Modeling of Novel Single Flow Zinc-Nickel Battery for Energy Storage System

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***Abstract*— The increasing demands for grid peak-shaving/load-leveling and renewable energy integration lead to fast development of electric energy storage techniques. A novel redox zinc-nickel flow battery system with single flow channel has been proposed recently. This single flow zinc-nickel battery system provides a cost-effective solution for grid energy storage because not only does it possess high efficiency and long life cycle, it also has no requirement for the expensive ion exchange membranes. In this paper, the basic characteristics including its principle and current research progress are introduced. And based on the electrical characteristics of the battery, an equivalent circuit battery model is proposed. Experimental validations show that the model provides a good indication of battery performance under both steady and dynamic conditions. The steady state output of the scaled-up 200Ah battery is also estimated by the model and compared with experiment results. At last, the possible improvement in the battery for future applications is discussed.**

Keywords—battery energy storage; zinc-nickel battery; flow battery; battery modeling

I. INTRODUCTION

In the development of modern power system, energy storage techniques have become one of the hottest areas as it can provide solutions for some critical problems including: renewable energy integration, peak shaving and load leveling, voltage regulation and frequency control, emergency backup power supply, etc [1,2]. Currently pumped hydro is the most widely used large-scale energy storage technology in the world. The major drawback with such systems is the geological restriction as the locations where pumped hydro is feasible is often distant from where the storage system is needed. In contrast, battery energy storage systems (BESS) have less limitation in site selection and are able to provide power and energy in a wide range, making them more flexible for all kinds of applications [2,3].

There are currently various batteries technologies at different stages of development that are available for integration of BESS. Among them, development of redox flow batteries (RFB) characterized by the long life cycles, high charge/ discharge efficiencies, have been rapidly advanced in recent years [3]. Some technically developed RFB such as the vanadium redox battery (VRB) system, zinc–bromine battery system and polysulphide–bromine system have been commercially available. These batteries possess two flowing passages because both the positive and negative reactions take place in solutions. Ion exchange membranes separating the electrolyte of positive electrode and the negative electrode are then required to prevent the unwanted transport processes through the membranes. But the membranes are very expensive and require complex maintenance, which make up a large percentage of the total cost of those flow batteries.

A novel redox flow battery system, single flow zinc–nickel battery system, has been proposed by J. Cheng and Zhang et al. [4]. Unlike the flow battery systems illustrated above, the single flow zinc-nickel battery possesses only one flowing passage, therefore the complexity of the mechanical and hydraulic structures is greatly reduced. And more importantly, there would be no requirement for the expensive ion exchange membrane anymore, which will greatly reduce the cost of the battery. In addition, the battery uses only abundant and relatively green materials with low levels of toxicity, and a fairly high level of safety, making it a highly cost-efficient alternative to large-scale power system storage. Table I [1-3, 8] provides a comparison between the single flow zinc-nickel battery and three other types of batteries for energy storage system.

In this work, we aim to illustrate the basic characteristics of the single flow battery including its reactions and current research progress, then a comprehensive electrical model of the single flow zinc-nickel batteries will be proposed based on its electrical characteristics. This model will be of great help in understanding and evaluating the performance of the battery of this type especially for system level simulation and applications.

This paper is organized in the following manners: Section II presents the reaction principles of the single flow zinc-nickel battery and its research progress. Section III provides the electrical equivalent circuit modeling of the battery including

TABLE I. COMPARISON BETWEEN BATTERIES

Battery	Energy Efficiency (%)	Cycle life	Cost ($/kWh)
Lead-acid	70~92	500~1000	200~400
Lithium-Ion	85~95	1000-	600~2500
VRB	65~85	10000+	150~1000
Single flow Zinc-nickel	65~85	5000~10000	300~500

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parameter identifications and extractions from experiment data. Then in Section IV, the result of model validation and a simulation example are given based on the scaled-up 200Ah battery, conclusion and possible future work are given in Section V.

II. Reaction Principles and Current Research

The development history of zinc–nickel battery can date back to over a century ago when German patent was applied by Dun and Haslacher in 1887, and U.S. Patent by Thomas Edison in 1901. Traditional zinc–nickel batteries were designed in a sealed configuration with non-flowing electrolyte. The life cycle of the batteries are however limited because of the zinc dendrite formation upon charging. The non-uniform deposition occurs on the negative electrode and will gradually accumulate towards the positive electrode and finally cause internal short circuit.

