

Constant-Power Characterization of a 5 kW Vanadium Redox Flow Battery Stack

Pavan Kumar V¹, Sreenivas Jayanti^{1,2}, Raghuram Chetty¹

¹Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036, INDIA

²Corresponding Author

ABSTRACT

For large-scale stationary energy storage applications, flow batteries are gaining attention all over the world. Numerous studies have been done on flow batteries since their invention. Almost all the studies are based on the constant current cycling of flow batteries. In the present work, we explore a different perspective of a flow battery and characterize the power, energy, and efficiency characteristics of a 5-kW scale vanadium redox flow battery system through constant power cycling tests. Different ratios of charge power to discharge power characteristics of solar, wind, and peak shaving applications have been incorporated in the test protocol. It is shown that, over the range of testing, the round-trip energy efficiency and the fractional energy utilization depend linearly on the power at which the battery is charged or discharged.

Keywords: Vanadium redox flow battery, Constant power cycling, Energy storage, Cell stack

NOMENCLATURE

Abbreviations

VRFB	Vanadium Redox Flow Battery
ESS	Energy Storage System
PV	Photo Voltaic solar energy conversion
SoC	State of Charge
OCV	Open circuit voltage

1. INTRODUCTION

Global warming and climate change encourage the world to seek effective ways to reduce greenhouse gas emissions; thus, renewable energy sources have gained more attention due to their low environmental impact. Solar and wind energy are the most widely used renewable energy sources. These energies depend on solar irradiation and wind speed, which are intermittent and variable. This limits their use in applications where assured or round-the-clock power is required [1].

Energy from the wind farm depends on the speed of the wind. Wind power fluctuates within the short range of time intervals. Jia et al. [2] showed that a 6 MW rating windfarm fluctuates between 2.5 MW and 5.5 MW in 25 seconds, thus reflecting the highly unpredictable nature of wind farms. Geographical location, seasonal conditions, and time decide the power extraction from the solar energy resource. The seven-day PV profile presented by Parameswarappa et al. [3] shows large variability in power during insolation time as well as in the cumulative energy extracted on a day-to-day basis. A utility-scale electrical power plant is best operated continuously at its design condition while continuing to supply electricity as per the consumer demand, and leveling the peaks in demand ("peak shaving") is a major concern for these plants. Increasing demand for renewable energy sources has therefore given a fresh impetus to the development of efficient energy storage systems (ESS). The ESS has to charge during low demand hours and discharge for short times during peak hours. In contrast, in a solar PV system integrated with residential load [3], charging occurs relatively quickly, and discharge occurs over a long period. Thus, the ESS requires to

operate at different powers depending on the absorption and demand of the power.

Several energy storage devices are available for the above applications, such as secondary batteries (e.g., lead-acid, Li-ion, and flow batteries), hydrogen storage devices, flywheels, and electrochemical supercapacitors [4]. Amongst these, flow batteries are regarded as the most promising candidates for large-scale stationary storage applications. Generally, secondary batteries involve converting chemical into electrical energy through simultaneous redox reactions occurring at solid electrodes in a suitable supporting electrolyte. The concept is the same for flow batteries; however, the electrolyte solution is stored separately in external tanks containing dissolved redox couples. The electrolyte solution is pumped through the battery stack compartment, where the electron transfer reactions occur at the electrode surface. Unlike conventional batteries, redox flow batteries (RFB) are not size-limited for energy storage capacity. Although various flow batteries have been undergoing development for the last 30 years, vanadium redox flow batteries are the most appealing because they employ both anolyte and catholyte as the same materials. VRFB's have the advantage of minor crossover, long cycle life, no emission of toxic vapors, etc. [5].

