Round trip efficiency	70%	90%	65%	85%	78%
Depth of discharge (DoD)	1	1	1	1	1
Self-discharge (%)	0	0	0	0	0
Construction time (year)	1	1	1	1	1
Cycle life (cycle)	2000	1000	120	500	8272
Electricity price	0.05 $/kWh for all application except the bill management, power quality and power reliability are 0.1 $/kWh Schmidt et.al. (2019)				

Table 3 showed the power, discharge time and annual cycle of each application used in the large-scale energy storage and Table 4 showed the input parameters of each flow battery in the LCOS model.

After that, sensitivity of the input parameters that affect the LCOS by changing the parameter in the model and considered the sensitivity of each parameter and competitive of each technology and compare the commercial potential of each of flow batteries in each application and then compare with vanadium flow battery and lithium ion battery.

3.2 Evaluation of materials and safety of flow batteries

The method of evaluation of materials of flow batteries are to evaluate the materials used in the flow batteries including the toxicity and safety of the materials when operating the flow batteries. We looked at the materials used in the cell that are made since they are produced that what chemicals used to produce and we considered the safety of all of the chemicals in the systems. We considered the toxicity and flammability of electrolytes used in flow batteries.

The parameters of toxicity of electrolytes that considered are the LD50 values of each chemical and for the flammable is considered the flash point temperature.

After that, we considered the contamination in soils of the electrolyte by the solubility of each chemical and then considered the recycling ability and electrolyte management of each flow battery technology by study and compare the method of technology of recycling electrolyte in recovery and management of each flow battery. We analyzed the method in each step. The method of recovery electrolyte is divided into 4 main steps. The first step is the leaching or extraction of the electrolyte by using solvent, the second step is the precipitation step by adding chemical or adjust pH, the third step is filtering to separate all of the solid of electrolytes and the last step is to prepare the new electrolyte by concentrated for using again. The cost of chemicals used in step was considered and compared the cost of each technology.

Chapter 4

Results and discussion

4.1 The investment cost of each flow battery

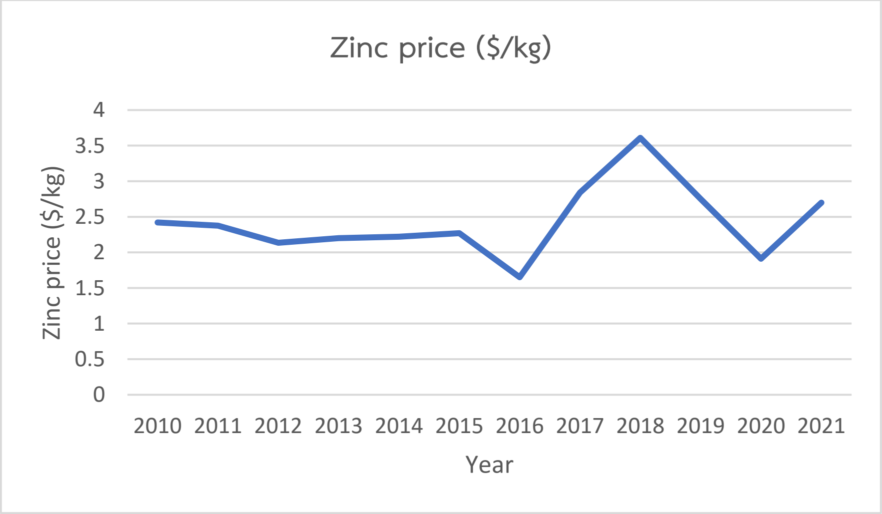

Figure 2 Zinc price ($/kg) trend from 2010 to 2021

For the anode electrode, the zinc air flow battery used zinc granules. The average cost of zinc is 2.07 $/kg. (https://www.usgs.gov/centers/nmic/zinc-statistics-and-information, Mineral industrial survey) The cost of zinc is the average cost in 2020. Figure 2 showed the trend of zinc price from 2010 to 2021 that the lowest zinc price is 1.65 $/kg in 2016 and highest zinc price is 3.61 $/kg in 2018. (https://www.usgs.gov/centers/nmic/zinc-statistics-and-information, Mineral industrial survey (USGS))

The anode for the zinc iodine flow battery, zinc iron flow battery, zinc manganese flow battery and vanadium flow battery used carbon felt or graphite felt. The cost of carbon felt is 2.9$/m^2. The cost of carbon felt is obtained from Alibaba.com.

For the cathode electrode, the zinc air flow battery used carbon black BP-2000 (Black pearl 2000, Carbot Corporation), carbon black (VXC-72, Carbot Corporation), polytetrafluoroethylene (PTFE), manganese dioxide (MnO_2), nickel foam and oxygen (O_2), the cost of BP-2000 is 50$/kg , carbon black (VXC-72) is 10 $/kg, PTFE is 14.8 $/kg , MnO_2 is 1.99$/kg and nickel foam is 10-50 $/m^2. The cost of PTFE, MnO_2 and nickel foam are obtained from Alibaba.com. Oxygen(O_2) is from atmosphere, so it is free. For the zinc iodine flow battery, zinc iron flow battery, zinc manganese dioxide flow battery and vanadium flow battery used carbon felt. The cost of carbon felt is 2.9 $/m^2. The cost of carbon felt is obtained from Alibaba.com.

For the membrane, the zinc air flow battery used the polyethylene/polypropylene (PE/PP) membrane, the cost of PE/PP membrane is 5 $/kg. The cost of PE/PP membrane is from Alibaba.com. Zinc iodine flow battery used Naffion 115 membrane. The cost of Nafion 115 membrane is 500-700$/m^2. (Xie et al., 2018) For the zinc iron flow battery and vanadium flow battery used Nafion 117 membrane. The cost of Nafion 117 membrane is 400 $/m^2 (Minke and Turek, 2018) and for the manganese dioxide flow battery, it doesn't use membrane.

For the bipolar plate, all of flow batteries used graphite plate. The cost of graphite plate is 3-30 $/m^2. The cost of bipolar plate is obtained from Alibaba.com.

For the electrolytes, zinc air flow battery used KOH, the cost of KOH is 1.39 $/kg. Zinc iodine flow battery used $ZnBr_2$ and KI. The cost of $ZnBr_2$ is 7.1 $/kg and the KI is 33$/kg. Zinc iron flow battery used $FeCl_2$, $FeCl_3$, $ZnCl_2$ and NH_4Cl. The cost of $FeCl_2$, $FeCl_3$, $ZnCl_2$ and NH_4Cl are 1.94 $/kg,0.65 $/kg, 1.53 $/kg, and 0.93 $/kg. Zinc manganese dioxide flow batteries used $ZnSO_4$ and $MnSO_4$. The cost of $ZnSO_4$ is 0.38 $/kg and the cost of $MnSO_4$ is 0.885 $/kg and for the vanadium flow battery used vanadium and sulfuric acid. The cost of vanadium is 26.6 $/kg and sulfuric acid is 0.06 $/kg. The costs of electrolytes are obtained from Alibaba.com. The costs of electrolytes are the costs for 1 metric ton of electrolytes and industrial grade.

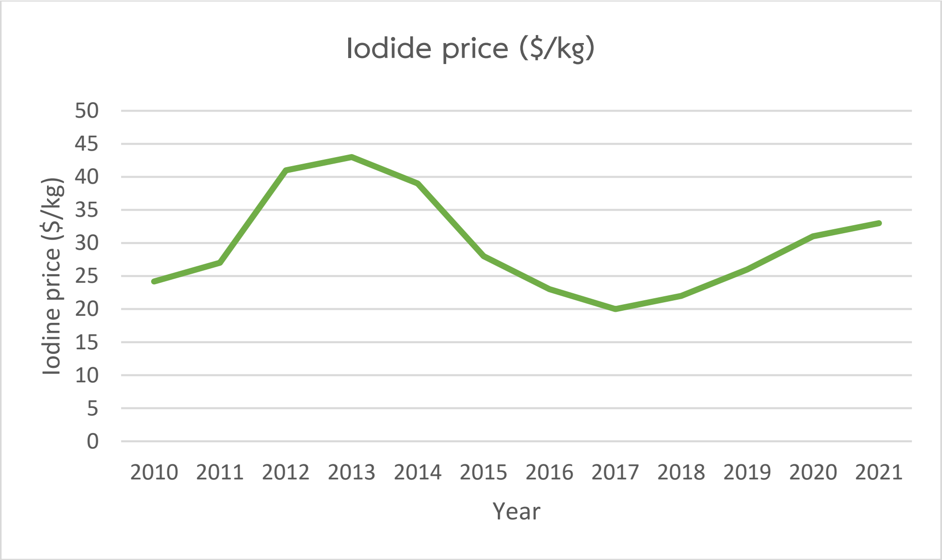

Figure 3 Iodine price ($/kg) trend from 2010 to 2021

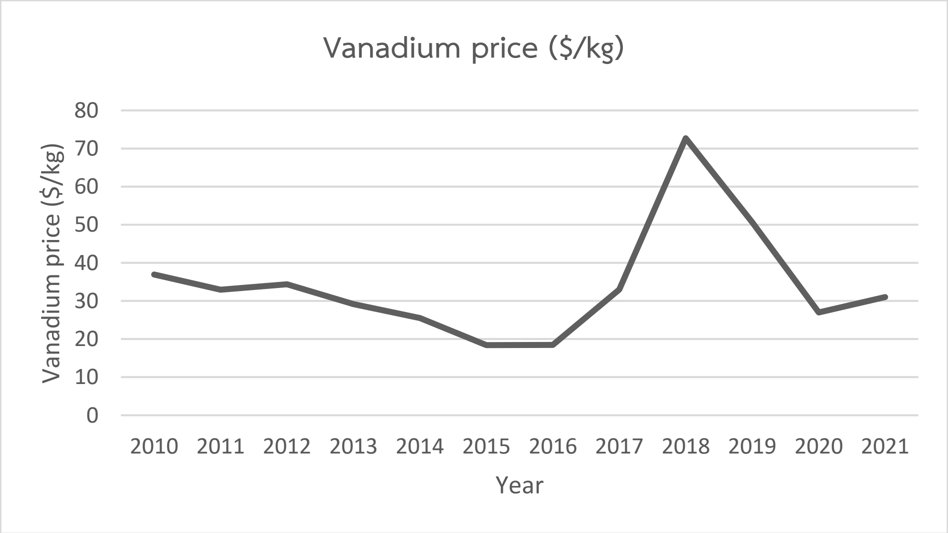

Figure 4 Vanadium price ($/kg) trend from 2010 to 2021

Figure 3 and Figure 4 showed the trend of iodine and vanadium price for electrolytes used in the flow battery. Figured 3 showed the highest price of iodine is 43 $/kg in 2013 and lowest price of iodine is 20 $/kg in 2017 and figure 4 showed the highest price of vanadium is 72.7 $/kg in 2018 and the lowest price is 18.4 $/kg in 2016. The electrolyte of iodine and vanadium are more expensive than other flow battery systems. (Mineral Industrial surveys, National Minerals Information Center)

For the anode, zinc and carbon felt electrodes are not expensive. The cathode of the zinc air flow battery is more expensive than the other flow batteries because of the high cost of carbon black (BP-2000) and nickel foam. The membrane is the most expensive of the system of the flow batteries. Membrane for the zinc air flow battery is cheaper than others and for electrolytes, the electrolytes for zinc iodine flow battery and vanadium flow battery are expensive, but electrolytes for other systems are not expensive.