By making the electrolyte flowing, the mass transport of zincate will change from diffusion control to convection control, thus the thickness of the diffusion layer can be substantially reduced. As a result, the zinc deposition can become more uniform and flat such that life cycle of the novel zinc-nickel flow battery can be extended remarkably [4-6]. The principal reactions of the single flow zinc-nickel battery are as follows:

Cathode:

$$2NiOOH + 2H_2O + 2e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} 2Ni(OH)_2 + 2OH^-$$

Anode:

$$Zn + 2OH^- \underset{charge}{\overset{discharge}{\rightleftarrows}} Zn(OH)_2 + 2e^-$$

Overall:

$$Zn + 2H_2O + 2NiOOH \underset{charge}{\overset{discharge}{\rightleftarrows}} 2Ni(OH)_2 + Zn(OH)_2$$

The schematic of the battery is illustrated below in Fig.1. The positive electrodes are nickel oxide and the negative electrodes are zinc. The electrolyte is continuously circulated to feed reactants to the battery stacks by a pump.

There are several research groups worldwide who have conducted studies on the characterization of the single flow zinc–nickel battery, targeting further improvement for practical applications of the battery. Cheng et al. [4, 5] carried out battery cycling experiments on the single flow zinc-nickel batteries and have achieved 220 charge–discharge cycles while keeping the coulomb and energy efficiencies about 98% and 88%, respectively. They also compared different negative substrates and found that the cadmium substrate is better for suppressing the hydrogen evolution. Ito et al. [6] achieved 1500 deep cycles by utilizing a deep-discharge reconditioning step every 15 charging-discharging cycles.

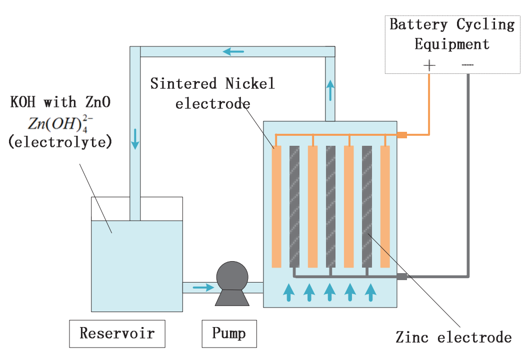

Fig. 1. Schematic of the experimental apparatus

Most of the studies were conducted on the chemical characteristics on the single flow zinc-nickel battery, but there have been no reported studies examining the electrical characteristics of the single flow zinc-nickel battery yet. In this work, we aim at describing the electrical output of the batteries and will give a dynamic electrical model based on its electrical characteristics. This model will be of great help in understanding and evaluating the performance of the battery especially for system level simulation and applications.

III. Electrical Equivalent Circuit Modeling

Mathematical battery model aims to predict the performance of a battery given a specific set of parameters. Since the technological feasibility of the single flow zinc-nickel technology has been demonstrated, an electrical model is essential for further evaluation and simulation in application of the flow battery system.

The modified Thevenin circuit model [7] possesses both high accuracy and comprehensibility, as each part of the model can be related with certain physical meanings of the battery. So it is chosen in illustrating the electrical characteristics of the single flow zinc-nickel flow battery. The equivalent circuit of the model is shown in Fig.2. The battery output voltage may be described mathematically as follows:

$$U_{batt} = OCV + R_i \cdot i + U_{Trans\_s} + U_{Trans\_l} \tag{1}$$

The model consists of four main parts: a controlled voltage source representing the OCV (open circuit voltage) of the battery, an internal resistance R_i, two RC circuits and a paralleled self-discharging resistance R_{self_disch}. OCV stands for the equilibrium potential of the battery reaction and in theory is a monotonic function of state of charge (SOC); resistor R_i is the sum of internal resistance of the circuit and those of the electrodes; two RC circuits denotes the capacitive effects arisen from double-layer formation at the electrode/solution interface, which affects the transient response of the battery. U_{trans_s} and U_{trans_l} are the transient voltage response of the RC circuit with short and long time constant respectively, both of which are determined by the RC circuits. The self-discharging resistance stands for the loss of coulomb efficiency in the reaction, mainly due to the self-discharging of zinc and side reactions of gas evolution.

