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Dynamic Modeling of Sodium Sulfur Battery Grid Storage Units

Engin Baran

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Dynamic Modeling of Sodium Sulfur Battery Grid Storage Units

Engin Baran

Thesis submitted to the
Benjamin M. Statler College of Engineering and Mineral Resources
at **West Virginia University**

in partial fulfillment of the requirements
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in
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Abstract

Dynamic Modeling of Sodium Sulfur Battery Grid Storage Units

Engin Baran

Due to the development of a high-technology-society, power demand has been increasing year after year. Therefore, new materials and development approaches in battery systems seek for a solution to store large amounts of energy. Among these new battery types, sodium sulfur batteries are a new practical and economical competitive solution in electrical energy storage systems. However, development of new batteries is a slow and an expensive practice.

The purpose of this study is to adapt a transient lumped computational model for a sodium sulfur battery cell to multi-cells of sodium sulfur battery module by using MATLAB/Simulink. Based on a non-linear battery model, different battery modules are presented and analyzed to predict the electrochemical behavior of the cells. Case studies are validated with simulations and experimental results from literatures. Presented model is designed to aid in the design process and calculation of state of charge of sodium sulfur battery storage units.

Dedication

I dedicate my thesis work to my loving parents and many friends. A special feeling of gratitude to my loving parents, Bulent and Gulden Baran whose words of encouragement and push for tenacity ring in my ears. My uncle (Burak Orkut) has never left my side and is very special. Their love is my mortal power.

I also dedicate this thesis to my many friends who have supported me throughout the process. I will always appreciate all they have done, especially Hayri Sezer for helping me to learn this project and discussing my results, Berk Demirgok, Brooke Anne Marie Nickelson, Emily Schack, Ozcan Ozmen, Serdar & Merve Bilgili, Sercan & Seda Babakiray, Sercan Ergungor and Tyler Davis for their motivation and encouragement. They helped me to overcome all the difficulties that I encountered during the course of this work and achieve my goals.

Finally, this thesis is dedicated to all those who believe in the richness of learning.

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Nomenclature

a	chemical activity
E_0	open-circuit voltage
E^0	cell potential
e	electron
F	the Faraday constant
I	current
I_0	exchange current density
i_0^*	reference current density
n	number of electrons
Q	capacity of a battery
P	power
R	universal gas constant
R_0	electrical resistance of the battery
T	temperature
SOC	state of charge
DOD	depth of discharge

Greeks

α	transfer coefficient
β	tortuosity factor
ε	porosity or volume fraction
η_{act}	activation potential

Subscripts

A	anode
C	cathode
E	electrolyte

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CHAPTER 1: INTRODUCTION

In recent decades, large-scale stationary battery energy storage has grown at a higher rate than any other sector due to the concern on fossil fuels (i.e. coal, oil and natural gas), nuclear fuel supply security and climate change. There are currently many methods of implementing energy storage, ranging from compressed air energy storage (CAES) to sodium-sulfur battery storage. Table 1.1 summarizes installed energy storage capacity [1]. Pumped hydro and CAES are the most common two forms of energy storage used worldwide. However, the major problem with pumped hydro and CAES storage is that there are few locations which have the required geological layout that allows these methods to be used. On the other hand, battery energy storage systems (BESS) are pad mounted in design and they can be put into any traditional electrical substation [2].

Due to the increased demand for energy and rapidly aging electric transmission, there is a need to produce and deliver energy more efficiently [2]. Therefore, distributed generation has become popular in electrical power generation recently. Electric power produced by renewable energy sources (RES), such as wind energy and photovoltaic (PV) energy may require energy storage systems. Two BESS applications can be mentioned [3]:

- I. Energy Applications: Involve the storage system discharge over periods of hours (typically one discharge cycle per day) with correspondingly long charging periods. Load leveling and peak shaving are some of energy applications.
- II. Power Applications: Involve comparatively short periods of discharge (seconds to minutes), short recharging periods, and often require many cycles per day. Frequency and voltage regulation, power quality, renewable generation smoothing and ramp rate control are some of power applications.

In this scenario, among new battery types and different methods of implementing energy storage, sodium-sulfur batteries offer new practical, economical, reliable performance solution to store large amount of energy. Other battery types, such as lead-acid, nickel-cadmium, and lithium-ion batteries can also be used for energy storage as well. Yet different designs need to be done for grid applications. Sodium-sulfur batteries are rechargeable and medium to high-temperature battery technologies that provide attractive solutions for many large-scale, electric utility energy storage applications.

Table 1.1: Summary: Experience with Energy Storage [1].

Source: U.S. Department of Energy, Energy Efficiency and Renewable Energy (EERE)

Technology	Installed (U.S. total)	Facility Size Range	Commercially Available
Pumped Hydroelectric	22 GW at 150 facilities in 19 states – almost exclusively utility – owned and operated	Up to 2.1 GW	Yes
Compressed Air Energy Storage (CAES)	110 MW in Alabama (utility owned and operated)	25 MW to 350 MW	Yes
Batteries	More than 70 MW installed by utilities in 10 states	From 100 W to 20 MW	Conventional and Advanced Batteries Yes
Flywheels	Dozens of units. Increasing use as subsystems for onsite emergency back-up power systems.	A few kW to tens of kiloWatts	Steel, low rpm Yes Advanced composite Near Commercial
Superconducting Magnetic Energy Storage (SMES)	Numerous facilities with at least 100 MW of combined capacity in at least 5 states.	1 – 10 MW (micro-SMES) 10 – 100 MW	Micro-SMES Yes 10 – 100 MW Developmental
Advanced or “Super” Capacitors	Millions of units for standby power. Emerging use: hybrid and electric vehicles	Watts to tens of kiloWatts	Yes

1.1 Motivation

Huge amount of power supply is necessary in the world due to the development of a high-technology society. At present, over 80% of the energy used by the mankind comes from non-renewable energy sources, such as fossil fuels and nuclear fuels. Fossil fuel has been a very convenient way to power the energy demand but it also brings severe consequences. There are a number of problems associated with fossil fuels. These problems are limited amount of resources, increased demand for fossil fuels and the adverse impact on the environment. The main byproducts of the combustion of fossil fuels, carbon dioxide and nitrous oxide, are greenhouse gases. Greenhouse gases are major contributors to global warming. Therefore, over the last decade, driven by limited fossil fuel supply and global warming, sustainable power generations such as wind power, solar power (thermal, photovoltaic and concentrated), hydroelectric power, tidal power, geothermal energy and biomass have been increasingly integrated into the existing power grids. From a wide range of renewable energy resources (RES), wind and solar energy are the focus of this study.

However, electrical energy harnessed from photovoltaic or wind turbine stations tend to be unsteady and not reliable since it is affected by weather conditions (solar radiation and wind speed). The generated electric power output is not only unpredictable but also it may fall or peak in periods. In order not to waste or discard this energy, an electric energy storage system (EES) can be a solution to balance supply and demand of electricity generation, distribution, and usage. Building an excessive energy generation capacity can be avoided by large-scale electric energy storage to meet short-term peak demand for electricity [4].

Secondary batteries are also known as rechargeable or storage batteries that are used in grid energy storage applications for renewable energy uses. Common applications for a battery energy storage system (BESS) are peak shaving and load leveling are shown in Figure 1.1 and Figure 1.2, respectively [5].

Figure 1.1: Daily peak shaving [5].