The total investment cost of the zinc air is 122.91-194.17 $/kW, zinc iodine is 613.97-858.63 $/kW, zinc iron is 616.17-667.58 $/kW, zinc manganese dioxide is 193.9-483.81 $/kW and for vanadium flow battery is 512.21-551.47 $/kW. For most applications are using at discharge time 1-10 h so the investment cost in energy term for zinc air is 12.91-194.17 $/kWh, zinc iodine is 61.3-858.63 $/kWh, zinc iron is 61.6-667.58 $/kWh, zinc manganese dioxide is 19.39-483.81 $/kWh and vanadium flow battery is 51.22-551.47 $/kWh. If compare the total investment cost of each technology, the cost of zinc air flow battery is less than zinc manganese dioxide flow battery, vanadium flow battery, and less than zinc iodine and zinc iron flow battery. The investment cost details showed in Figure 5 to Figure 9.

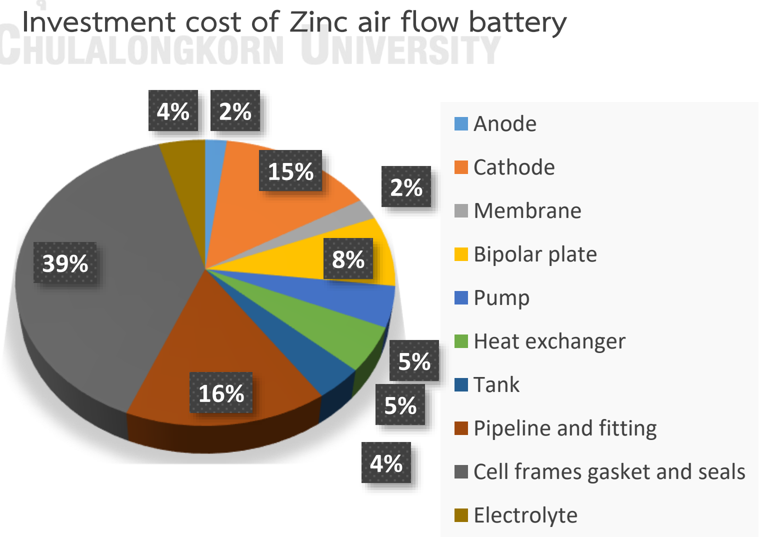

Figure 5 Investment cost of zinc air flow battery

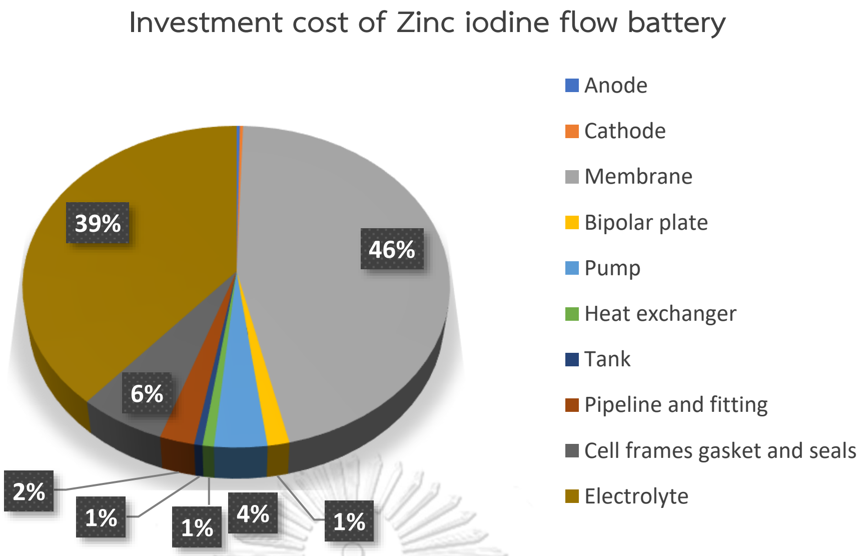

Figure 6 Investment cost of zinc iodine flow battery

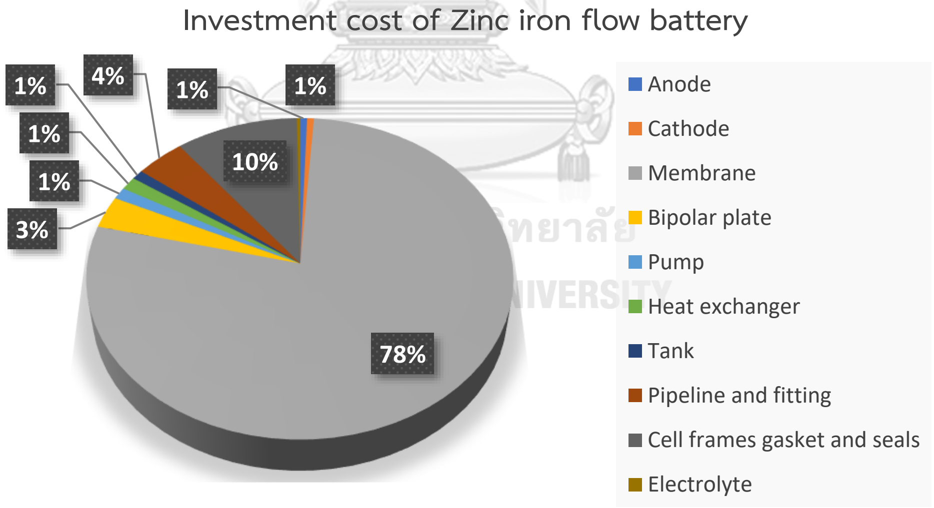

Figure 7 Investment cost of zinc iron flow battery

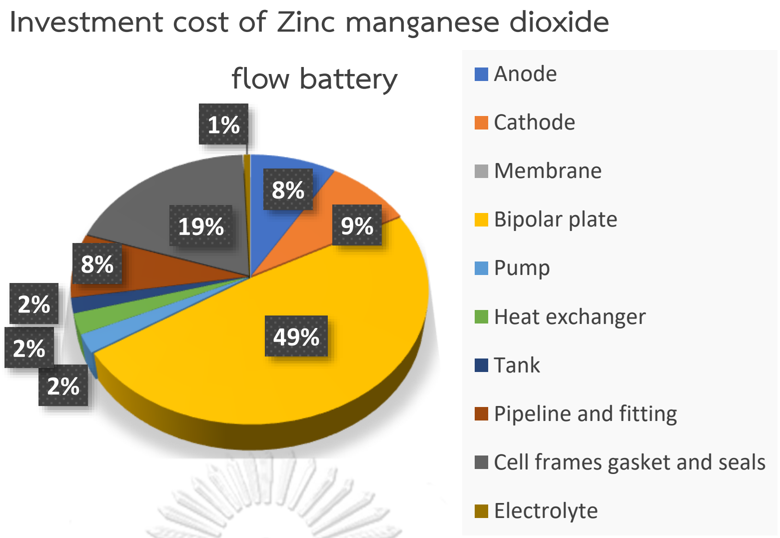

Figure 8 Investment cost of zinc manganese dioxide flow battery

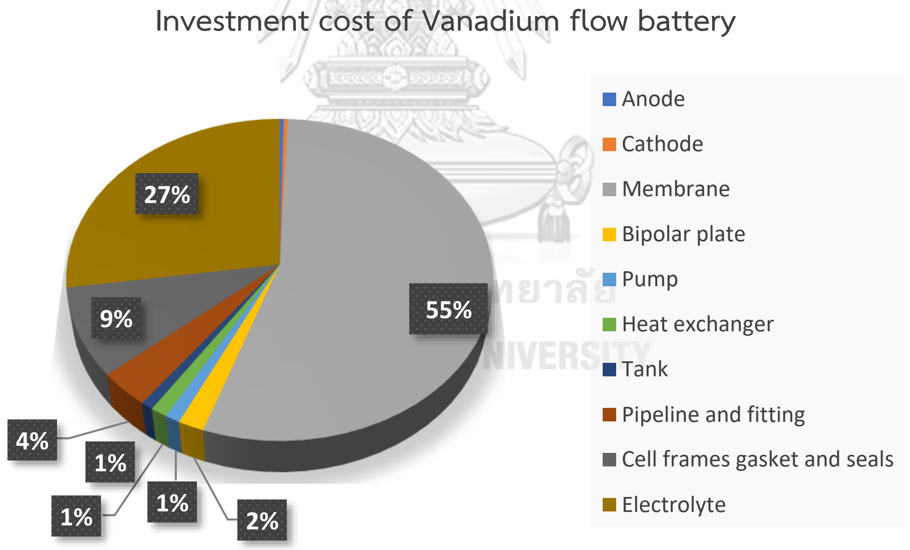

Figure 9 Investment cost of vanadium flow battery

Figure 5 to Figure 9 showed the investment cost of zinc-based flow batteries and vanadium flow battery. The investment cost including the anode, cathode, membrane, bipolar plate, pump, heat exchanger, tank, pipeline and fitting, cell frames gasket and seals, and electrolytes. Most of the investment cost have come from the membrane for every flow battery except the zinc air flow battery. The investment cost for zinc air flow battery is mostly from gasket frame and seal, pipeline and fitting and cathode. The membrane and electrolyte for the zinc air flow battery are cheap but the cathode of zinc air flow battery is expensive than other systems because the cathode for the zinc air flow battery is made from materials such as carbon black BP-2000 and VXC-72 and nickel foam that is high cost while the cathode for the other systems is made from carbon felt that is cheap. The Investment cost of zinc iodine flow battery and vanadium flow battery mostly come from membrane and electrolytes that is 55% and 27% for vanadium flow battery and 46% and 39% for zinc iodine flow battery while electrolytes for the zinc iron flow battery and zinc manganese flow battery is only 1% and 4 %. The investment cost of zinc air flow battery is cheaper than other flow batteries.