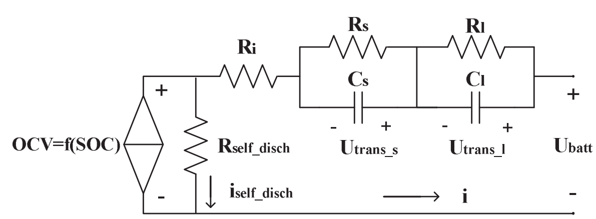

Fig. 2. Electrical model of single flow zinc-nickel battery based on Thevenin circuit

In the following of this section, the parameter identification method with stepped current and least-squared-fitting (LSF) will be illustrated in part A; the corresponding experiments conducted are introduced in part B; and the parameters identification results as function of current and SOC are given in Part C.

A. Parameter identification method

Most Parameters in the model (OCV, R_i, two RC circuits) can be identified at a stepped current from steady state to zero, as illustrated in Fig.3. The corresponding voltage response of the battery includes three parts: the instantaneous response, followed by a slow voltage recovery, and finally the stable state is reached. At a single SOC point when current changes, the model parameters can be identified by the voltage variation during the following three phases:

1) When current changed, series resistor R_i is responsible for the instantaneous voltage drop of the step response. It can be defined with equation (2).

$$R_i = dU/dI \tag{2}$$

2) The following transient response of the voltage is characterized by the RC circuits. The parameters of the RC networks can be determined by fitting the short- and long-time constants of the step response, using the LSF method.

3) The open circuit voltage is normally measured as the steady-state terminal voltage. The traditional way to identify accurate OCV requires the voltage reaching the steady state that may take hours to days, which is not so practical. A simpler method to identify the OCV and RC circuits together is adopted together using the LSF method. When current drops to zero, the output voltage of the battery can be expressed by:

$$U_{batt} = OCV + U_s \cdot e^{-\frac{t}{\tau_s}} + U_l \cdot e^{-\frac{t}{\tau_l}} \tag{3}$$

where U_s and U_l stand for the initial state of RC circuits at the moment when current changes. In general they equal to the voltage drops on R_s and R_l under the steady current respectively. Using (3) to fit the transient voltage curve when i=0, then OCV and short- and long-time constants can be obtained easily.

For example, the voltage transient curve at the end of charging at 1C charging current cases is shown below in red dot line in Fig.4. The relaxation time takes 30min and voltage is recorded every 5s. The fitting results as marked in green line were obtained using the proposed method. The fitting error is shown in Fig.4 as well as summarized in Table II. The fitting result well matches the experiment data. Using the obtained time constant as well as the initial state of RC circuit, the parameters of the two RC circuits can be calculated accordingly.

In determining the self-discharging resistance and current, the following equation can be applied:

$$R_{self\_disch} = OCV/i_{self\_disch} = OCV/(1-\eta)i \tag{4}$$

where η is the coulomb efficiency of the battery, which is greatly affected by the quantity and morphology of zinc deposition on negative electrodes.

TABLE II. FUNCTION FITTING RESULTS

Max error(V)	OCV(V)	U_s(V)	U_l(V)	τ_s(s)	τ_l(s)
0.0012	1.834	0.01426	0.02379	13.62	176.0