According to Northern Pacific Systems, peak shaving is the process of reducing the amount of energy purchased from the utility company during peak hours when charges are highest [6]. On the other hand, load leveling allows storing power during low demand and low cost generation and deliver energy from energy storage devices during periods of high demand [7].

Figure 1.2: Daily load leveling [5].

A rechargeable battery consists of reversible cell reactions that allow them to recharge, or regain their cell potential, by passing an electric current through it in the opposite direction to the current flow during discharge. It is comprised of one or many electrochemical cells. On the other hand, the non-rechargeable batteries are also known as primary batteries which are used once, and after its life span it has to be discarded. That means in primary battery cells, the chemical reactions are responsible for delivering electrical energy which are irreversible. Therefore, rechargeable batteries are a type of energy accumulator used for electrochemical energy storage.

Rechargeable batteries are widely used in industrial and automotive applications. There are many different energy storage technologies. Those technologies include lead-acid, nickel cadmium (NiCd), nickel metal hydride (NiMh), lithium ion (Li-ion), lithium-ion-cobalt (LiCoO₂), lithium ion polymer (Li-ion polymer) and sodium-sulfur (NaS) batteries. Each technology provides its own unique set of benefits including specific energy, years of service life, load characteristics, safety, price, self-discharge, environmental issues, maintenance requirements, and disposal.

NaS batteries are one of the emerging technologies in many large-scale, electric utility energy storage applications. NaS battery has many attractive features such as high energy density, high efficiency, and long cycle life [8]. NaS battery is made from cheap and abundant raw materials and it operates at relatively high temperatures around 300-360 °C [2, 9].

1.2 History of Sodium Sulfur Batteries

The sodium sulfur (NaS) battery is a relatively high ampere hour, rechargeable and high-temperature battery. The basic principle of sodium sulfur batteries was originally developed by Ford Motor Company of the U.S. in 1967 [10].

British Railways has developed the sodium sulfur battery for rail traction. In particular, British Rail considered some of the requirements of a sodium sulfur battery which would be needed to power a rail vehicle. Their analysis indicated that a sodium sulfur battery could be a financially competitive with the diesel fuel cost in 1979 [11]. Similarly, there has been research on sodium sulfur battery for naval applications [12] and space applications [13] in the early 1980's as well.

Moreover, a Japanese collaboration between NGK Insulator, Ltd., and Tokyo Electric Power Company (TEPCO) is the dominant organization that started producing sodium sulfur cells in 1984 [3, 14]. Their goal is to develop sodium sulfur cells (NAS cells) with sufficient energy capacity to use in battery energy storage systems [3].

Another research was done by Sandia National Laboratories and Beta Power, Inc. in 1990. The main goal of this research was to design a common sodium sulfur cell (and a module) that can be used in electric utility vans. Several cell configurations were evaluated and compared in terms of the medium risk option, calendar life and overall size of the cell [15].

As discussed above, sodium-sulfur batteries can be used for a wide variety of applications including renewable integration, peak shaving (Figure 1.1) and load leveling (Figure 1.2), emergency backup power and distributed energy storage system (DESS) [2]. Table 1.1 summarizes advantages and limitations of Sodium/sulfur technology [16]. It can be seen that sodium battery is suitable for large-scale, non-mobile applications such as grid energy storage.

Table 1.2: Advantages and limitations of Sodium/sulfur battery technology [16].

Characteristics	Comments
Advantages	
Potential low cost relative to other advanced batteries	Inexpensive raw materials. Sealed, no-maintenance configuration
High cycle life	Liquid electrodes
High energy efficiency	80+ % due to 100% coulombic efficiency
Insensitivity to ambient conditions	Sealed high-temperature systems
State-of-charge identification	High resistance at top of charge and straightforward current integration due to 100% coulombic operation
Limitations	
Thermal management	Effective enclosure required to maintain energy efficiency and provide adequate stand time
Safety	
Durable seals	Cell hermeticity required in a corrosive environment
Freeze-thaw durability	Due to the use of a ceramic electrolyte with limited fracture toughness that can be subjected to high levels of thermally driven mechanical stress

1.3 Research Objectives

The main objective of this study is to adapt a zero-dimensional, transient, lumped computational model for a sodium sulfur battery cell to multi-cells of sodium sulfur battery module by using MATLAB/Simulink. Important factors such as internal resistance, cell temperature, battery electromotive force, depth of discharge and state of charge are considered in the developed computational battery model. Moreover, the model is implemented to several sodium sulfur battery configurations (either in series or parallel) to predict the electrochemical behavior of the electrochemical storage system.

The proposed methodology is the model based approach where the parameters are obtained from the lumped model to be used as inputs to Simulink model. The main steps taken during the project are; various models (including different large scale energy storage technologies) are reviewed first from the literature in order to be familiar with sodium sulfur batteries. Then, these models aim to predict the operation of a battery module at various electrical networking of the battery configurations. Furthermore, several battery configurations are to be implemented and simulated in MATLAB/Simulink. The intention of the battery modeling is to predict charge and discharge states of the electrical energy storage system which can be integrated to renewable energy sources.

CHAPTER 2: LITERATURE SURVEY

2.1 Comparing Sodium Sulfur to Other Energy Storage Technologies

The energy storage technology is selected on the basis of the necessity of the system used. There are a variety of options available for both small and large scale energy systems. Reliability, efficiency, life span, capital cost per cycle and environmental impact are some criteria to select a best-fit energy storage technology.

Sodium sulfur batteries are another relatively new battery technology if it is compared to other energy storage technologies. A U.S. Electric Power Research Institute's (EPRI) paper entitled Electricity Energy Storage Technology Options states that sodium sulfur batteries are currently the third most widely used energy storage solution in the world.

Moreover, sodium sulfur batteries are one of the most beneficial and the lowest cost options for grid-scale energy storage. The defining characteristics of sodium sulfur batteries are high cycle life (2000-3000 cycles range), high pulse power capability, high power density and energy, nearly three times the density of lead-acid batteries. Sodium sulfur batteries have an ability to deliver power pulses up to five times of its rated capacity over a period up to 30 seconds continuously [17, 18]. Because of this ability of sodium sulfur battery, these batteries are considered economically viable for both power quality and energy management applications [17]. Grid Energy Storage report that was published by Department of Energy in December 2013 mentions that sodium sulfur batteries are somewhat behind Li-ion battery technology in terms of energy and power, but they can maintain longer discharges (up to four to eight hours) and may be more suitable for load leveling [19].

The Electricity Storage Association (ESA) compared energy storage technologies for high power and high energy applications as shown in Figure 2.1[20]. As it can be seen from Figure 2.1, sodium sulfur batteries are one of the most capable and reasonable energy storage candidates for applications in electric power systems.

<div> <div>● Fully capable and reasonable</div> <div>◐ Reasonable for this application</div> <div>○ Feasible but not quite practical or economical</div> <div>None Not feasible or economical</div> </div>				
Storage Technologies	Main Advantages (relative)	Disadvantages (Relative)	Power Application	Energy Application
Pumped Storage	High Capacity, Low Cost	Special Site Requirement		●
CAES	High Capacity, Low Cost	Special Site Requirement, Need Gas Fuel		●
Flow Batteries: PSB VRB ZnBr	High Capacity, Independent Power and Energy Ratings	Low Energy Density	◐	●
Metal-Air	Very High Energy Density	Electric Charging is Difficult		●
NaS	High Power & Energy Densities, High Efficiency	Production Cost, Safety Concerns (addressed in design)	●	●
Li-ion	High Power & Energy Densities, High Efficiency	High Production Cost, Requires Special Charging Circuit	●	○
Ni-Cd	High Power & Energy Densities, Efficiency		●	◐
Other Advanced Batteries	High Power & Energy Densities, High Efficiency	High Production Cost	●	○
Lead-Acid	Low Capital Cost	Limited Cycle Life when Deeply Discharged	●	○
Flywheels	High Power	Low Energy density	●	○
SMES, DSMES	High Power	Low Energy Density, High Production Cost	●	
E.C. Capacitors	Long Cycle Life, High Efficiency	Low Energy Density	●	◐

Figure 2.1: Comparing energy storage technologies for high power and high energy applications [20].