4.2 LCOS in each application using in large scale energy storage

4.2.1 LCOS in term of cost per energy ($/kWh) in each flow battery technology

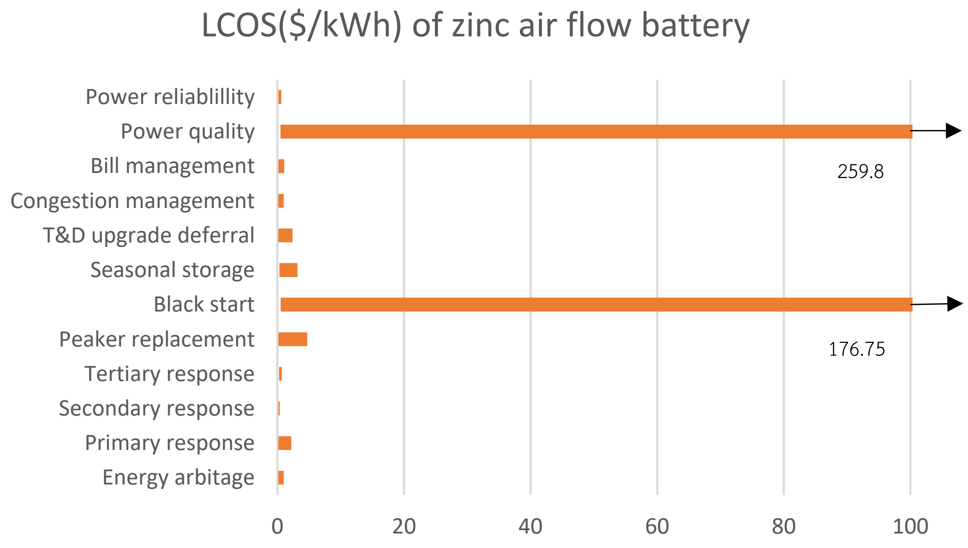

Figure 10 LCOS($/kWh) of zinc air flow battery

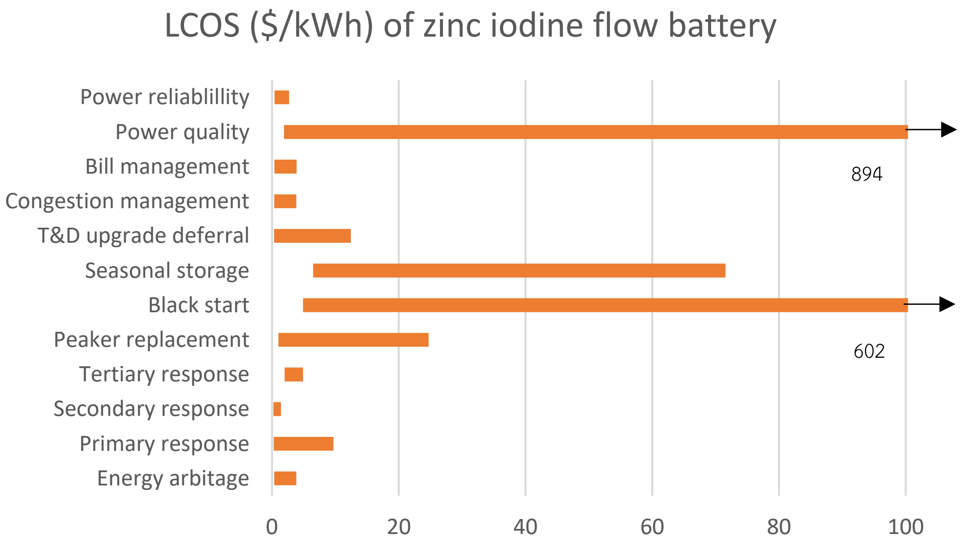

Figure 11 LCOS ($/kWh) of zinc iodine flow battery

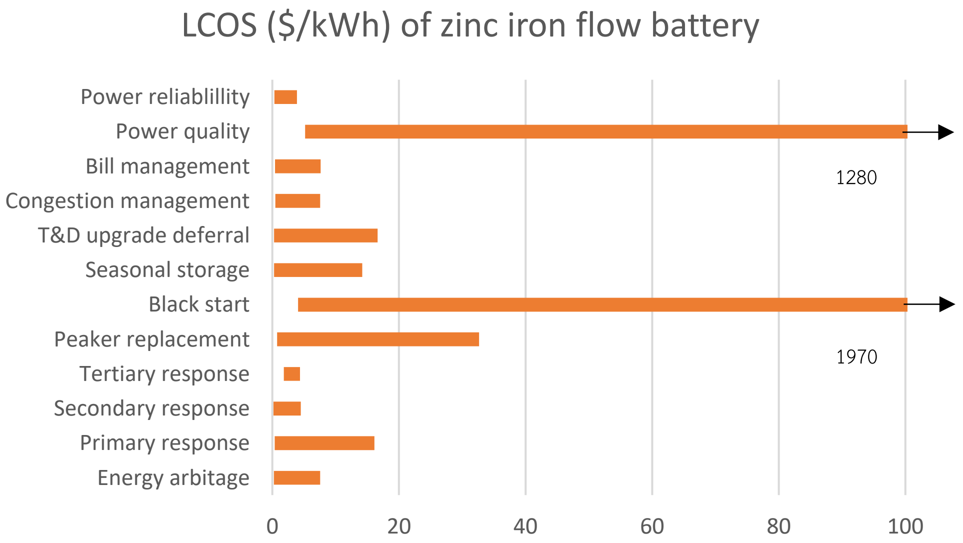

Figure 12 LCOS($/kWh) of zinc iron flow battery

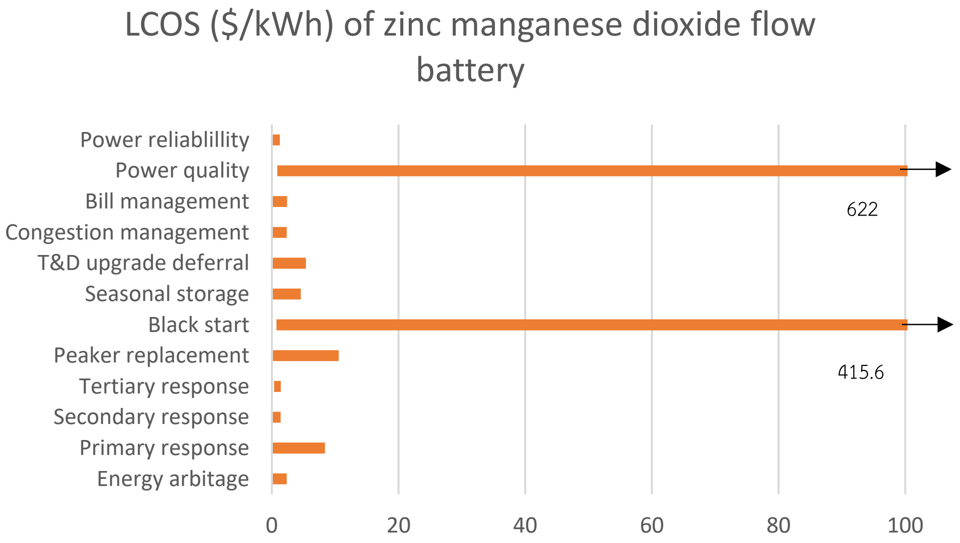

Figure 13 LCOS($/kWh) of zinc manganese dioxide flow battery

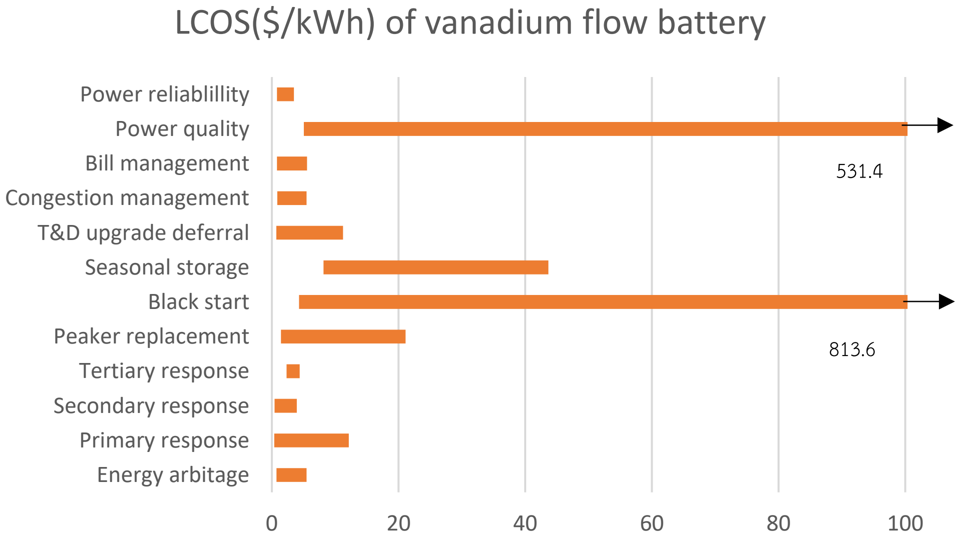

Figure 14 LCOS($/kWh) of vanadium flow battery

Figure 10 to Figure 14 showed the LCOS in term of cost per energy of each technology for 12 applications using in large scale energy storage. The LCOS of all technologies are between 0.1-30 $/kWh except the application of seasonal storage and black start which is using high power and energy because of high discharge time. For zinc air flow battery, the LCOS is about 0.1-5 $/kWh. Zinc iodine flow battery is about 0.3-13 $/kWh. Zinc iron flow battery is about 0.3-30 $/kWh. Zinc manganese flow battery is about 0.1-5 $/kWh and vanadium flow battery is about 3-20 $/kWh. If consider the LCOS in the same application, such as the energy arbitrage application at low power and energy, The LCOS of the Zinc iron is greater than Vanadium , Zinc iodine, Zinc manganese, and Zinc air flow battery (Zinc iron > Vanadium > Zinc iodine > Zinc manganese >Zinc air), but for the high power and energy, the LCOS of Vanadium flow battery is greater than Zinc iodine, Zinc iron, Zinc manganese and Zinc air flow battery (Vanadium > Zinc iodine > Zinc iron > Zinc manganese > Zinc air flow battery) and for other application, the zinc iodine, zinc iron and vanadium are very competitive, in some application The LCOS of Zinc iodine is more than zinc iron and vanadium and some application The LCOS of Zinc iron is more than vanadium and zinc iodine). The LCOS of zinc air flow battery for all applications is the lowest, so zinc air flow battery is the most cost-effective.