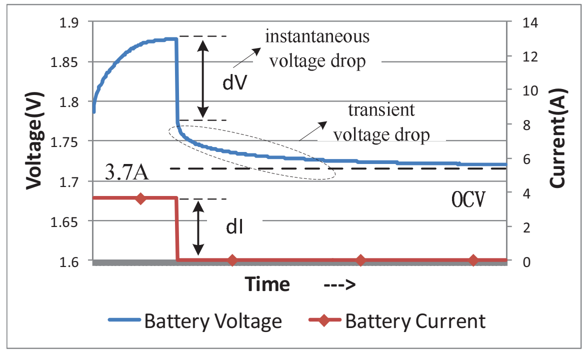

Fig.3. Transient response to a step load-current event

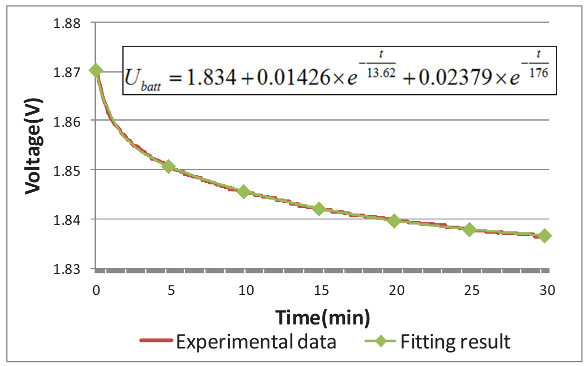

Fig.4. Voltage relaxation and function fitting curve at end of charging

Generally during the normal discharging, zinc deposition may not be completely removed from the electrodes. Then the remaining deposition will cause distinct coulomb efficiency loss along with working cycles. For the traditional non-flowing nickel-zinc battery, the coulomb efficiency is relatively low as the deposition of zinc tends to be non-uniform and dendritic, the coulomb efficiency loss with the cycles is more obvious. According to the past studies the lifetime of the non-flowing nickel-zinc battery was only hundreds of cycles [9] when distinct capacity loss or even internal short-circuit took place. However, for the single flow nickel-zinc battery, the coulomb efficiency is relatively higher as the deposition is more uniform and flat, so the internal short-circuit can substantially be avoided. It's difficult to accurately predict the efficiency of the battery but according to the experimental results, the efficiency is basically above 98%. So here η is assumed to be 1 and self-discharging resistance is therefore assumed to be infinity.

B. Experimental procedures

The experiments for the identification of model parameters are introduced in this part. A 3.7Ah single flow zinc-nickel battery was assembled in the lab with the same experimental schematic shown in Fig.1. Four sheets of sintered nickel oxide plates were used as the positive electrodes while three nickel-plated stainless steels as negative electrode substrates were sandwiched between the positive electrodes. Reagent grade of

1 Mol ZnO in 10 Mol KOH solution was prepared as the electrolyte.

The battery cycles tests were carried out with a battery test system CT-3008W (ShenZhen Neware Corp., China) at room temperature. Charging was terminated when battery was charged to the rated capacity of 3.7Ah, and SOC is defined to be 90% at this point. And discharging was terminated when the voltage dropped to 1.2 V at 1C current, and SOC is defined to be 10% at this point.

The SOC in the model is calculated as follows:

$$SOC = SOC_0 + \eta \cdot \int_0^t idt / C_{batt} \tag{5}$$

where SOC_0 is the initial value of SOC, and C_{batt} is the rated capacity of the battery.

In order to obtain the relationship between model parameters and SOC, several stepped intervals should be created at different SOC points. Hence pulse charging and discharging experiments were conducted. Fig. 5 shows a typical pulse charging/discharge curve with 1C current. Eight points are evenly chosen during charging and discharging process between SOC 10% and 90%. At each point, the battery current steps down to zero and rest for 30 min similar to the transient response of a step load current in Fig.3 The pulse experiments are also conducted at different current to see the effect of different current on model parameters.

C. Model extraction results

1) Open-circuit voltage

Using experimental results obtained in section B, the values of OCV at each SOC interval with different current were determined and shown in Fig.6. It can be observed that parameter difference among the OCV curves for different currents are small, indicating that the OCV value is independent of currents, which is also true in theory. But there exists some difference between the OCV curves at charging and those at discharging, so the extracted function of OCV for charging and discharging should be separated.

The single variable functions of SOC for OCV curves are extracted with LSF method, shown in equations (6) and (7):

$$OCV(SOC)_{charging} = 1.316 + 5.326 \times SOC - 28.52 \times SOC^2 + 80.78 \times SOC^3 - 122.2 \times SOC^4 + 93.73 \times SOC^5 - 28.60 \times SOC^6 \tag{6}$$

$$OCV(SOC)_{discharging} = 1.868 - 0.1703 \times SOC - 2.726 \times SOC^2 + 12.28 \times SOC^3 - 23.19 \times SOC^4 + 21.03 \times SOC^5 - 7.589 \times SOC^6 \tag{7}$$