2.1.1 Existing Installations

Sodium sulfur battery installations have seen rapid growth in recent years. The greatest sodium sulfur battery energy storage systems size is 34 MW * 7 hour in Aomori, Japan, forming a hybrid system with 51 MW wind farm [21]. Table 2.1 is examples of installed large scale sodium sulfur BESS [3, 17, 21].

Table 2.1: List of sodium sulfur battery energy storage systems (BESS) [3, 17, 21].

Name and Location	Application	Power	Energy	Cell Size& Configuration	Battery Manufacturer
Rokkasho-Futamata Wind Farm, Aomori, Japan	Load leveling and spinning reserve	34 MW	238 MWh	17 sets of 2 MW NGK Insulators NAS battery units	NGK Insulators LTD (battery)
Yerba Buena Battery Energy Storage System Pilot Project, San Jose, CA, USA		4 MW			NGK Insulators LTD (battery)/ S&C Electric Co.
Long Island, New York Bus Terminal Energy Storage System, NY, USA	Load shifting	1.2 MW	6.5 MWh	20 ea. 50 kW (60 kW peak) NAS battery modules	NGK Insulators LTD (battery)/ABB Inc. (integration and balance of system)
AEP Sodium Sulfur Distributed Energy Storage System at Chemical Station, N. Charleston, WV, USA	Substation upgrade deferral	1.0 MW	7.2 MWh	50 kW NAS battery modules, 20 ea.	NGK Insulators LTD (battery)/ S&C Electric Co. (balance of system)
EDF, La Réunion, France	N/A	1.0 MW	7.2 MWh	Total 384 NAS cells (32(S)×12(P))	NGK Insulators LTD (battery)

Note: The disparity in the rate assumptions, ranging from ~5 hours to 7 hours.

2.2 Chemistry and Cell Structure

A sodium sulfur battery cell consists of molten sulfur (S) at the positive electrode and molten sodium (Na) at the negative electrode. Sodium sulfur batteries have an operating temperature between 300° and 360° C (572° and 680° F) to maintain Na and S at molten states and low resistance values. The medium separating the two electrodes is a kind of solid ceramic which serves as both the electrolyte and a separator simultaneously. Sodium β'' -Alumina (beta double prime alumina) is a fast ion conductor material and is used as a separator in several types of molten salt electrochemical cells such as NaS and sodium nickel chloride (ZEBRA) cells [19].

A sodium sulfur battery works based on the electrochemical reaction between sodium and sulfur and formation of sodium polysulfide (Na_2S_x). Figure 2.2 below shows the operating principle of sodium sulfur batteries when current flows during charging and discharging phases, where NA, Na^+ , S, Na_2S_x and e^- refer to elemental sodium, sodium ion, elemental sulfur, sodium polysulfide and electron, respectively. The value of x can be between 2 to 5, depending on its actual process of charge/discharge [22].

Figure 2.2: Chemical mechanism for the NaS battery [22].

During discharge phase, electrons are stripped off the molten elemental sodium metal (one negatively charged electron for every sodium atom) leading to formation of the sodium-ions (Na^+) within a sodium based electrode (anode) as shown in reaction (2.3.1). Then, sodium ions pass through the electrolyte into a sulfur based electrode (cathode). The positively charged sodium-ions moving into a sulfur based electrode balance the electron charge flow. The electrons given off by the sodium metal move through an electrical load, such as resistor, wire, etc. and back into the battery at the positive electrode, where another electron reacts with sulfur to form S_x^{2-} to generate sodium polysulfide (NaS_x) in cathode as shown in reaction (2.3.2). The overall reaction is expressed as (2.3.3).

During charge phase, the whole process is the reverse process of discharging phase [2, 23, 24]. In this process, the sodium polysulfide decomposed to sodium and sulfur, respectively, and return to the anode and cathode. An external current pulls electrons from the positive electrode and injects them into the negative electrode. Energy is stored through the transfer of ions to the negative electrode [23]. The general cell structure of the sodium sulfur battery is shown in Figure 2.3 [17].

Figure 2.3: Sodium sulfur tubular cell structure [17].

One of the special specifications of sodium sulfur battery is that reactions which involve the formation and decomposition of various polysulfide determines the way sodium sulfur battery charges and discharges [25]. Sodium sulfur batteries do not have self-discharge problems if they are used at nominal operating conditions [17]. However, the act of over-charge and over-discharge is a critical issue if sodium sulfur battery energy storage system is used in micro-grid applications. When the battery is over-charged, it causes a huge resistance in cathode. In this case, a current being compelled to pass through the battery can damage it. Overheating might result from overcharging, cell failure, or a failure of the thermal management of the batteries. On the other hand, if the battery is over-discharged, the amount of sodium will be less in the anode. This may lead to degradation of the solid electrolyte.

2.3 Important Factors in Sodium Sulfur Battery Modeling

Part of the research for this thesis involves creating a sodium sulfur battery model. In order to model sodium sulfur batteries accurately, there are some important factors that have to be discussed. These important factors are introduced and discussed in the next section.

2.3.1 Internal Resistance

One of the most important parameters in cell performance of sodium sulfur batteries is internal resistance. The cell resistance determines the maximum power from the cell and it is the major source of the cell's internal heating when thermal management of batteries is considered [26]. A paper published by Hussien, et al. [9] mentions that the internal resistance of sodium sulfur battery consists of the ohmic resistance associated with electrolyte resistance, plate resistance, fluid resistance, and the resistance associated with the polarization effect.

The internal resistance varies based on depth of discharge and temperature of the cell during charging and discharging operation. Figure 2.4 shows how internal resistance behaves for an individual NAS cell at different temperature and depth of discharge (DOD) [9, 26]. It should be noted that nominal capacity of a NAS cell is 628 Ah and those NAS cells are produced by NGK Insulators [27].

Figure 2.4: NAS battery cell charge/discharge resistance vs. DOD at different temperature [26].

One of the observations from Figure 2.4 (Experimental data) is that the internal resistance reduces as the temperature increases from 280° to 360°C. Also it can be observed that at the end of charging and discharging operation polarization effect tends to increase the internal resistance [9].

Another important concept is the practical operating temperature of the NaS battery. Upon the examination of the phase diagram is shown in Figure 2.5 [25, 28]. In order to have a proper operation of the cell, the sodium polysulfide melt needs to stay in the liquid phase. In fact, the operating temperature is in the range 300 to 400°C and when the polysulfide melt reaches the composition Na_2S_3 , the discharge is

normally terminated in order to avoid precipitation of solids [25]. Any shortcomings in the cell seals will allow the escape of sulfur and cause failure in the NaS cells. Therefore, the operating temperature of NAS battery is maintained at the same level, which is in the range 300 to 350°C [17]. During charging or standby state, the battery temperature drops gradually. If the temperature goes outside of this range (the lower limit is 300°C in NAS battery), the heater installed in the battery module will be activated to raise the temperature to the operating temperature range [17].