4.2.2 LCOS in term of cost per power ($/kW) in each flow battery technology

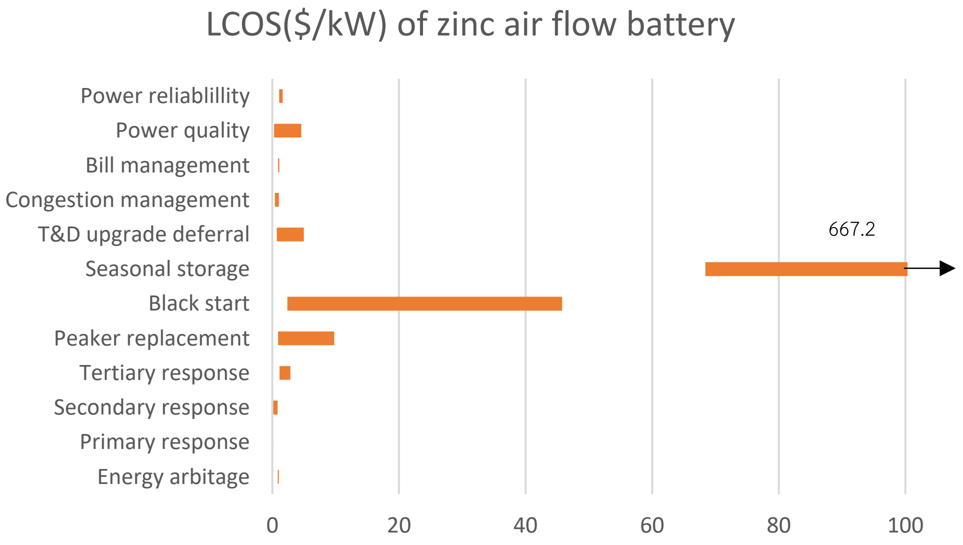

Figure 15 LCOS($/kW) of zinc air flow battery

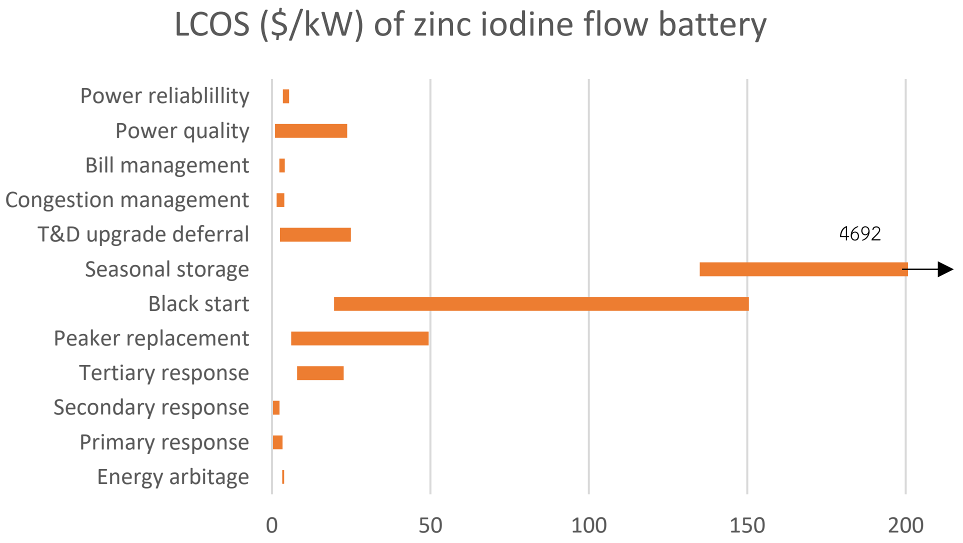

Figure 16 LCOS ($/kW) of zinc iodine flow battery

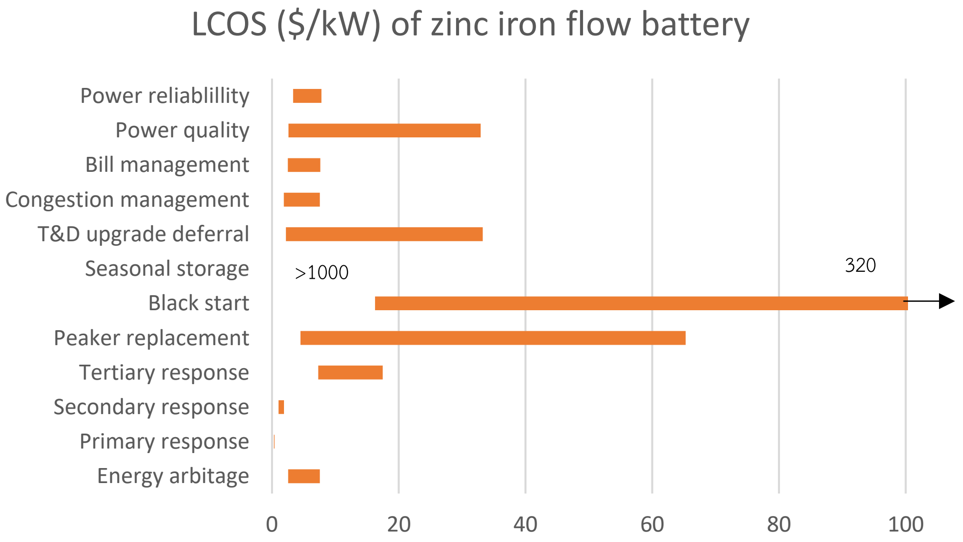

Figure 17 LCOS($/kW) of zinc iron flow battery

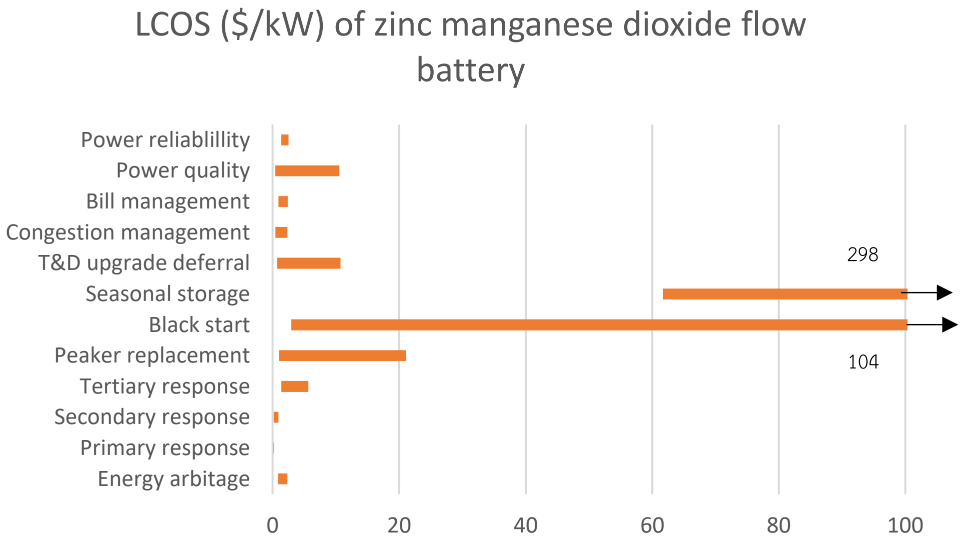

Figure 18 LCOS($/kW) of zinc manganese dioxide flow battery

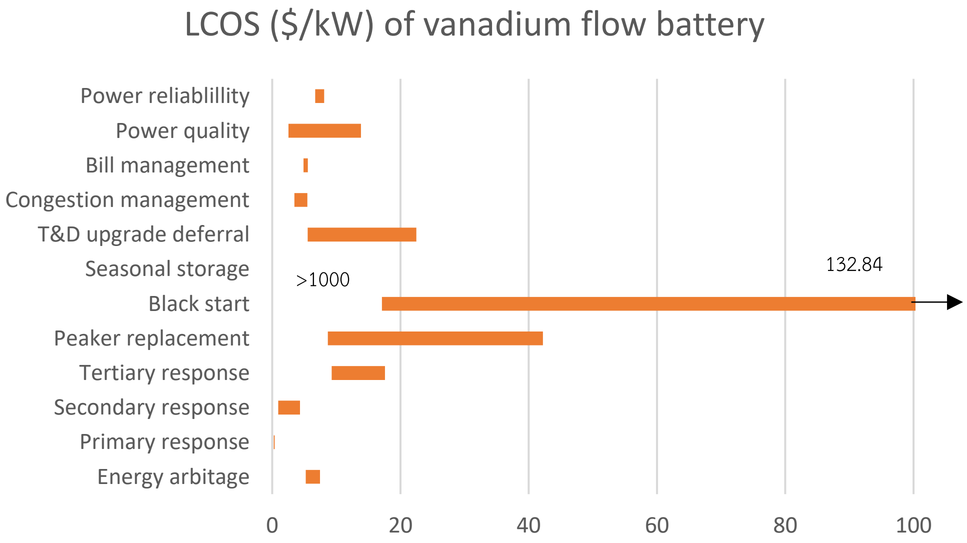

Figure 19 LCOS($/kW) of vanadium flow battery

Figure 15 to Figure 19 showed the LCOS in term of cost per power of each technology for 12 applications used in large scale energy storage. The LCOS of all technologies are between 0.1-60 $/kW except the application of seasonal storage and black start which is using high energy of these applications because of high discharge time. For zinc air flow battery, the LCOS is about 0.15-9.5 $/kW. Zinc iodine flow battery is about 0.3-50 $/kWh. Zinc iron flow battery is about 0.3-65 $/kW. Zinc manganese flow battery is about 0.2-21 $/kW and vanadium flow battery is about 0.23-22.5 $/kWh. The LCOS for application of seasonal storage and black start are more than 100 $/kW. The LCOS is depending on the application using in large scale energy storage. If use at the high power and high discharge time, the LCOS is less than using at low power and low discharge time. If consider the LCOS in the same application such as energy arbitrage application at high and low power and energy. The LCOS of the Zinc iron is greater than Vanadium , Zinc iodine, Zinc manganese and Zinc air flow battery (Zinc iron > Vanadium > Zinc iodine > Zinc manganese >Zinc air flow battery) and for other applications, zinc iodine, zinc iron and zinc manganese dioxide is very competitive in the LCOS, The LCOS in some application; LCOS of Vanadium flow battery is greater than Zinc iodine and Zinc iron, and in some application, the Zinc iodine is greater than vanadium flow battery and zinc iron flow battery depending on the application but the zinc air flow battery is also the lowest of LCOS in all application, so zinc air flow battery is the most cost effective.