2) Internal resistance

The internal resistance as the function of SOC and current is also obtained as shown in Fig.7. Unlike OCV, the value of internal resistance is independent of both current and charging/discharging mode. Single variable function of SOC to represent the resistance is also extracted:

$$Ri(SOC) = 0.1394 - 1.204 \times SOC + 5.355 \times SOC^2 - 12.53 \times SOC^3 + 16.19 \times SOC^4 - 10.92 \times SOC^5 + 3.011 \times SOC^6 \tag{8}$$

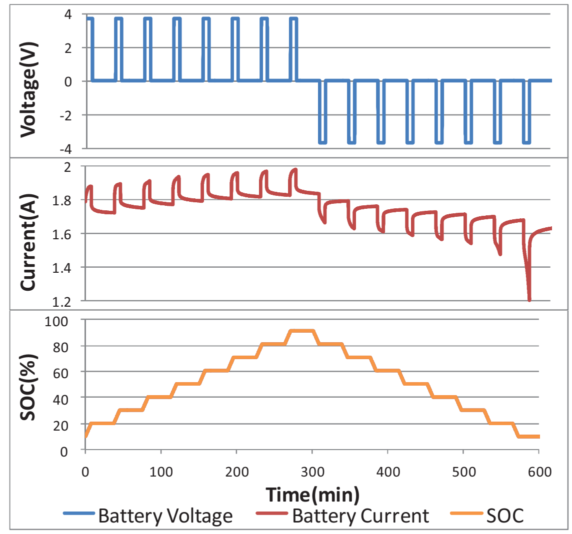

Fig.5. Pulse charging and discharging experiment

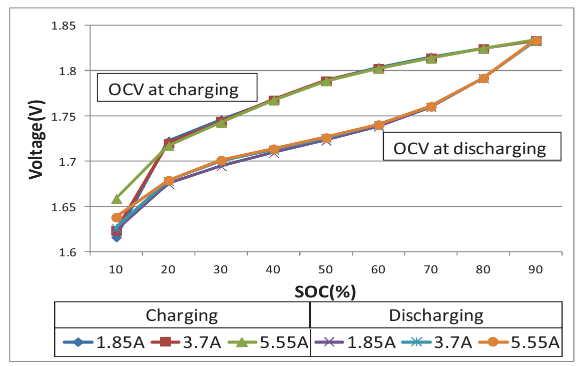

Fig.6. OCV curve at charging and discharging

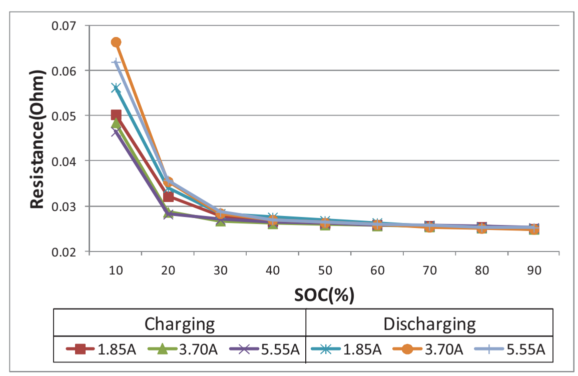

Fig.7. Extracted value of resistance

The variation tendency of the internal resistance can reflect the changes in reactants and products of the positive electrode. As $Ni(OH)_2$ is of poor electrical conductivity while NiOOH is of good conductivity. During charging, $Ni(OH)_2$ will be oxidated to NiOOH, so that the internal resistance drops significantly. As for the discharging, the reaction happens reversely. The internal resistance is a good indication of the SOC of positive electrode. It's quite different from other batteries like the lithium battery, whose internal resistance

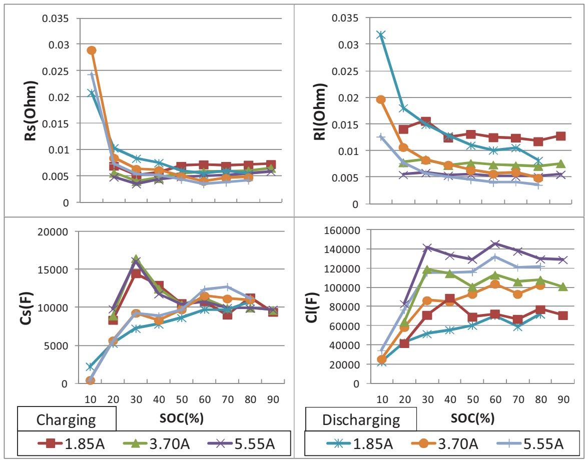

Fig.8. Extracted value of R_s, R_l, C_s and C_l at charging

keeps almost constant all though the charging/discharging cycle.