Figure 2.5: The $\text{Na}_2\text{S}/\text{S}$ phase diagram according to Gupta and Tischer (1972) and Oci (1973) [25, 28].

Furthermore, the life cycle resistance (R_{lc}) which depends upon the number of the charge-discharge cycles already experienced by the battery can affect the internal resistance. The life cycle resistance determines the remaining available maximum pulse power and voltage output of the battery. Figure 2.6 shows the change of deterioration cell resistance with the number of charging-discharging cycles in the range 300 to 350°C. [9, 26, 29]. It can be observed that the internal resistance increases with the number

of cycles. R_{ic} is zero in a new battery and as the battery is used, the value increases. The use of the NaS battery at the grid level requires high current density operation that can cause cell deterioration, thus cell deterioration causes lower sulfur utilization and lower energy efficiency. When the battery is constructed and managed properly, a calendar life of at least 15 years at 300 cycles each year can be expected, the given annual losses were converted to per-cycle losses. The NaS battery is capable of 2500 cycles to full depth of discharge (DOD) or 4500 cycles to 90% DoD which both at a discharge rate between 8.5 and 10.5 hours [30].

Figure 2.6: NaS cell deterioration resistance vs. charge-discharge cycle (Manufacturer Data) [9, 26, 29].

As a result, it can be seen from Figure 2.4 and Figure 2.6 that analytical expressions in closed-form are difficult to derive because of the non-linear characteristics of the resistances. Therefore, this major problem has to be solved in order to create a sodium sulfur battery electrical model.

2.3.2 Temperature Effect

Sodium sulfur batteries have unique thermal considerations. The Na and S located at the electrodes need to be kept at a low resistance. So, the batteries need to operate at elevated temperatures [31]. During discharging state, two exothermic reactions, which are the Joule heating associated with ohmic loss and the entropy-heating associated with the electrochemical reaction, occur simultaneously in the cell [32]. However, during charging state, even though Joule heating is still present, the battery absorbs heat due to the internal endothermic chemical reaction. Thus, the battery temperature is gradually lowered [9, 31]. During the idle state, the battery's temperature decreases at a rate greater than charging state because of no ohmic heating is presented at this stage.

Finally, Hussien, et al. [9] points out that the effect of temperature on the internal resistance is very important as it determines the limit to the battery's peak power output. Pulse power output with larger currents generates more joule heat by internal resistance.

2.3.3 Battery Electromotive Force

By and large, the electromotive force (EMF) of sodium sulfur batteries depends on the depth of discharge, sometimes abbreviated to DoD. DoD is defined as the fraction of the elemental sulfur which has been converted to Na_2S_3 [25]. The theoretical capacity of the cell is the capacity calculated from the mass of sulfur in the cell assuming complete conversion to Na_2S_3 [25].

Figure 2.7: The relationship between depth of charge and voltage of sodium sulfur battery [33].

As illustrated in Figure 2.7 [33], the EMF is relatively constant except in the vicinity of the end of a charge or a discharge. It can be observed that the voltage rises toward the end of the charge and falls toward the end of the discharge with a reduction in the molar proportion of sulfur. The composition of the sodium polysulfide generated at the positive electrode changes with respect to DoD.

Moreover, in the single-phase region the molar proportion of sulfur reduces and the voltage drops substantially as the cell keeps discharging as shown in Figure 2.8 [9]. At approximately 55% and 100% state of discharge, the knee starts to occur at 350°C. Hussien, et al. [9] mentions that, in practice, sodium sulfur battery is limited to discharge less than 100% of its theoretical capacity because of the more corrosive properties of Na_2S_3 . Therefore, sodium sulfur battery is designed to stop discharging before all the sodium transfers to active electrode.

Figure 2.8: NAS cell electromotive force vs. depth of discharge (DOD) [9].

2.3.4 Summary

In order to develop a battery model for sodium sulfur batteries, the most important characteristics of the battery which are the depth of discharge, battery electromotive force, internal resistance and the temperature effect have to be considered.

Based on the literature review in this chapter, it is imperative that a predictive model for sodium sulfur battery could be a useful design tool. In the current study, the results of a computational lumped model for a NaS cell developed by of Fan Wu [34], were used as inputs to create models for both a cell and multiple cells electrical networks via MATLAB/Simulink. The newly developed dynamic electrical model takes into account parameters such as open-circuit voltage, cell voltage, ohmic resistance and activation potential in order to simulate the NaS battery module.

The lumped computational model and a dynamic electrical model for the battery module will be elucidated in Chapter 3 and Chapter 4, respectively.

CHAPTER 3: COMPUTATIONAL LUMPED MODEL

3.1 Introduction

To understand how a NaS battery functions and stores electric energy, it is necessary to introduce some generalities about electrochemistry. The relationship between Gibbs free energy and electrochemical cell potential and other fundamental equations such as the Nernst equation, Butler-Volmer equation and open-circuit voltage (OCV) describe the basic operation of a NaS battery. Fan Wu's zero-dimensional, computational lumped model is mentioned after reviewing key factors in the electrochemical in this chapter.

3.2 Gibbs Free Energy, Nerst Equation and the Butler-Volmer Equation

The maximum electric energy (or work done) that can be delivered from any electrochemical cell depends on the change in Gibbs energy of the overall reaction in the cell, ΔG° , [16].

$$\Delta G^\circ = -nFE^\circ \quad (3.2.1)$$

where n is the number of electrons exchanged in an electrochemical reaction, F is the Faraday's constant (96,485 C/mole), and E° is the cell potential. Two electrons are produced during the overall reaction of a NaS battery. Therefore, the above equation becomes

$$\Delta G^\circ = -2FE^\circ \quad (3.2.2)$$

when rearranged, it yields

$$E^{\circ} = \frac{-\Delta G^{\circ}}{2F} \quad (3.2.3)$$

where E° is the electromotive force (EMF) or reversible open circuit voltage (OCV) for a NaS battery [29].

The charge is produced by the Gibbs energy of the system (The Gibbs function of formation) is defined as

$$G = H - TS \quad (3.2.4)$$

where H is the enthalpy in Joules, T is the Kelvin temperature, and S is the entropy in Joule/Kelvin.

The altered form of the Gibbs free energy equation given in [34], yields the well-known Nernst equation as (3.2.5) or (3.2.6).

$$E = \frac{-\Delta g_f^{\circ}}{2F} - \frac{RT}{2F} \ln \left(\frac{a_{Na_2S_x}}{(a_{Na})^2 (a_S)^x} \right) \quad (3.2.5)$$

or

$$E = E^0 - \frac{RT}{2F} \ln \left(\frac{a_{Na_2S_x}}{(a_{Na})^2 (a_S)^x} \right) \quad (3.2.6)$$

where, E^0 is the EMF at standard condition, $a_{Na_2S_x}$, a_{Na} and a_S are the chemical activity for Na_2S_x , Na and S, respectively, and R is the universal gas constant.

The voltage of a battery cell is considered as the electrical potential difference between the electrodes of the cell. If there is no current flow through the battery cell, the measurable potential difference is the equilibrium cell voltage or open circuit voltage [35]. When a voltage applied to the cell terminals, it is not exactly equal to the equilibrium voltage. A current will flow and the terminal voltage of the cell will shift

from its equilibrium cell voltage value. When a current flows through the cell, this changing of cell voltage is called polarization. The magnitude of the voltage shift caused by polarization is called overvoltage.