4.3 Sensitivity analysis of input parameters

4.3.1 Sensitivity analysis of input parameters at 0.2 MW and discharge time 1 hour

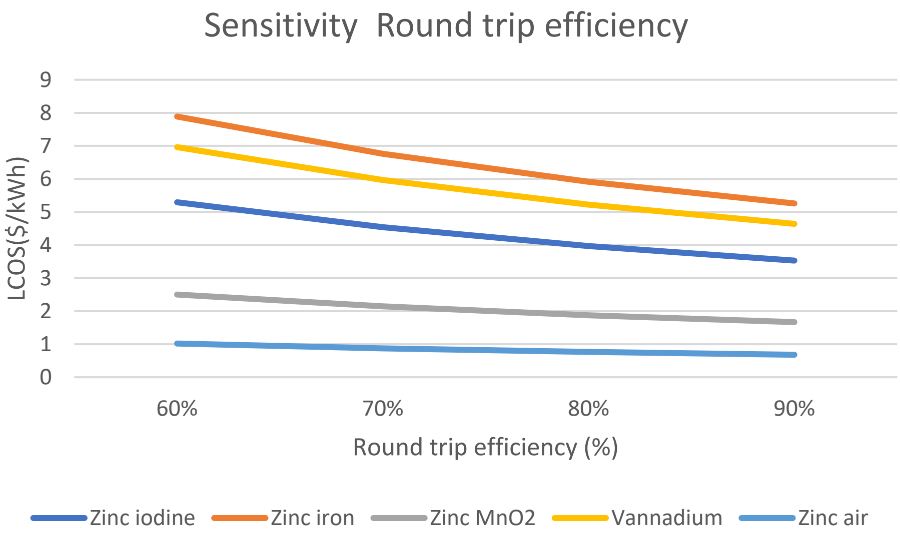

Figure 20 Sensitivity analysis of round-trip efficiency at low power and energy

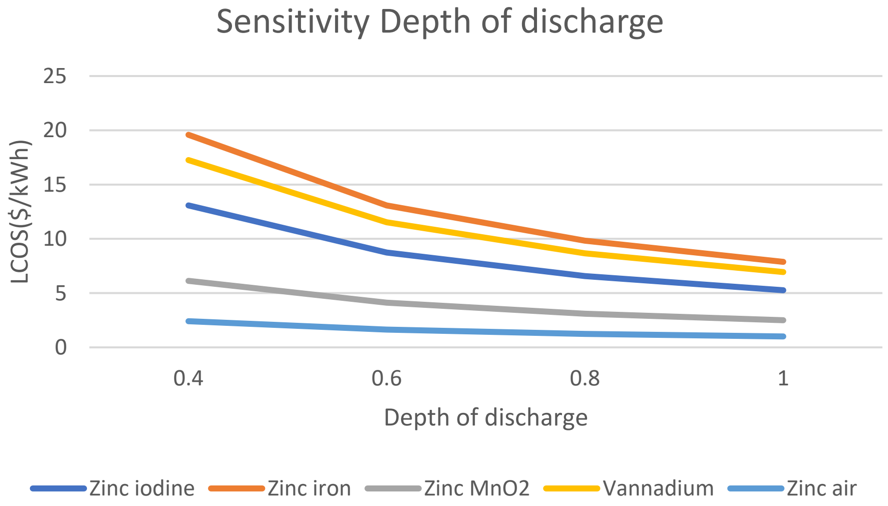

Figure 21 Sensitivity analysis of depth of discharge at low power and energy

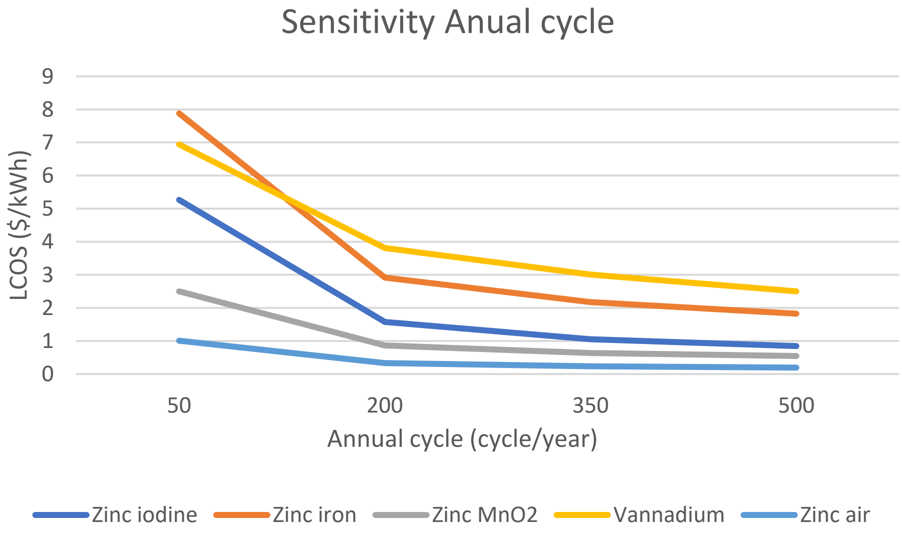

Figure 22 Sensitivity analysis of annual cycle at low power and energy

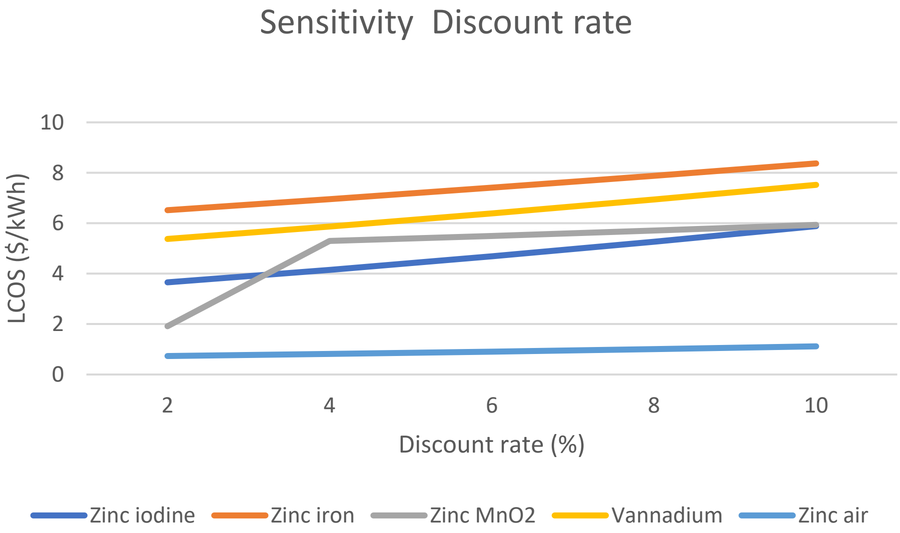

Figure 23 Sensitivity analysis of discount rate at low power and energy

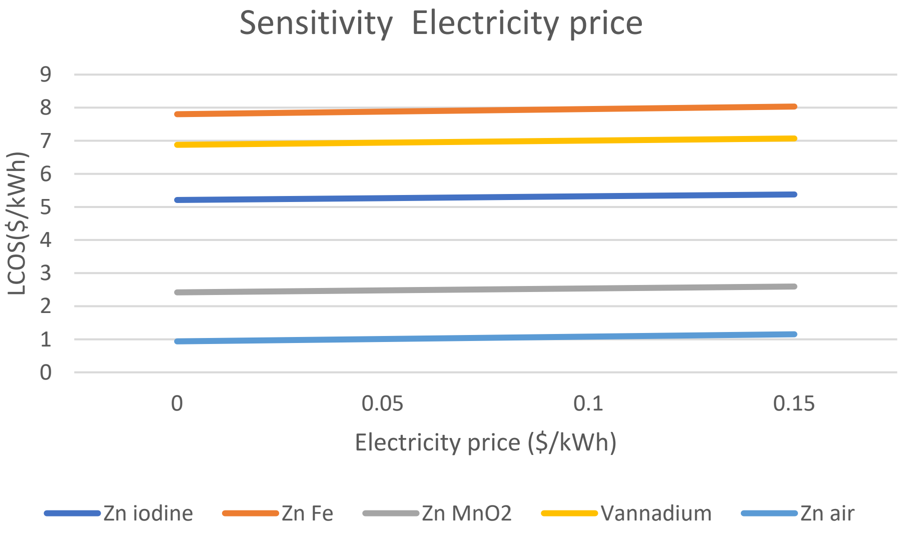

Figure 24 Sensitivity analysis of electricity price at low power and energy

4.3.2 Sensitivity analysis of input parameters at 2000 MW and discharge time 10 hours

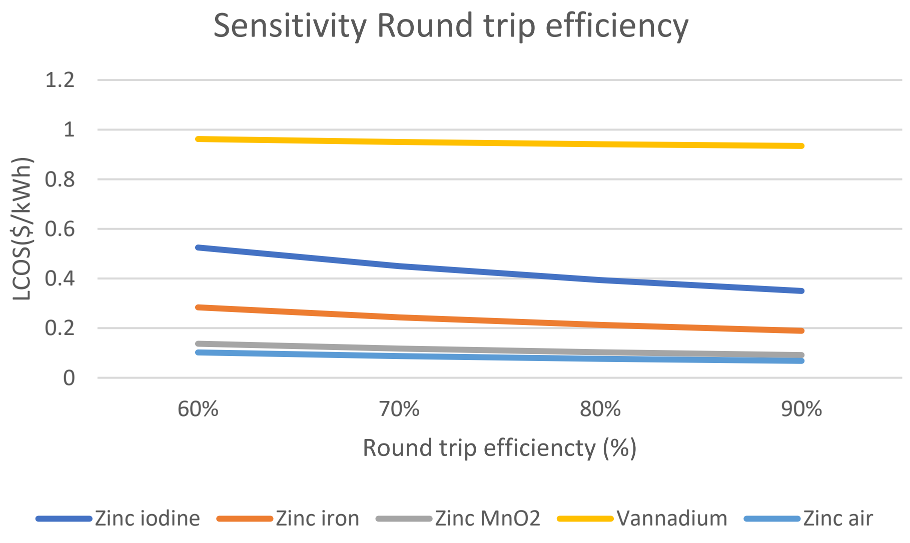

Figure 25 Sensitivity analysis of round-trip efficiency at high power and energy

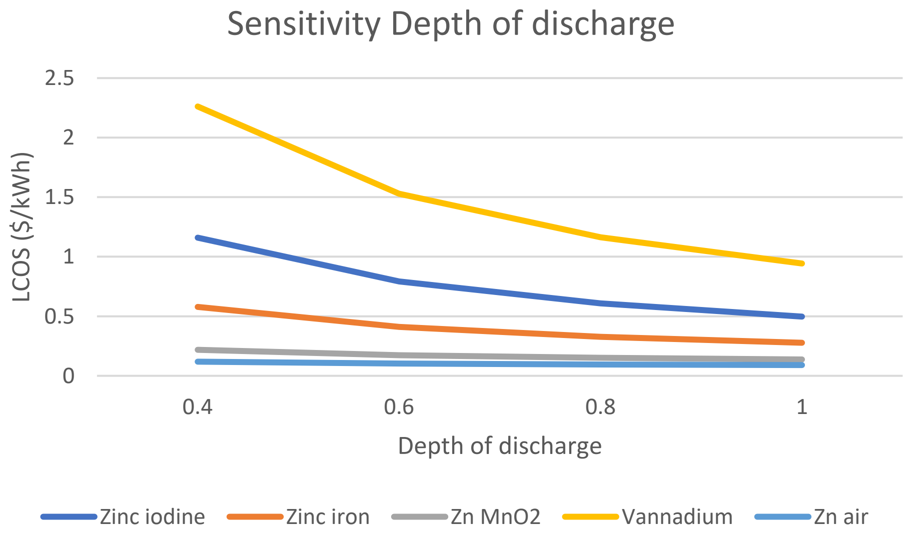

Figure 26 Sensitivity analysis of Depth of discharge at high power and energy

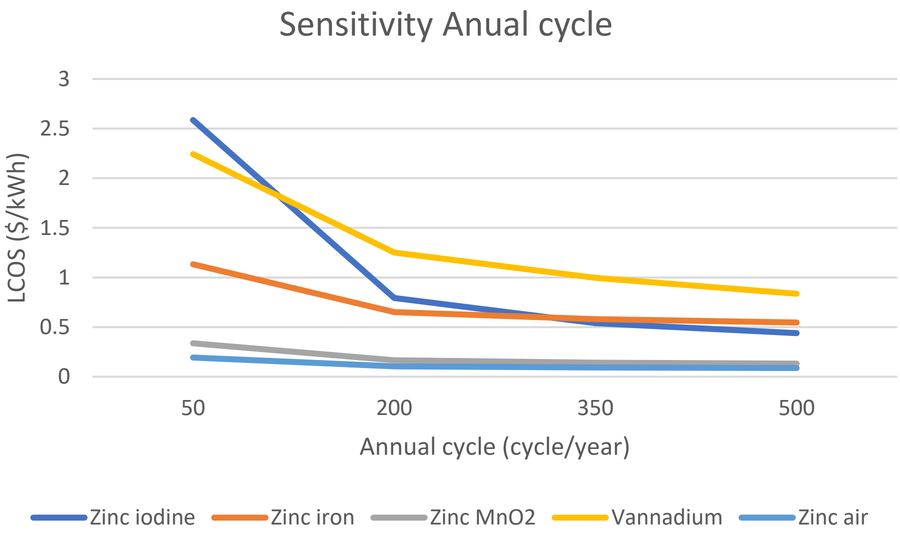

Figure 27 Sensitivity analysis of annual cycle at high power and energy

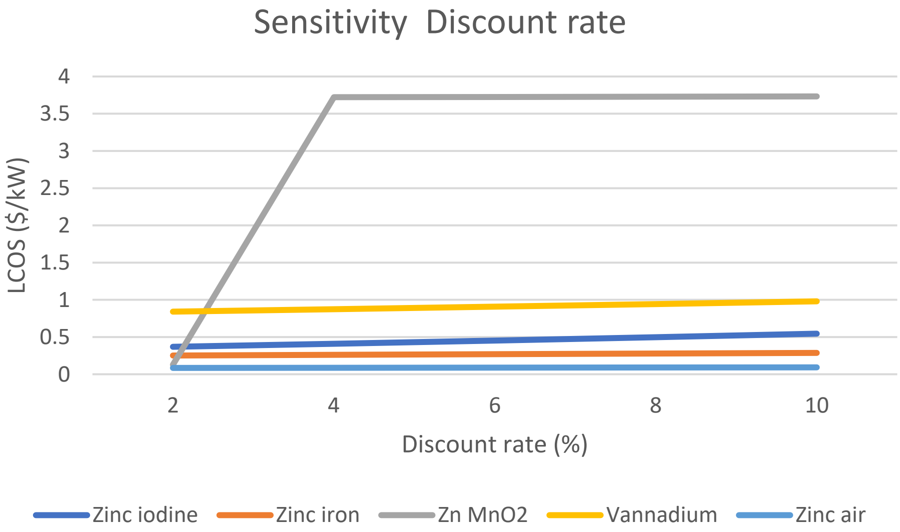

Figure 28 Sensitivity analysis of discount rate at high power and energy

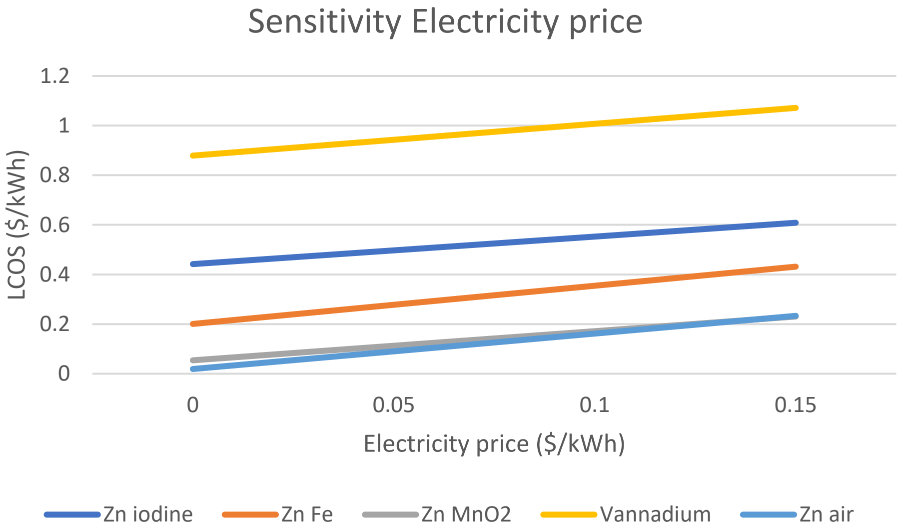

Figure 29 Sensitivity analysis of electricity price at high power and energy

From Figure 20 to Figure 29 showed the sensitivity analysis of input parameters including round trip efficiency, depth of discharge, annual cycle, discount rate, and electricity price at low and high power and energy, For using at the low power and energy (0.2 MW and 1 h discharge time) showed that round trip efficiency and depth of discharge are very sensitive to the LCOS model. The flow battery that is the lowest LCOS is the least affect to the LCOS such as zinc air flow battery when changing the round-trip efficiency and depth of discharge. The annual cycle is affected the LCOS in using between 50 to 200 cycles per year. The zinc iron and zinc iodine are very competitive in the LCOS at an annual cycle between 350 to 500 cycles per year. Electricity price is the least affected to the LCOS model. For at high power and energy (2000 MW and 10 h discharge time), the LCOS for high power and energy is less than using at low power and energy. Electricity price is affected to the LCOS model at high power and energy more than at low power and energy. Zinc air flow battery and zinc manganese dioxide flow battery are very competitive in LCOS at high power and high energy and the discount rate is the least affect to the LCOS model by using at high power and energy.

4.4 Evaluation of materials and safety of each flow battery

For evaluation of materials and safety of each flow battery, zinc air flow battery is safe because zinc is not flammable, non-toxic, and environmentally friendly. Zinc is stable and it doesn't react violently with moisture and oxygen in the air so it doesn't explode and safe. Electrolyte KOH, Carbon black, and MnO_2 are not flammable and non-toxic. Zinc oxide is non-toxic, environmentally friendly, and not flammable. Normally, the flow batteries operate at room temperature to keep electrolytes to be a liquid phase, so they don't flammable. The data of flash point temperature is from the Material Safety Data Sheet (MSDS) in Sigma Aldrich.

For zinc iodine flow battery, zinc iron flow battery, zinc manganese dioxide flow battery and vanadium flow battery, carbon felt electrode and the bipolar plate is made from the carbon, it is not flammable and it can work with high temperature (1000-1450 °C, Specification of carbon felt in alibaba.com). Electrolytes for zinc iodine flow battery including KI and $ZnBr_2$ are not flammable and non-toxic. Electrolytes for zinc iron flow battery including $FeCl_2$, $FeCl_3$, $ZnCl_2$, and NH_4Cl are not flammable and non-toxic, for zinc manganese dioxide flow battery, electrolyte $MnSO_4$ is non-toxic and not flammable and for vanadium flow battery, electrolyte of vanadyl sulfate is toxicity but it is not flammable. working conditions. If the electrolyte is leaking, all of the chemicals are not flammable and don't have toxic vapor. Most of the membrane used in flow battery system are Nafion membrane. It is made from the polymer of sulfonated tetrafluoroethylene. It is non-toxic because sulfonated is used in the detergent or washing powder. The flow battery normally operates at room temperature and don't occur the thermal runaway. Thermal runaway occurs when the batteries have too much heat in the systems that is one important factor for safety evaluation that should be considered because if thermal runaways occur, the flow battery will be flammable and then explode. The current and voltage of the flow battery should be not too high, and when we considered the zinc-based flow battery, zinc gives too much energy but it is stable and not flammable, so little chances of thermal runaways occur, so it is safe. It can conclude that zinc-based flow batteries are safe for operating flow batteries in large scale energy storage with appropriate working conditions.