2. Details of Experimental Work

2.1 Motivation

Most of the existing work on the kW-scale vanadium redox flow batteries (VRFBs) is based on the constant current operation. Zhao et al. [6] reported a kW-scale VRFB charge-discharge cycling at constant current density 70 mA/cm^2 with an average power output of 1.14 kW. Park et al. [7] also reported similar cycling at 60 mA/cm^2 and 90 mA/cm^2 on the kW scale VRFB with 76% and 70% energy efficiencies. Recently, Gundlapalli et al. [8] compared the performance of three kW-scale stacks through constant current cycling test protocol. As a characterizing technique, constant current density operation is consistent with the perspective of battery operation as an electrochemical reaction where the battery voltage depends on the overpotential which itself is directly linked to the current density. However, in a practical application, the battery characteristics over an operating range of state of charge (SoC) are of interest. Since the open circuit voltage (OCV) of a flow battery varies significantly over a charge or discharge

cycle (unlike in the case of a lead-acid battery or a lithium-ion battery), constant current density operation is not equivalent to constant power output. During charge-discharge cycling, as the state of charge (SoC) increases (or decreases) with charging (discharging) time, the cell voltage increases (decreases). In order to obtain a desired quantum of power, the battery current will be lower at high SoCs (i.e., towards the end of a charging cycle) than at low SoCs (towards the beginning of charging cycle). In case of discharging, the battery current will be especially high at low SoCs because the discharge capacity in large flow batteries is often limited by concentration polarization. The extent of energy that can be extracted from a battery would therefore depend on the power required and is better reflected in constant-power cycling.

In the present work, constant power cycling characterization of a flow battery stack has been carried out employing variable ratios of charging power to discharging power.

2.2 Material and methods

A 5 kW VRFB stack was assembled with 22 cells of 1500 cm^2 active area, as shown in Fig. 1. The overall structure of the cells and the stack are similar to those of the 8-cell stack reported elsewhere [8]. Thermally treated graphite felt electrodes with 4.6 mm thickness were employed as electrodes, and Nafion 117 was used as the proton exchange membrane cum separator. Electrodes were cut into the active area size and deployed on the thick bipolar graphite plates with a serpentine flow field. Silicone gaskets were used for making the stack leak-proof and getting the required compression. Two copper plates were placed as current collectors at both ends of the stack, followed by aluminum endplates and tightened with nuts and bolts. 1.6 M VO_2^{2+} electrolyte solution was prepared by dissolving VOSO_4 salt in $5 \text{ M H}_2\text{SO}_4$. In the dissolved state, other oxidation species (VO_2^+ , V^{3+} , and V^{2+}) were prepared by dual step charging [8]. All the characterization was done with 35 liters of the volume of the electrolyte on each side.

Electrochemical characterizations were done with a battery cycler (Bitrode battery cycler). Voltage cutoff for charging and discharging was set to 1.7 V and 0.8 V per cell. Charge-discharge cycling was carried out at constant power subject to voltage limits for the stack and current limitations of the battery cycler. Different power combination protocols were employed for the testing, as presented in Table 2.



Fig.1. 5 kW VRFB stack with 22 cells of 1500 cm² active area and external manifolds for electrolyte circulation.

Table.1: Specifications of 5 kW VRFB stack

Graphite felt	Thickness – 4.6 mm Geometrical area- 1500 cm ²
Number of cells	22
Bipolar plates	Graphite plates
Membrane material	Nafion 117
Electrolyte	1.6 M VOSO ₄ in 5 M H ₂ SO ₄
Volume of the electrolyte	35 liters

2.3 Results

Polarization was carried out on the stack with varying current densities ranging from 120 mA/cm² to 10 mA/cm² for 45 seconds at each current density. Maximum power of 5.6 kW obtained at 120 mA/cm² current density as shown in Fig. 2. The test protocol also included an OCV measurement step which enabled the determination of the overpotential at the beginning and at the end of the discharge step. From these observations, overpotential and power are correlated, as shown in Fig. 3. One can see that, as expected, for extracting higher power, higher overpotential is required because a higher current density operation is required, which increases the activation and ohmic overpotentials.

The present results show that over a short discharge step, the overpotential varies linearly with power.