These polarization components can be classified into activation polarization, concentration polarization, and ohmic polarization. Depending on the circumstances, any of these polarization effects may be dominant.

3.2.1 Activation Polarization

Activation loss is generated at the very surface of the working electrode, where electron transfer occurs [36]. Many spontaneous reactions are slow, thus the extra power is needed to force the reaction to proceed at the speed required by the current. This minimum energy must be presented if a collision between two atoms or molecules is to result in a chemical reaction. In NaS battery, when the minimum required energy is presented, the reaction tends towards the formation of sodium polysulfides and electricity, as opposed to the reverse [34, 35]. In Fan Wu's study [34], some empirical equations are explained to describe the electrical current on an electrode depends on the electrode overpotential for modeling of NaS battery.

Another important term which needs to be known to understand the lumped model is the exchange current density. The exchange current is the magnitude of partial anodic and cathodic currents which are equal at equilibrium. Exchange current density is the current in the absence of net electrolysis and at zero over-potential. In the lumped model, exchange current density in the cathode is formulated differently between the process of charge ($I > 0$) and discharge ($I < 0$) [34].

For discharging ($I < 0$),

$$i_0 = i_0^* \frac{(y_s)^m}{1 + \left(\frac{1}{y_s}\right)^n} = i_0^* \left(\frac{y_s^{m+n}}{1 + y_s^n} \right) \quad (3.2.7)$$

For charging ($I > 0$),

$$i_0 = i_0^* \frac{(y_{Na_2S_x})^m}{1 + \left(\frac{1}{y_{Na_2S_x}}\right)^n} = i_0^* \left(\frac{y_s^{m+n}}{1 + y_s^n} \right) \quad (3.2.8)$$

where, i_0^* is a reference current density (A/cm²), y refers to mass fraction of different species, m and n are empirical model parameters.

The activation potential (η_{act}), also known as the over-potential (η), can be calculated from the Butler-Volmer equation can be expressed as [34]

$$\eta_{act} = \frac{2\alpha RT}{nF} \sinh^{-1} \left(\frac{i}{2i_0} \right) \quad (3.2.9)$$

where n is the number of electrons exchanged in an electrochemical reaction, F is the Faraday's constant (96,485 C/mole), R is the universal gas constant, T is temperature (in Kelvin), α is the transfer coefficient, i_0 is the exchange current density, and i is the current.

3.2.2 Ohmic Polarization

Ohmic polarization is a common effect in every electronic device, and it is one of the main varieties in NaS battery as well. Ohmic polarization appears or disappears instantaneously on current flow. Therefore, ohmic polarization (V_{ohmic}) follows Ohm's law which is defined as

$$V_{ohmic} = R_{ohmic} \times I \quad (3.2.10)$$

where I denotes the cell current and R_{ohmic} is the electrical resistance of the battery. As it can be seen (3.2.10), ohmic loss is strictly proportional to the current. However, if a concentration profile develops, the magnitude of the ohmic drop may change [36]. In Fan Wu's study [34], the resistance of the battery is calculated from the effective conductivity, σ^{eff} at each control volume, as shown in Figure 3.1.

Figure 3.1: Control volumes used for lumped model of NaS battery [34].

$$\sigma_A^{eff} = \sigma_{Na} \quad (3.2.11)$$

$$\sigma_E^{eff} = \sigma_E \quad (3.2.12)$$

$$\sigma_C^{eff} = \varepsilon_S^\beta \sigma_S + \varepsilon_{Na_2S_x}^\beta \sigma_{Na_2S_x} + \varepsilon_{mesh}^\beta \sigma_{mesh} \quad (3.2.13)$$

where ε denotes the porosity or volume fraction of each substance, β is the tortuosity factor, the subscript A, E and C denote anode, electrolyte and cathode, respectively, and the rest subscripts denote each species and the carbon mesh at the cathode electrode.

Moreover, ohmic polarization applies to both ionic and electronic current. The electronic conductivity is often higher than the ionic conductivity. It should be noted that the electrolyte ohmic drop depends on the conductivity, which in turn depends on the concentration of the ions in the solution.

3.2.3 Concentration Polarization

This type of common polarization can cause the electrode may suffer a significant voltage loss due to concentration polarization. Concentration polarization is mainly located in the thin transport layer surrounding the electrodes [36].

When the battery is charged or discharged, chemical reactions take place at the electrodes (according to equations 2.3.1 and 2.3.2). It can be seen from these equations that reactants are consumed and products are formed. The concentration of the reacting species at the electrode surface get disturbed. This rise in the concentration overvoltage is an extra voltage needed to keep the reaction rate regardless of the concentration disturbance, and thus provide the requested current [35].

Moreover, it is necessary to track the mass transport within the control volume in order to calculate concentration loss. In Fan Wu's zero-dimensional model, this concentration loss is not calculated. This loss is due to limiting the actual simulation effectiveness [34]. However, a proposed model in Fan Wu's study can be used for further study.

3.3 Zero-Dimensional, Lumped Model

Fan Wu's zero-dimensional lumped model for a single cell NaS battery [34] predicts the transient of the cell voltage (voltage of the battery), open circuit voltage (OCV) and temperature at a constant charge or discharge current. These results are compared to those from experiments and predicted by Kawamoto and Kusakabe [37].

Figure 3.2: Charge/discharge characteristics of the cell operated at 130/130 mA/cm² charge/discharge current density [37].

Figure 3.3: Voltage results at 130/130 mA/cm² [34].

As it can be seen from Figure 3.2 and Figure 3.3, the result obtained from Fan Wu's model shows good agreement with Kawamoto and Kusakabe's calculated and measured results [37]. The same operation time and trend, and the OCV and cell voltage are consistent with what is shown in the literature. It can also be observed that there is somewhat large discrepancies exist at the end of the charging and the very beginning of discharging [34]. This behavior is usual since the concentration polarization is neglected in Fan Wu's model.

3.4 Summary

In this chapter, important electrochemical concepts, polarization components, OCV and cell voltage are introduced. Based on the expressions described, the total cell voltage equation (3.2.14) for a single NaS battery cell is calculated.

$$V_0 = E_0 \pm IR_o - \eta_{act} \quad (3.2.14)$$

After the generalities about electrochemistry discussed in this chapter, a zero-dimensional, transient, lumped computational model for a single NaS battery cell which was developed by Fan Wu [34] is elucidated and made comparisons between the presented model and Kawamoto and Kusakabe's results next.

Fan Wu's model is derived from integral analysis of the transport of mass, energy and charge throughout the battery. The processes are coupled with the use of Faraday's law of electrolysis, and solutions for the species concentrations, electrical potential and current density are produced with respect to time. Averaged surface area of the beta-alumina (cm^2) is one of the most important parameters in the model to observe the behavior of the charge and discharge characteristics of the NaS battery modules.

Finally, Fan Wu's model for a single cell is used to combine multiple NaS battery cells with different configurations. In fact, this model is modified to analyze charge/discharge of the cell at constant power, which are explained in Chapter 4.

CHAPTER 4: DYNAMIC MODEL OF SODIUM SULFUR BATTERY AND SIMULATION RESULTS

In this chapter, several battery models from literature are reviewed and described for modeling a sodium sulfur battery module. Based on the lumped model in MATLAB which discussed in Chapter 3, a Simulink model was built in order to create a battery module in this chapter. There is a link between the lumped model and a Simulink model in order to build a dynamic model of sodium sulfur batteries. The lumped model provides data such as open-circuit voltage, ohmic resistance, activation loss, and concentration loss for a NaS cell. These data are used as inputs in the Simulink model and solves the equation (3.2.14) simultaneously.