Table 5 Toxicity and flammable of electrolyte in each flow battery

Electrolytes	LD50 (mg/kg)	Toxicity	Flammable
Potassium hydroxide (KOH)	333	✗	✗
Zinc Bromide ($ZnBr_2$)	1.447	✓	✗
Potassium iodide (KI)	2779	✗	✗
Zinc chloride ($ZnCl_2$)	329	✗	✗
Ferrous chloride ($FeCl_2$)	500	✗	✗
Ferric chloride ($FeCl_3$)	450	✗	✗
Ammonium chloride (NH_4Cl)	1650	✗	✗
Zinc sulphate ($ZnSO_4$)	200	✗	✗
Manganese sulphate ($MnSO_4$)	2150	✗	✗
Vanadium sulfate	74.1	✓	✗
Sulfuric acid (H_2SO_4)	2140	✗	✗

Table 5 showed the LD50 value and flammable of electrolyte, most of the electrolytes in each flow battery system are non-toxic because have a high value of LD50 but it has some electrolyte like Vanadyl sulfate and zinc bromide is needed to be careful in the system because of low value of LD50 and for the flammable of electrolyte, all of the electrolytes are not flammable because there is not have flash point temperature and inorganic chemicals didn't flammable, so it is safe for operating the flow battery for large scale energy storage. The data of LD50 are obtained from the material safety data sheet (MSDS).

Table 6 Solubility of electrolytes in each flow battery system

Electrolytes	Solubility (per 100 part of solvent)	Part of Solvent Per 1 part of solute	Solubility level
Potassium hydroxide (KOH)	1320	0.075	Very soluable
Zinc oxide (ZnO)	0.0042	23809	Insoluable
Zinc Bromide ($ZnBr_2$)	390	0.26	Very soluable
Potassium iodide (KI)	127.5	0.784	Very soluable
Zinc chloride ($ZnCl_2$)	432	0.231	Very soluable
Ferrous chloride ($FeCl_2$)	64.4	1.55	Freely soluble
Ferric chloride ($FeCl_3$)	74.4	1.344	Freely soluble

Ammonium chloride (NH_4Cl)	29.4	3.4	Freely soluble
Zinc sulphate ($ZnSO_4$)	42	2.38	Freely soluble
Manganese sulphate ($MnSO_4$)	98.47	1.015	Freely soluble
Vanadyl sulfate ($VOSO_4$)	17.82	5.61	Freely soluable
Sulfuric acid (H_2SO_4)	Infinity	0	Very soluable

Table 6 showed the solubility of electrolytes in each flow battery system, the results show that all of the electrolytes are soluble in water except the ZnO generated from the zinc air flow battery system that is not soluble, so all of the electrolytes, have a chance of the soil contaminated in the water underground, so it needs to be careful and manages in the large scale energy storage. The data of solubility are obtained from Perry Chemical Engineering Handbook 7th edition.

4.5 Electrolyte recycle and management of each flow battery system

The method of recycle and management of electrolyte in each flow battery system are divided into the 4 main steps including extraction or leaching to remove the metal ion that undesired, precipitation of sediment or undesired solid, filtration and prepare the new electrolyte by rebalancing , neutralization or concentrated the solution to desired concentration.

For the vanadium flow battery, it used the method of solvent extraction with the NaOH or Na_2CO_3 as the solvent to remove the V_2O_5 and other undesired metal then adjust the pH to 10-12 for precipitation the undesired solid and adding the ammonia solution and carboxyl chemicals for removing the byproduct of di and tri of the vanadium compound in amine complex and removing anion and filtration, after that, it is using the purification method by heating under the nitrogen atmosphere and using sulfuric acid to recover vanadyl sulfate.

For zinc air flow battery, the electrolyte management of KOH is using the calcium hydroxide ($Ca(OH)_2$) material or particles to capture the sediment of the zincate ion for reducing ZnO in the systems and add additive to reduce corrosion and sediment of ZnO and $Ca(OH)_2$ can capture the CO_2 in the form of carbonate. CO_2 comes from the air from atmosphere. The Second way to reduce CO_2 is the CO_2 absorption by using an amine-based solution; Piperazine solution or monoethanolamine solution (MEA) were used as absorbent. After that, ZnO will recover to Zn by electroplating to change the calcium zincate to zincate and prepare the new electrolytes and extraction again to remove contaminate.