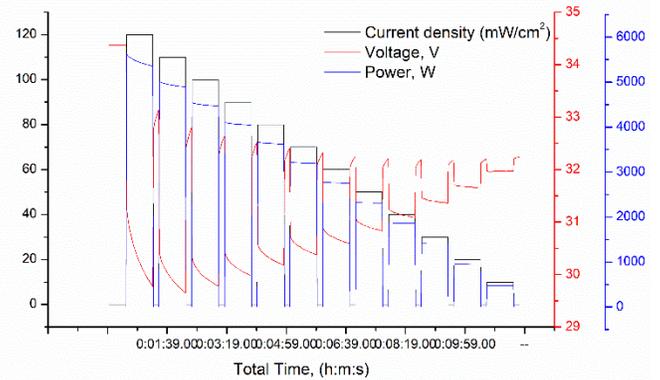


Fig. 2. Polarization plot of the 5 kW VRFB stack operated at current densities ranging from 120 mA/cm² to 10 mA/cm².



Fig. 3. Plot against over potential and power deduced from polarization plot.

From the linear variation of the overpotential with power, a nearly linear variation of overpotential with SoC may be expected if the SoC is not too low or not too high. In the present experiments, the charge/discharge cycles typically operated over an SoC range of 15 to 85% at low powers. The OCV was found to vary nearly linearly with SoC over this SoC interval. Over this range of SoC overpotential is solely dependant on current density, which is consistent with the results shown by Parameswarappa et al.[3] and J.Langer et al.[9]. Since the cycling protocols were carried out over fixed stack voltage ranges and higher power operation required higher overpotentials, the operating SoC range was lower at high powers. The measured discharge energy is plotted in Fig. 4 as a function of power for cases with

equal charging and discharging powers. One can see that the energy that can be discharged decreases almost linearly with power. The round-trip energy efficiency was also found to vary linearly under these conditions within an efficiency range of 75% to 80%.

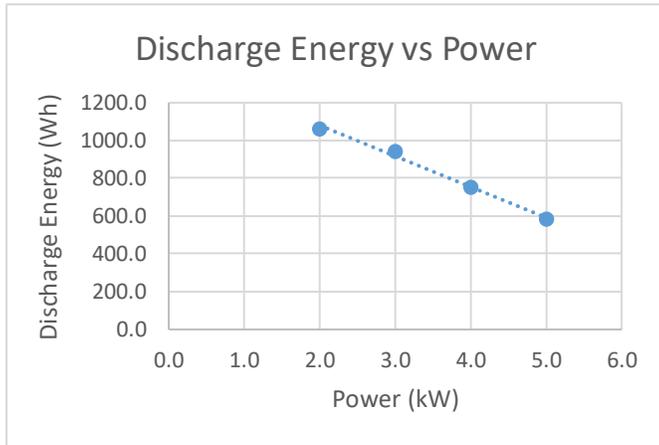


Fig. 4. Discharge energy against the discharge power of VRFB stack operated at 2-5 kW power.

Table 2. Efficiency data for 5 kW stack operated at constant powers

S.no	Ratio	P-Charge (kW)	P-Discharge (kW)	Energy Efficiency (%)
1	0.4	2	5	77.3
		1	2.5	79.1
2	0.7	2	3	80.4
		3	4.5	77.5
		1	1.5	79.4
3	1.0	2	2	82.1
		3	3	80.8
		4	4	78.2
		5	5	76.1
4	1.5	3	2	82.2
		4.5	3	75.1
		1.5	1	80.6

Constant-power cycling experiments carried out with unequal charging and discharging powers (see Table 2) showed that the energy charged as well as the round-trip energy efficiency depended primarily on the discharge energy. However, a reasonable, strong correlation was also observed with the charging power. Over the Pch/Pdis ratio range between 0.4 and 1.5, the efficiency was found to vary between 72 to 82%. A nearly linear variation in the energy efficiencies was observed with charge energy, as shown in Fig. 5. A similar correlation with a slightly higher regression coefficient (R^2 value of

0.94 vs. 0.92) was obtained when the round-trip energy efficiency was plotted against discharge energy. This may be a peculiarity of constant power cycling carried out under both current and voltage limits. At high discharge powers, the discharge step may be limited not by the lower limit of the stack voltage but by the battery current because in constant discharge power testing, the battery current increases towards the end due to a decrease in the battery voltage.