4.1 Battery Models

There are three models are elucidated in this section. Each of these models has some advantages and disadvantages in terms of different characteristics of sodium sulfur battery. The most suitable model was used to build a Simulink model after reviewing the literature.

4.1.1 Simple Model

This model is the simplest and the most commonly used battery model as shown in Figure 4.1[38]. It consists of a constant internal resistance (R) in series with an open-circuit voltage (E) where (V_b) is the terminal voltage of the battery [9, 39]. In fact, internal resistance is assumed to be constant in this model. If this model is considered for sodium sulfur battery modeling, it can be seen that it does not take into account the varying characteristic of the internal resistance of the battery with respect to depth of discharge and temperature changes. Therefore, it is not suitable in modeling a sodium sulfur battery.

As a result, this model can only be applied in case studies where the energy from E is assumed to be unlimited as Hussien, et al. [9].

Figure 4.1: Simple Model [38].

4.1.2 Thevenin Model

A Thevenin model is another commonly used battery model which consists of an ideal no-load battery voltage (E_0), series internal resistance (R) in series with parallel combination of overvoltage resistance (R_0) and capacitance (C_0) as seen in Figure 4.2 [9, 39, 40].

Figure 4.2: Thevenin battery model [9, 39, 40].

A Thevenin's battery model, which has been widely used to model the discharging dynamics of various types of batteries such as lead-acid, lithium-ion (Li-ion), Li-polymer, nickel metal hydride (NiMH),

and fuel cells, e.g. [41]. This model can depend on many factors such as the state of charge, the load, the temperature and under certain working condition the elements are assumed to be constant. All the values are a function of battery conditions. In addition, the internal open-circuit voltage drop in a sodium sulfur battery is not considered in this model [9]. Therefore, this battery modeling has a disadvantage in modeling the NaS battery because the elements are all assumed constant.

4.1.3 Modified Battery Model

A modified battery model is the most suitable configuration for the NaS battery. It is simple and most requirements for the NaS battery can be implemented in this model as shown in Figure 4.3 [9]. This model is called “Modified Battery Model” by [9], because it is based on the basic configuration of the simple battery model.

Figure 4.3: Sodium-sulfur battery cell equivalent circuit [9].

In this model, the resistances R_c and R_d are internal resistances for charge and discharge, respectively. The resistances R_c and R_d are a function of the temperature and depth of discharge. Depending on the direction of the current, only one of the charge or discharge resistances will affect the circuits due to the diodes [9, 26, 39]. R_l represents deterioration-resistance and E represents the cell's EMF as a function of discharge. All of these parameters were discussed at “Important Factors in Sodium Sulfur Battery Modeling” in Chapter 2.

4.2 A Predictive Model of a NaS Battery Cell in MATLAB/Simulink

Before discussing the proposed model of a NaS battery cell, Sarasua, et al. [17, 42] will be reviewed in this section. This paper developed a battery model for the NAS battery and implemented in MATLAB/Simulink with the help of SimPowerSystems toolbox. A schematic circuit is shown in Figure 4.4 [42].

Figure 4.4: Schematic circuit of NAS battery model [42].

The model takes into account the non-linear battery element characteristic during charging and another for discharging as well as the internal resistance dependence. V_i , R_{id} and R_{ic} are determined by using lookup tables in MATLAB/Simulink. The minus sign indicates the current is negative during discharge process and the positive sign indicates the current is positive during charging process as shown in Figure 4.4.

In particular, the model consists of three look-up tables based on the functions described below:

- The battery's open-circuit voltage is a function of state of charge ($V_{oc} = f(SOC)$),
- The battery's internal resistance for charging and discharging with respect to state of charge, respectively ($R_{ic} = f(SOC)$, $R_{id} = f(SOC)$).

This battery model is very useful for steady-state studies. Basically, the circuit takes into account the state of charge (SOC) and direction of current at 320°C. This model is implementation of modified battery model which is explained in Section 4.1.3. It calculates equation (4.1) and calculates the state of charge for each time step. It should be noted that the only power source is the NaS battery. 'A' block was created in SimPowerSystems toolbox (Simulink library) which takes the value of current to calculate state of charge in each time step. This study, the effects of charge-discharge lifecycle resistance were neglected in this work [42]. After this developed model's results were validated with Hussien, et al. [9], another model was developed by Sarasua, et al. [17] for 50 kW battery module which consists of 320 cells in series for obtaining a higher capacity storage device with higher voltage [17].

Furthermore, by using the similar look-up tables idea from [9, 17, 42], a sodium sulfur battery model was developed in MATLAB/Simulink by using Fan Wu's model [34]. This model takes into account ohmic resistance (R_o), activation potential (μ_{act}) and open-circuit voltage (E_0) as inputs which are the outputs of the lumped model for a NaS battery with beta-alumina as the solid electrolyte. Look-up tables are created by using them as inputs and equation (4.1) is computed simultaneously in order to provide cell voltage (V_o) as an output by using constant current density or constant power density as another input parameter to model in Simulink.

$$V_o = E_0 \pm IR_o - \eta_{act} \quad (4.1)$$

It should be noted that R_o depends on the sign of the current density (I), equation (4.1) can represent charge or discharge phases in the predictive model. In addition, the simulation results are presented as a function of time.

4.2.1 Created Simulink Model for a NaS Cell at Constant Current

Figure 4.5 and Figure 4.6 show implementation of a Simulink model for charging and discharging of a NaS battery model at constant current which is 130 mA/cm² (10.01 A), respectively. Equation (4.1) is implemented in the block in Figure 4.7 to calculate cell voltage (V_0).

Figure 4.5: A Simulink model created for charging a NaS battery cell.

Figure 4.6: A Simulink model created for discharging a NaS battery cell.

Figure 4.7: Inside of the NaS cell charging block shown in 4.5.

Look-up tables consist of data which are presented with respect to time in Figure 4.8, Figure 4.9 and open-circuit voltage part in Figure 4.10.

Figure 4.8: The resistance of the NaS cell vs. time.

The resistance of the battery with respect to time is shown in Figure 4.8. The effective conductivity changes during charging and discharging process. These changes are due to variation of the chemical composition of the cell components in charging and discharging process. The detailed formulization of the electrical conductivity is given by Fan Wu [34]. It can be seen that during charging the resistance is increasing and decreasing in discharging stage. This behavior is mainly due to the formation of sulfur and its huge resistance compared to the sodium polysulfide. In addition, the variation of cell resistance with respect to time is not linear. If the cell is over charged, it will generate huge resistance and it can cause damage to the cell. Therefore, controlling the state of charge level of the battery is very important to protect the NaS battery and get better performance.

Moreover, activation potential is shown in Figure 4.9 and open-circuit voltage is shown in Figure 4.10. The cell voltage (in Figure 4.10) is mainly influenced by the open-circuit voltage and activation potential. The loss from ohmic heating is less effective compared to the former two. The open-circuit voltage is a dominant factor in the battery. Because, it is not connected to any load in a circuit and represents the difference between of electrical potential between two terminals. On the other hand, activation potential is directly derived from the actual chemical reactions and the amount of all the reactants and products which the detailed formulization are given by Fan Wu [34]. All the results produced from the lumped computational model validated with J. L. Sudworth and A. R. Tilley, Mitoff, S. P. [25, 43] and a good agreement with literatures is observed.