For zinc iodine flow battery, the electrolyte management of KI and $ZnBr_2$ is using leaching and extraction to remove the undesired metal ion. After that, the electrolyte will concentrate, adjust pH to acid, and adding oxidizing agent such as hydrogen peroxide for oxidize the iodine to IO_3^-, filtration to remove the byproduct of iodine and solvent extraction with toluene or dimethyl benzene as the solvent, filter it again.

For zinc iron flow battery, precipitation by using crystallization to remove $FeCl_2$ and rebalancing electrolyte by using an organic reducing agent such as formic acid or methanol and have to remove NH_4 by using N_2H_4 and using H_2SO_4 as the oxidizing agent.

For zinc manganese flow battery, removing iron and organic matters by using leaching or extraction, remove remnants by using H_2SO_4 and separate the sour and dissolved residue, Next filtration to separate the zinc ion and electrolysis to recover

Zn and Mn. If it has excess Mn in the system, it has to do acid neutralization then precipitation by using NaOH and filtering and prepared the new electrolyte for using it again.

Compare each of technology, for vanadium flow battery technology has more steps than the zinc-based flow battery in the purification step but the chemicals in the system are not too much. If we compare it in management and recycle ability, zinc air flow battery is easier management than other systems because it doesn't have too much of electrolyte in the system, so easiest management and difference to other system in management only the the zincate ion and CO_2 occurs in the solution and KOH electrolyte has high solubility so little of sediment occur, while the electrolyte for zinc manganese and zinc iodine flow battery are low solubility than electrolyte of zinc air flow battery. Zinc manganese electrolyte have more sediment than Zinc iodine electrolyte, so zinc iodine electrolyte is easier management of sediment than zinc manganese flow battery. The zinc iron flow battery is the hardest electrolyte management. We compare each other by using the solubility of the electrolytes. High solubility is easier management than lower solubility. The solubility of electrolytes as show in Table 6.

Compare the solubility of electrolytes: KOH >$ZnCl_2$ > $ZnBr_2$ > Vanadyl sulfate > KI >$MnSO_4$ > $FeCl_2$ > $FeCl_3$ > $ZnSO_4$

In precipitation step, zinc air flow battery is easier management than zinc manganese dioxide, zinc iodine, zinc iron, and vanadium flow battery.

Table 7 Cost of chemicals used in each flow battery systems

Flow battery	Chemicals used in each step	Cost of chemicals ($/kg)
Vanadium	Sodium hydroxide (NaOH)	0.3$/kg
	Sodium carbonate (Na_2CO_3)	0.22 $/kg
	Ammonia solution (NH_3)	0.3 $/kg

	Sulfuric acid (H_2SO_4)	0.7$/kg
Zinc air	Monoethanolamine (MEA)	2 $/kg
	Calcium hydroxide ($Ca(OH)_2$)	1.5 $/kg
Zinc iodine	Toluene	1.5 $/kg
	Dimethylbenzene	1.2 $/kg
	Hypochlorite	0.65 $/kg
	Hydrogen peroxide	10-14 $/kg
Zinc iron	Manganese dioxide (MnO_2)	2 $/kg
	Hydrogen peroxide (H_2O_2)	10-14 $/kg
	Formic acid	0.55 $/kg
	Methanol	0.45 $/kg
	Hydrazine (N_2H_4)	32 $/kg
Zinc Manganese dioxide	Sulfuric acid (H_2SO_4)	0.7 $/kg
	Sodium hydroxide (NaOH)	0.3 $/kg

Table 7 showed the cost of chemical used in treatment and management of electrolytes in each flow battery system. The data of cost are obtained from Alibaba.com and the grade of chemicals are industrial grade.

The cost of chemicals used in each step showed that zinc manganese dioxide flow battery and vanadium flow battery are low cost of chemical used and chemical used in zinc air and zinc iodine flow battery are very competitive but for the zinc iron flow battery has the highest cost of chemicals used because of high cost of hydrogen peroxide (H_2O_2) and hydrazine (N_2H_4).

Chapter 5

Conclusion

5.1 Conclusion

In this work, zinc-based flow battery including zinc air flow battery, zinc iodine flow battery, zinc iron flow battery, zinc manganese flow battery and vanadium flow battery are evaluated the cost, materials, and safety for 12 large scale energy storage applications including energy arbitrage, primary response, secondary response, tertiary response, peaker replacement, black start, seasonal storage, T&D investment deferral, congestion management, bill management, power quality, and power reliability applications.

This work demonstrated that zinc air flow battery is the most cost-effective because of the lowest cost of investment cost and LCOS in all applications used in the large-scale energy storage. The investment cost of zinc air flow battery is 122.91-194.17 $/kW and 12.29-194.17 $/kWh and the LCOS of zinc air is between 0.1-5 $/kWh and 0.03-9.45 $/kW. The investment cost is not exceeding the target of the US Department of Energy that is 150$/kWh. (Gong et al., 2015) The Zinc iodine, Zinc iron and Vanadium flow battery are very competitive in the LCOS. The internal factors such as round-trip efficiency and depth of discharge are very sensitive to the LCOS and the external factor such as electricity price is sensitive to the LCOS at high power and energy using. The low LCOS are not affected to the LCOS model too much if the parameters in the model are changed. Using the flow battery at high power and energy is more cost-effective than using at low power and energy. For the materials and safety evaluation, all zinc-based flow batteries are safe for operating in large scale energy storage because all materials and chemicals are non-toxic and not flammable, but for the vanadium flow battery, the electrolyte is toxic, so it needs to be careful. All of electrolytes are soluble in water, so it needs to be careful in soil contaminated underwater in large-scale energy storage. For electrolyte management and recycle ability of each flow battery system, In precipitation step, zinc air flow battery is easier management than vanadium flow battery, zinc manganese dioxide flow battery, zinc iodine flow battery, and zinc iron flow battery, when considering the cost of chemical used in each step of recovery, the cost of chemical used in zinc air flow battery is not expensive, so zinc air flow battery is the best appropriate for use in large scale energy storage.

5.2 Recommendation

This work focused on evaluating the cost, materials and safety of each zinc based flow battery that is the new technology, so they need to have more researches to improve and develop the zinc based flow battery in the future and can use for large scale energy storage with high efficiency, high stability, and long cycle life with the most cost effective and safe materials. In the present research about zinc-based flow battery cannot commercialize and scale up for use in large-scale energy storage because of the problem mentioned above. This research showed that the cost of each flow battery is very competitive. The optimization of the cost and economic worthiness and optimize the performance should be considered in future work. The cost of the cathode of zinc air flow battery is too high, so it needs to improve and develop the cathode with low cost material with high efficiency, high stability, and long cycle life.

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Appendix A

Details for calculation of Levelized cost of storage (LCOS)

The model of LCOS including the investment cost, operating and maintenance cost, charging cost and electrical discharged and the input parameters in the model was showed in chapter 3 of this research. In following table showed the details for calculation the Levelized cost of storage (LCOS).

Table 8 Investment cost of zinc air flow battery in each application

	Investment at low power		Investment at high power	
Application	Minimum ($)	Maximum ($)	Minimum ($)	Maximum ($)
Energy arbitrage	2602.16	4027.36	389780000	532300000
Primary response	123053.96	194313.96	260216000	402736000
Secondary response	1247095	1959695	389780000	532300000
Tertiary response	758510	1114810	151702000	222962000
Peaker replacement	137306	208566	83049000	118679000
Black start	12470.95	19596.95	60680800	89184800
Seasonal storage	147831000	183461000	29037820000	29180340000
T&D upgrade deferral	137306	208566	90247000	125877000
Congestion management	130108	201368	75851000	111481000
Bill management	2602.16	4027.36	1660980	2373580
Power quality	6151.6183	9714.6183	1265090	1977690
Power reliability	2746.12	4171.32	1948900	2661500

Table 9 Investment cost of zinc iodine flow battery in each application

	Investment at low power		Investment at high power	
Application	Minimum ($)	Maximum ($)	Minimum ($)	Maximum ($)
Energy arbitrage	20724	17192.6	9672540000	10161860000
Primary response	622414.6	858650	2072400000	2561720000
Secondary response	7195275	8588800	9672540000	10161860000
Tertiary response	11514450	4313150	2302890000	2547550000
Peaker replacement	1458430	860630	1573675000	1696005000
Black start	71952.75	85888	921156000	1019020000
Seasonal storage	5373745000	441315000	1.69015E+12	1.69064E+12
T&D upgrade deferral	1458430	860630	1995905000	2118235000
Congestion management	1036200	859630	1151445000	1273775000
Bill management	20724	17192.6	31473500	33920100
Power quality	31057.3955	42932.35	8250850	10697450
Power reliability	29168.6	17212.6	48362700	50809300

Table 10 Investment cost of zinc iron flow battery in each application

	Investment at low power		Investment at high power	
Application	Minimum ($)	Maximum ($)	Minimum ($)	Maximum ($)
Energy arbitrage	12359.4	13387.6	1268340000	1371160000
Primary response	616206	667616	1235940000	1338760000
Secondary response	6166200	6680300	1268340000	1371160000
Tertiary response	3116850	3373900	623370000	674780000
Peaker	619770	671180	313485000	339190000

replacement				
Black start	61662	66803	249348000	269912000
Seasonal storage	329685000	355390000	8432340000	8535160000
T&D upgrade deferral	619770	671180	315285000	340990000
Congestion management	617970	669380	311685000	337390000
Bill management	12359.4	13387.6	6269700	6783800
Power quality	30810.03	33380.53	6170700	6684800
Power reliability	12395.4	13423.6	6341700	6855800

Table 11 Investment cost of zinc manganese dioxide in each application

	Investment at low power		Investment at high power	
Application	Minimum ($)	Maximum ($)	Minimum ($)	Maximum ($)
Energy arbitrage	3921.2	9696.2	431000000	1010820000
Primary response	193943.2	483830	392120000	971940000
Secondary response	1944400	4840600	431000000	1010820000
Tertiary response	1012700	2439050	202540000	492450000
Peaker replacement	198220	485810	103430000	248385000
Black start	19444	48406	81016000	196980000
Seasonal storage	122870000	253905000	9027800000	9607620000
T&D upgrade deferral	198220	485810	105590000	250545000
Congestion management	196060	484810	101270000	246225000
Bill management	3921.2	9696.2	2068600	4967700
Power quality	9696.836	24191.35	1949800	4848900

Power reliability	3964.4	9716.2	2155000	5054100

Table 12 Investment cost of vanadium flow battery in each application

	Investment at low power		Investment at high power	
Application	Minimum ($)	Maximum ($)	Minimum ($)	Maximum ($)
Energy arbitrage	12359.4	13387.6	1268340000	1371160000
Primary response	616206	667616	1235940000	1338760000
Secondary response	6166200	6680300	1268340000	1371160000
Tertiary response	3116850	3373900	623370000	674780000
Peaker replacement	619770	671180	313485000	339190000
Black start	61662	66803	249348000	269912000
Seasonal storage	329685000	355390000	8432340000	8535160000
T&D upgrade deferral	619770	671180	315285000	340990000
Congestion management	617970	669380	311685000	337390000
Bill management	12359.4	13387.6	6269700	6783800
Power quality	30810.03	33380.53	6170700	6684800
Power reliability	12395.4	13423.6	6341700	6855800