3) RC circuits

The values of R_s, R_l, C_s *and* C_l extracted at each SOC interval are shown respectively in Fig. 8. It can be observed that RC values vary in terms of both current and SOC. The RC values at each point are stored in a look-up table, and the relationships between RC parameters and SOC as well as current are implemented with interpolation method.

Using the extracted battery model parameters, the electrical battery model can be established and be applied for simulation and evaluations under various cases.

IV. Model Validations and Simulations

To validate the proposed model for the single flow zinc-nickel battery, a simulation platform was set up in Matlab. Validations are done under both the continuous and pulse current conditions. By comparing the simulation with experimental results, we can find out whether the model is accurate enough under both steady and dynamic cases.

The first test is to charge/discharge the battery with different constant current. Terminal voltage of the battery was recorded in experiments and compared with those obtained in simulations, as shown in Fig. 9(a) and (b). During charging, the maximum error is 0.018V; while during discharging, the maximum error is 0.1V, taking place at the end of discharging. It's because that in our model, the charging efficiency in (5) was assumed to be 100%, while in reality the efficiency was around 98%~99%. Except the end, the error stays within 0.02V.

The second test is pulse charging-discharging of the battery. As shown in Fig. 10, simulation results match experimental data well with the average error of 0.005V and maximum error of 0.293V.

The above results indicate that the proposed electrical battery model can predict both steady-state and dynamic

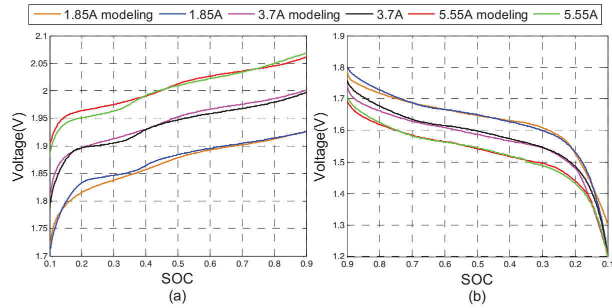

Fig.9. Comparison between simulation and experimental results at continuous current (a) at charging; (b) at discharging

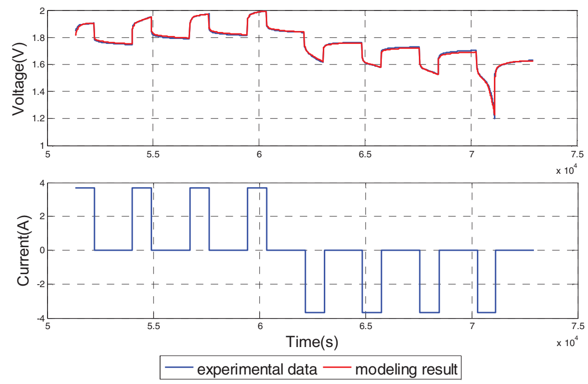

Fig.10. Comparison between simulation and experimental results at pulse current

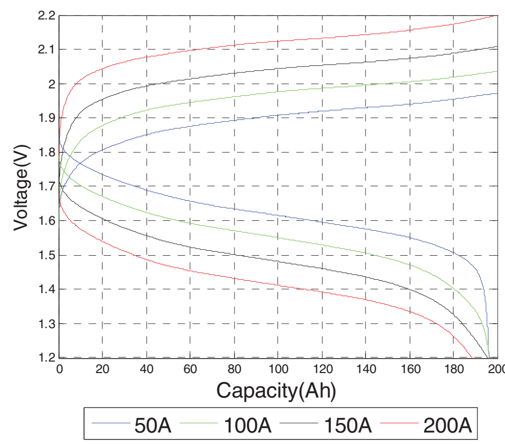

Fig.11. Charge–discharge curves at different current rate

voltage responses accurately. Hence the model can be used to predict the voltage and power output of the battery under various operation states with no need to conduct experiments every time. Next, the obtained model is used to estimate a 200Ah single flow zinc-nickel battery.