Figure 4.9: Activation overpotential vs. time.

Figure 4.10: V_{cell} and open-circuit voltage vs. time.

Another important terms which need to be known to understand is State of Charge (SOC) or its counterpart, Depth of Discharge (DOD), is often used. By and large, in order to operate the BESS continuously, the battery SOC needs to be controlled within a certain range which is 20-90% in sodium sulfur battery [29]. The battery SOC is calculated by using equation (4.2),

$$\text{SOC} = \text{SOC}_{\text{ini}} - \int \frac{I_{\text{Bat}}}{Q_{\text{bat}}} dt \quad (4.2)$$

where I_{Bat} is DC current of the battery (A), SOC_{ini} is initial SOC of the battery (Ah) and Q_{bat} rated battery capacity (Ah). Naoki Hirai and Motohiro Fukuhara's patent [33] which explains a method for calculating state of charge of NaS battery, defines that the integrating value of the discharge currents may be subtracted from the battery's rated capacity at the time of a discharge, while the integrated value of the charge currents may be added to the SOC before the charge to calculate the updated value for the SOC at the time of a charge.

4.2.2 Created Simulink Model for a NaS Cell at Constant Power

Based on a given algorithm for synthesize the behavior of a parallel array of cells, with their charge and discharge characteristic, a computer program was developed by Mitoff, S. P. [43]. The results of this paper predicted that they would deliver about the same power in the parallel connection. In contrast, the lumped model, developed by Fan Wu [34], works at constant current for the NaS cell. This model is modified to deliver a constant power for the NaS battery cell. After reviewing a constant power for the NaS battery cell model structure in MATLAB/Simulink, variable demand analyses are presented in the next section. Variable power demand analyses are done by sinusoidal wave power and continual step changes of power.

In order to keep the power constant, iterative steps have to be implemented for each time step in MATLAB. If current and cell voltage are known for the battery, power of first iteration is defined as

$$P_1 = V_1 \times I_1 \quad (4.3)$$

Then, P_1 needs to be the same for the second iteration which is P_2 ,

$$P_1 = P_2 = V_1 \times I_1 = V_2 \times I_2 \quad (4.4)$$

when (4.4) is rearranged, it yields

$$I_2 = \frac{V_1 \times I_1}{V_2} \quad (4.5)$$

It should be noted that the maximum power available from a cell is defined as, [25],

$$P_{max} = \frac{V_o^2}{4R} \quad (4.6)$$

where R is the load resistance of the cell at a particular depth of discharge and V_o is the open circuit voltage of the cell. Since the open circuit voltage is the lowest at the end of discharge, the peak power calculations are conservative.

Figure 4.11 and Figure 4.12 show implementation of a Simulink model for charging and discharging of a NaS battery model at constant power density which is 100 mW/cm^2 (7.7 W), respectively.

Figure 4.11: A Simulink model for charging the NaS cell that produces constant power.

Figure 4.12: A Simulink model for discharging the NaS cell that produces constant power.

Figure 4.13 shows the behavior of the current density with respect to time. The current variation is a result of an applied constant power. In order to keep the power at the same level during the cell operation, current density must be changed as a result of cell potential variation as shown in Figure 4.14. This is assured by implementing an iterative method in each time step of an iteration. As it can be seen in Figure 4.15, constant power both charge and discharge stages are provided.

Figure 4.13: Current density vs. time.

Figure 4.14: Cell voltage and open-circuit voltage vs. time.

Figure 4.15: Constant power density (7.7 Watt) vs. time.

4.2.2.1 Variable Power Demand for a NaS Battery Cell

When large-scale renewable energy sources such as wind and photovoltaic are integrated into power grids on remote islands, power frequencies tend to fluctuate due to intermittent power outputs from renewable energy sources. Therefore, it is really important to produce desired output power continuously from a battery with the effective frequency response.

In the first case of variable power demand, Fan Wu's single cell model was used to simulate, cell current and voltage change for one cycle (charge and discharge). Given input power (Sinusoidal wave power) can be seen in Figure 4.16, cell current and voltage behavior which correspond oscillated power demand are shown in Figure 4.17 and 4.18, respectively.

Figure 4.16: Sinusoidal wave power density vs. time.

Figure 4.17: Current density vs. time when sinusoidal wave power input is given.

Figure 4.18: Cell voltage and open circuit voltage when sinusoidal power input is given.

In the second case of variable power demand, the same model, which is used for sinusoidal wave input power, changed to continual step changes of power. Given input power (Step changes of power) can be seen in Figure 4.19, cell current and voltage behavior which correspond oscillated power demand are shown in Figure 4.20 and 4.21, respectively.

Figure 4.19: Step changes of power density vs. time.

It can be observed from Figure 4.19 that the input power oscillated between 0 and -40.69 mW/cm^2 . The reason of having a negative values in power density is because of power is delivered from the NaS battery.

Figure 4.20: Current density vs. time when step changes of power is given.

Figure 4.21: Cell voltage and open circuit voltage when step changes of power is given.

In order to validate the obtained results, given step changes of power input model is compared with the experimental result of the NAS battery cell for peak shaving application by Hussien, et al. [9] in Figure 4.22.

- 4 hours of constant power discharging at 84 W
- 3 hours of constant power discharging at 136 W
- 4 hours of constant power discharging at 84 W
- 2 hours standby
- 9 hours of constant power charging at 135 W

Figure 4.22: Voltage-current behavior of a NAS cell (Experimental) [9].

Even though the cell specifications are not exactly the same, a similar trend can be seen in cell voltage and cell current in Figure 4.22. The results obtained from these simulations are in a good agreement with the cell voltage and current variation. They would be expected for variable power demand.

4.3 Sodium Sulfur Battery Module Design Considerations

This section gives a description of modern battery configurations for a sodium sulfur battery technology. The most extensive reference for batteries is “Handbook of Batteries” by D. Linden and T. B. Reddy, this explains basic options for networking sodium sulfur cells such as long-series strings, total parallel connection and series-parallel array [16]. These configurations are elucidated in this section.

Electrical networking is one of the most important battery module design considerations. Individual cells will fail during the lifetime of a battery which causes a degradation of electrical performance. Some battery configurations with higher voltages, such as 200+ V, the impact of small numbers of cell failures can be significant. Thus, the effects of cell failure must be mitigated or controlled in the battery [16].

Moreover, electrical networking options that are explained below consists of series and parallel connection of the cells in the module. When the cells are connected in series, the required battery voltage can be produced. Another important topic is having the required battery capacity. If the cell capacity is less than the required battery capacity, cells need to be connected in parallel.

4.3.1 Long-Series Strings Electrical Network

Requirements for this connection option, as shown in Figure 4.23, are a low resistance and can be capable of carrying normal operating currents in case of failing of a cell [16]. Otherwise, a single cell failure forces the entire string to become inoperative since the cells in a string are connected in series. This network option with large number of cells is not recommended by D. Linden and T. B. Reddy [16]. The first cell to recharge can have a high overvoltage, which is proportional to the number of cells in a string. High overvoltage can be higher if a string contains numerous failed cells.

A Simulink model created to simulate long-series strings networking option. Simulation results are presented in section 4.4 for 4 parallel/5 series configuration.

Figure 4.23: Long-series networking of sodium beta cells [16].