Table 13 Operating and maintenance cost of zinc air flow battery

	Investment at low power		Investment at high power	
Application	Minimum ($)	Maximum ($)	Minimum ($)	Maximum ($)
Energy arbitrage	12359.4	13387.6	1268340000	1371160000
Primary response	616206	667616	1235940000	1338760000
Secondary	6166200	6680300	1268340000	1371160000

response				
Tertiary response	3116850	3373900	623370000	674780000
Peaker replacement	619770	671180	313485000	339190000
Black start	61662	66803	249348000	269912000
Seasonal storage	329685000	355390000	8432340000	8535160000
T&D upgrade deferral	619770	671180	315285000	340990000
Congestion management	617970	669380	311685000	337390000
Bill management	12359.4	13387.6	6269700	6783800
Power quality	30810.03	33380.53	6170700	6684800
Power reliability	12395.4	13423.6	6341700	6855800

Table 14 Operating and maintenance cost of zinc air flow battery

	Operating and maintenance cost ($)	Operating and maintenance cost ($)
Application	At low power and energy	At high power and energy
Energy arbitrage	1045.20153	129125087.1
Primary response	52149.4811	112476224.3
Secondary response	526428.444	150276459.6
Tertiary response	261914.082	52842186.28
Peaker replacement	52106.0415	27159433.36
Black start	5206.70424	20953126.57
Seasonal storage	26081152.9	184135763.1
T&D upgrade deferral	52145.772	31940031.24
Congestion management	52260.0763	28986525.53
Bill management	1045.20153	609265.5678
Power quality	2603.33587	524182.5235
Power reliability	1049.08226	645625.4357

Table 15 Operating and maintenance cost of zinc iodine flow battery

	Operating and maintenance cost ($)	Operating and maintenance cost ($)
Application	At low power and energy	At high power and energy
Energy arbitrage	1838.70561	187017741.6
Primary response	97114.967	194229934
Secondary response	947519.345	189503869.1
Tertiary response	458700.395	91935280.32
Peaker replacement	91637.5649	46116903.13
Black start	9160.96504	36696031.6
Seasonal storage	45804825.2	183275129.8
T&D upgrade deferral	91672.1131	46899515.84
Congestion management	91935.2803	46899515.84
Bill management	1838.70561	937990.3168
Power quality	4583.60566	927446.9388
Power reliability	1838.70561	935088.7082

Table 16 Operating and maintenance cost of zinc iron flow battery

	Operating and maintenance cost ($)	Operating and maintenance cost ($)
Application	At low power and energy	At high power and energy
Energy arbitrage	890.208626	89898091.97
Primary response	47794.5795	95589158.97
Secondary response	453581.944	90716388.73
Tertiary response	222139.397	44510431.29
Peaker replacement	44380.3465	22309548.91
Black start	4436.68697	17771151.72
Seasonal storage	22183434.8	88760693.06
T&D upgrade deferral	44396.7054	22509986.11
Congestion management	44510.4313	22509986.11

Bill management	890.208626	450199.7222
Power quality	2219.83527	447679.7167
Power reliability	890.208626	449490.4599

Table 17 Operating and maintenance cost of zinc manganese dioxide flow battery

	Operating and maintenance cost ($)	Operating and maintenance cost ($)
Application	At low power and energy	At high power and energy
Energy arbitrage	1680.53619	170217687.7
Primary response	87770.1596	175540319.2
Secondary response	857722.695	171544539.1
Tertiary response	419290.543	84026809.51
Peaker replacement	83766.0968	42134355.82
Black start	8374.063	33543243.47
Seasonal storage	41870315	167532193.6
T&D upgrade deferral	83797.3708	42633370.69
Congestion management	84026.8095	42633370.69
Bill management	1680.53619	852667.4138
Power quality	4189.86854	846399.864
Power reliability	1680.53619	851088.4387

Table 18 Operating and maintenance cost of vanadium flow battery

	Operating and maintenance cost ($)	Operating and maintenance cost ($)
Application	At low power and energy	At high power and energy
Energy arbitrage	1760.36643	176325347.4
Primary response	91249.1507	182498175.9
Secondary response	887327.146	177354143
Tertiary response	439630.481	87875521.24
Peaker replacement	87851.3753	43955418.13

Black start	8782.63847	35142374.31
Seasonal storage	43913192.3	175678972.6
T&D upgrade deferral	87879.319	44124201.27
Congestion management	88018.3217	44124201.27
Bill management	1760.36643	882484.0254
Power quality	4393.96595	879918.5741
Power reliability	1760.36643	881626.737

Table 19 Charging cost of each flow battery in each application

Flow battery	Zinc air flow battery	Zinc iodine flow battery	Zinc iron flow battery	Zinc manganese flow battery	Vanadium flow battery
Application	Charging cost ($/kWh)				
Energy arbitrage	0.071428571	0.055555556	0.076923077	0.058823529	0.064102564
Primary response	0.071428571	0.055555556	0.076923077	0.058823529	0.064102564
Secondary response	0.071428571	0.055555556	0.076923077	0.058823529	0.064102564
Tertiary response	0.071428571	0.055555556	0.076923077	0.058823529	0.064102564
Peaker replacement	0.071428571	0.055555556	0.076923077	0.058823529	0.064102564
Black start	0.071428571	0.055555556	0.076923077	0.058823529	0.064102564
Seasonal storage	0.071428571	0.055555556	0.076923077	0.058823529	0.064102564
T&D upgrade deferral	0.071428571	0.055555556	0.076923077	0.058823529	0.064102564
Congestion management	0.071428571	0.055555556	0.076923077	0.058823529	0.064102564

Bill management	0.142857143	0.111111111	0.153846154	0.117647059	0.128205128
Power quality	0.142857143	0.111111111	0.153846154	0.117647059	0.128205128
Power reliability	0.142857143	0.111111111	0.153846154	0.117647059	0.128205128

Table 20 LCOS of zinc air flow battery in term of power and energy

	LCOS ($/kWh)		LCOS($/kW)	
Application	Minimum	Maximum	Minimum	Maximum
Energy arbitrage	0.086259	1.005082	0.74276	1.005082
Primary response	0.103332	2.181235	0.031425	0.115532
Secondary response	0.079788	0.379297	0.072763	0.819944
Tertiary response	0.25967	0.692291	1.03868	2.769165
Peaker replacement	0.141314	4.726072	0.847886	9.452144
Black start	0.53161	176.7505	2.126441	44.18763
Seasonal storage	0.332327	3.180994	63.65403	667.1986
T&D upgrade deferral	0.086204	2.407026	0.689629	4.814051
Congestion management	0.096783	1.005082	0.387131	1.005082
Bill management	0.161159	1.07651	0.814189	1.07651
Power quality	0.505721	259.792	0.25286	4.416465
Power reliability	0.157687	0.623289	0.984257	1.617603

Table 21 LCOS of zinc iodine flow battery in term of power and energy

	LCOS ($/kWh)		LCOS($/kW)	
Application	Minimum	Maximum	Minimum	Maximum
Energy arbitrage	0.342903	3.823763	3.233982	3.823763
Primary response	0.283996	9.688146	0.146145	3.333115
Secondary response	0.229528	1.401366	0.301176	2.381598
Tertiary response	1.984336	4.895098	7.937342	22.59664
Peaker replacement	1.006044	24.70786	6.036266	49.41572
Black start	4.895098	602.0549	19.58039	150.5137
Seasonal storage	6.483072	71.56619	135.0098	4692.558
T&D upgrade deferral	0.313908	12.45003	2.511267	24.90006
Congestion management	0.358664	3.823763	1.434656	3.896061
Bill management	0.384382	3.879319	2.306295	4.050105
Power quality	1.897024	894.0715	0.948512	23.73084
Power reliability	0.398459	2.700383	3.403989	5.400766

Table 22 LCOS of zinc iron flow battery in term of power and energy

	LCOS ($/kWh)		LCOS($/kW)	
Application	Minimum	Maximum	Minimum	Maximum
Energy arbitrage	0.255338	7.548993	2.553378	7.548993
Primary response	0.37544	16.11581	0.299265	0.398492
Secondary response	0.182018	4.490176	1.043034	1.899687
Tertiary response	1.824548	4.369944	7.29819	17.47977
Peaker replacement	0.750502	32.64358	4.503009	65.28717

Black start	4.063072	1280.14	16.25229	320.035
Seasonal storage	0.27083	14.21107	317.9718	546.339
T&D upgrade deferral	0.274815	16.62638	2.198516	33.25276
Congestion management	0.468488	7.548993	1.873952	7.548993
Bill management	0.416295	7.625917	2.497772	7.625917
Power quality	5.187936	1937.437	2.593968	32.93643
Power reliability	0.332261	3.899301	3.322609	7.798603

Table 23 LCOS of zinc manganese dioxide flow battery in term of power and energy

	LCOS ($/kWh)		LCOS($/kW)	
Application	Minimum	Maximum	Minimum	Maximum
Energy arbitrage	0.084551	2.3459	0.845507	2.3459
Primary response	0.141559	8.389814	0.083295	0.226067
Secondary response	0.076214	1.374561	0.176458	0.929494
Tertiary response	0.346868	1.415774	1.38747	5.663096
Peaker replacement	0.16562	10.56292	0.993721	21.12583
Black start	0.738638	415.6229	2.954551	103.9057
Seasonal storage	0.143613	4.568681	61.69715	297.9199
T&D upgrade deferral	0.08727	5.362918	0.698159	10.72584
Congestion management	0.114058	2.3459	0.456232	2.3459
Bill management	0.155023	2.404723	0.930136	2.404723
Power quality	0.84401	621.9564	0.422005	10.57326
Power reliability	0.143374	1.263195	1.370101	2.526391

Table 24 LCOS of vanadium flow battery in term of power and energy

	LCOS ($/kWh)		LCOS($/kW)	
Application	Minimum	Maximum	Minimum	Maximum
Energy arbitrage	0.735164	5.481089	5.227634	7.453107
Primary response	0.364318	12.15241	0.228374	0.378995
Secondary response	0.428769	3.940399	0.930095	4.342825
Tertiary response	2.321188	4.396719	9.284753	17.58688
Peaker replacement	1.444692	21.10279	8.66815	42.20558
Black start	4.278202	531.3834	17.11281	132.8459
Seasonal storage	8.163375	43.66716	1042.11	16328.34
T&D upgrade deferral	0.692069	11.23676	5.536554	22.47351
Congestion management	0.863678	5.481089	3.454711	5.481089
Bill management	0.813375	5.545191	4.880248	5.545191
Power quality	5.049089	813.609	2.524545	13.83135
Power reliability	0.799266	3.480987	6.713168	8.094133

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