As for the latest development, single flow zinc-nickel batteries have been scaled-up to 200Ah (320Wh) in capacity by the group of J. Cheng, making the battery more suitable for large-scale grid energy storage. The charge–discharge

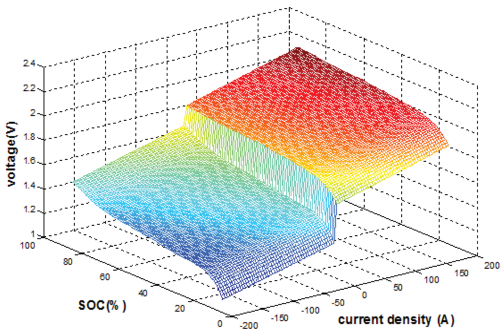

Fig.12. Steady voltage output as a function of current and SOC

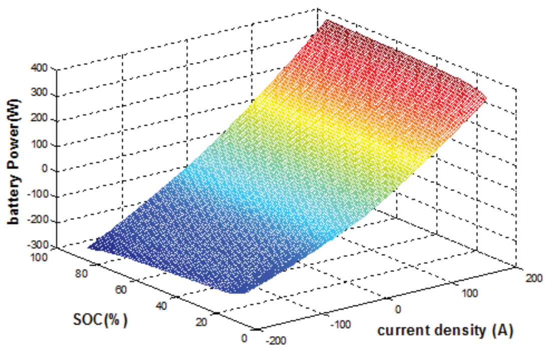

Fig.13. Steady power output as a function of current and SOC

TABLE III. OUTPUT VOLTAGE/POWER AND ENERGY EFFICIENCY

Current (A)	Average charging voltage (V)	Average discharging voltage (V)	Average Output Power (W)	Energy efficiency (%)
Experimental Data				
50	1.8917	1.6203	81	83.40
100	1.9585	1.5457	155	77.94
150	2.0286	1.4793	217.5	71.60
200	2.1129	1.4215	284	65.47
Simulation Results				
50	1.8919	1.6200	81	85.63
100	1.9643	1.5528	155	79.05
150	2.0366	1.4857	223	72.95
200	2.1090	1.4186	283	67.26

performances of the 200Ah (320Wh) battery were tested at constant current of 0.25C (50A), 0.5C (100A), 0.75C (150A) and 1C (200A) respectively, as is shown below in Fig.11. The modeling technique is applied on the scaled-up 200Ah battery to estimate steady state output voltage of the battery and the corresponding curves are shown in Fig.12 while the output power is shown in Fig.13 as a function of current and SOC. Note that for the coordinate of the figures, current >0 means the battery are operating at charging state while current <0 means discharging; Power >0 means the charging power while Power <0 means discharging power.

The output voltage, power and energy efficiency of the 200Ah battery in the simulation are also listed in Table III. Comparing the experimental data with simulation results, the model is adequately able to estimate the average output voltage and power of the battery with good accuracy. Hence, the proposed model in this paper is proved to be a good indication of the battery electrical performance under various cases.

From the above results we can see that the single flow zinc-nickel batteries can achieve an energy efficiency of more than 75% at current of less than 100A. Considering its low cost and a fairly high level of safety, the single flow zinc-nickel battery provides a competitive choice for battery technologies at this scale.

V. CONCLUSIONS

In this paper, the primary characteristics of the novel single flow zinc-nickel battery is illustrated and based on that, the electrical equivalent circuit model is established for the first time. The parameters in battery model are identified by a variety of experiments, carried on a small-capacity batter in the lab. According to the simulation and experiment verifications, the model can well estimate the performance of the batteries under different conditions. The model is also proved to be validated for large-scale single flow zinc-nickel battery. Since the single flow zinc-nickel battery will be a high cost-efficient alternative to large-scale power system storage, the proposed model would be a very useful tool in future system design and evaluations. Future work includes implementation of the model in the embedded system as part of the battery management system (BMS) and state of charge (SOC) estimation.

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