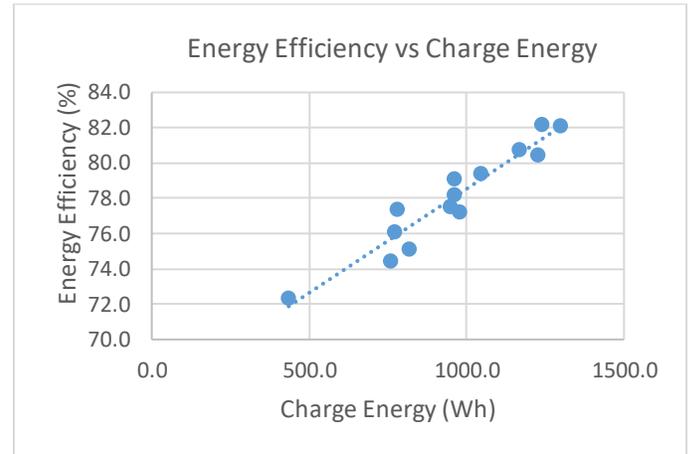


Fig. 5. Energy efficiencies of the 5 kW VRFB stack operated at different powers against the energy during the charging.

3. Conclusions

Constant power cycling protocols were employed on a 5 kW VRFB stack to replicate the real-time operations with solar PV and wind energy. Results show that the discharge energy decreases linearly with increasing power. The round-trip energy efficiency varies linearly, with discharge energy in the range of 72 to 82% for discharge powers in the range of 1 to 5 kW.

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REFERENCE

- [1] R. López-Vizcaíno, E. Mena, M. Millán, M. A. Rodrigo, and J. Lobato, "Performance of a vanadium redox flow battery for the storage of electricity produced in photovoltaic solar panels," *Renew. Energy*, vol. 114, pp. 1123–1133, 2017, doi: 10.1016/j.renene.2017.07.118.

- [2] H. Jia, Y. Fu, Y. Zhang, and W. He, "Design of hybrid energy storage control system for wind farms based on flow battery and electric double-layer capacitor," *Asia-Pacific Power Energy Eng. Conf. APPEEC*, no. 10, 2010, doi: 10.1109/APPEEC.2010.5448720.
- [3] P. Parmeshwarappa, R. Gundlapalli, and S. Jayanti, "Power and Energy Rating Considerations in Integration of Flow Battery with Solar PV and Residential Load," *Batteries*, vol. 7, 2021.
- [4] M. Skyllas-Kazacos, M. H. Chakrabarti, S. A. Hajimolana, F. S. Mjalli, and M. Saleem, "Progress in Flow Battery Research and Development," *J. Electrochem. Soc.*, vol. 158, no. 8, p. R55, 2011, doi: 10.1149/1.3599565.
- [5] C. Ding, H. Zhang, X. Li, T. Liu, and F. Xing, "Vanadium flow battery for energy storage: Prospects and challenges," *J. Phys. Chem. Lett.*, vol. 4, no. 8, pp. 1281–1294, 2013, doi: 10.1021/jz4001032.
- [6] P. Zhao, H. Zhang, H. Zhou, J. Chen, S. Gao, and B. Yi, "Characteristics and performance of 10 kW class all-vanadium redox-flow battery stack," *J. Power Sources*, vol. 162, no. 2 SPEC. ISS., pp. 1416–1420, 2006, doi: 10.1016/j.jpowsour.2006.08.016.
- [7] D. J. Park, K. S. Jeon, C. H. Ryu, and G. J. Hwang, "Performance of the all-vanadium redox flow battery stack," *J. Ind. Eng. Chem.*, vol. 45, pp. 387–390, 2017, doi: 10.1016/j.jiec.2016.10.007.
- [8] R. Gundlapalli and S. Jayanti, "Case studies of operational failures of vanadium redox flow battery stacks, diagnoses and remedial actions," *J. Energy Storage*, vol. 33, no. August 2020, p. 102078, 2021, doi: 10.1016/j.est.2020.102078.
- [9] J. Langner, J. Melke, H. Ehrenberg, and C. Roth, "Determination of Overpotentials in All Vanadium Redox Flow Batteries," *ECS Trans.*, vol. 58, no. 37, pp. 1–7, 2014, doi: 10.1149/05837.0001ecst.