4.3.2 Total Parallel Connection Electrical Network

If this connection option (shown in Figure 4.24) is used, the resistance of each failed cell needs to be high to prevent discharge of remaining cells in parallel. This condition is not a useful connection option in practice. An extra device needs to be attached to each cell, in series, which causes the cell to go to an open-circuit condition if there is a cell failure. However, no success has been achieved with the development of such a device until now [16].

Figure 4.24: Total parallel networking of sodium-beta cells [16].

4.3.3 Series-Parallel Array Electrical Network

This connection option (shown in Figure 4.25) provides a compromise between long-series and total parallel options. The failure of one of the cells in this configuration removes the other cells from the string along with its contribution to the battery energy. A cell failure results in recharge of the remaining cells in the string by other parallel strings. Moreover, using large-capacity cells in this connection option can cause a cell failure, because the number of parallel paths in a battery is small [16].

Figure 4.25: Series-parallel array networking of sodium-beta cells [16].

4.4 A Predictive Model of a NaS Battery Module in MATLAB/Simulink

One of the objectives of this study is to create NaS battery modules in Simulink. These case studies will be presented, with their results, in this section. It should be noted that all cells assumed to be identical and the cell operates at the constant temperature which is 335° C (635° F). The following battery models are presented below:

- The NaS battery module configuration with bundle of 20 cells in parallel with constant power.
- The NaS battery module configuration with 4 parallel and 5 series (Similar to the long-series strings electrical network).
- The NaS battery module configuration with 2 series and 5 parallel.

4.4.1 The NaS Battery Module Configuration with Bundle of 20 Cells in Parallel with Constant Power

One of studies is done by Mitoff S. P. [43], is to simulate charge and discharge curves for the 20 cell bundle in parallel with constant power. As it can be seen in Figure 4.26 [43], each cell produces a constant power which 3.21 W. Similar specifications used to simulate 20 cell bundle in parallel and the following result produced in Figure 4.27. When these two results are compared, charging time for Simulink solution is less than Mitoff, S. P.'s result [43]. Even though discharging time for both figures are around 7 hours, the discharge curve does not start until around 1.75 V, in Figure 4.27. One of the main problems of this simulation is the missing information from the specifications for the cell, proposed by Mitoff, S. P. [43].

In order to get similar results, the surface area of the beta-alumina needs to be modified (chosen at 4.5 times bigger). A comparable trend was obtained while observing an increase of charge and discharge in cell voltage, due to a higher surface area.

Figure 4.26: Parallel 20 cell bundle charging and discharging curves [38].

Figure 4.27: Simulation results of bundle of 20-cell in parallel (surface area assumed 350 cm³).

4.4.2 The NaS Battery Module Configuration with 4 Parallel/5 Series

In this case study, an electrical network of 4 P/5 S NaS battery cell module configuration in Figure 4.28 was developed in a Simulink, as shown in Figure 4.31. The module is charged and discharged at constant current which is 200 mA/cm² (15.4 A). However, the current at each branch in the system has 50 mA/cm² since there are 4 branches in the system. If the results are compared in Figure 4.29 and Figure 4.30, it can be seen that predicted battery module charges at around 12 hours, while discharging at around 13 hours.

Figure 4.28: Electrical network of 4 P/5 S NaS battery cell module configuration.

Figure 4.29: A NaS battery (charged/discharged at 200 mA/cm²) cell voltage, open-circuit voltage, and activation potential vs. time.

Constant Current = 200 mA/cm², 4 Parallel/5 Series NaS Battery Module Configuration

Figure 4.30: Open-circuit voltage, predicted cell voltage vs. time for 4 P/5 S case.

Figure 4.31: A Simulink model for 4 P / 5 S case constant current charging state.

4.4.3 The NaS Battery Module Configuration with 2 Series/5 Parallel

In this case study, an electrical network, as shown in Figure 4.32, was developed in a Simulink model, as shown in Figure 4.35. The module is charged and discharged at constant current which is 100 mA/cm² (7.7 A). However, each branch in the system has 20 mA/cm², since there are 5 branches in the system. If the results are compared in Figure 4.33 and Figure 4.34, it can be seen that predicted battery module charges at around 30.5 hours, while discharging at around 35 hours.

Figure 4.32: An electrical network of 2 S/5 P NaS battery module configuration.

Figure 4.33: A NaS battery cell (charged/discharged at 100 mA/cm²) voltage, open-circuit voltage, and activation potential vs. time.

Constant Current = 100 mA/cm², 2 Series/5 Parallel NaS Battery Module Configuration

Figure 4.34: Open-circuit voltage, predicted cell voltage vs. time for 2 S/5 P case.

Figure 4.35: A Simulink model for 5 P/2 S case at constant current charging.

CHAPTER 5: CONCLUSIONS AND FUTURE WORK

A non-linear sodium sulfur battery model is developed in MATLAB/Simulink. This model cooperates fully with a zero-dimensional lumped computational model for NaS battery. This model is a suitable model for fast performance simulation of a NaS battery module.

Almost all simulation studies have room for improvement when it comes to modeling and the study conducted here is no exception, particularly when it comes to modeling the sodium sulfur battery.

The model of the sodium sulfur battery is developed to account for several aspects of the operation of the battery in this study:

- The ability to effectively deliver energy which in turn is affected by several factors:
 - The effect of state of charge of the battery on the internal resistance.
 - The effect of the temperature of the battery on the internal resistance.
 - The effect of state of charge on the batteries open-circuit voltage.

On the other hand, the following aspects have to be implemented in order to have a more comprehensive model in the further study:

- The effect of the number of discharge-recharge cycles on the internal resistance.
- The decrease in battery capacity over the number of discharge-recharge cycles.

In particular, to simplify the calculation of cell voltage, open-circuit voltage, losses and state of charge, all the models in this study are simulated based on the constant temperature and identical cell approach. This constant temperature assumption ignores the heating and cooling of the NaS battery while it operates. A more realistic model would seek to incorporate these thermal aspects, modeling not only heat generated or absorbed by sodium sulfur battery.

More specifically, new study cases can be created similar to the practical examples if the simulated cells show variation between each other in terms of different temperature and capacity. In that case, temperature can be defined as a function of state of charge. An example of a more realistic model could be created by using a look-up table, by adding an extra dimension to the library of Simulink models. Using a look-up table idea which is learned from the literatures, a general model for the sodium sulfur battery can be created inside of a Simulink library to simulate large-scale battery energy storage systems.

The prediction of multiple sodium sulfur battery cell configurations show similarities with the results in the literatures. Accuracy of calculation of the cell voltage and state of charge, has the potential to be increased if one or two dimensional computational lumped models are used. The results are obtained from the lumped model, it can be seen that the cell voltage is mainly influenced by the open-circuit voltage and activation over-potential. While the loss from ohmic heat has less influence compared to all factors. Some factors, such as the double layer capacitance and concentration losses are neglected in the current model. In order to have a better model, these losses could be included for a further study.

Another implementation, which is modified from Fan Wu's study [34], is to show the NaS cell current and voltage behavior when there is oscillated power demand. If the battery is operating at a given power level, lower output voltage would require more output current which in turn would lead to higher losses. The major predictions drawn from this variable power demand model is optimistic when it is compared with literature.

All batteries require power converters if they are to be used in the bulk power system. The interaction between the battery and the power converter connecting it to the larger grid is not modeled at all in this study. However, it has to be considered to model of a renewable smart grid with battery storage.

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