Journal of Power Sources 284 (2015) 547–553

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Shunt currents in vanadium flow batteries: Measurement, modelling and implications for efficiency

H. Fink*, M. Remy

ZAE Bayern, Energy Storage, Walther-Meißner-Str. 6, 85748 Garching, Germany

HIGHLIGHTS

- We investigate a mini flow battery stack with external hydraulic system.
- We measure the shunt currents directly during battery operation and standby.
- We model shunt current effects for various flow frame geometries and cell figures.
- Inner cells discharge faster; outer cells are charged during charge conservation.

ARTICLE INFO

Article history:
Received 17 November 2014
Received in revised form
16 February 2015
Accepted 8 March 2015
Available online 10 March 2015

Keywords:
Redox flow battery
Shunt currents
Coulombic efficiency
Stack efficiency

ABSTRACT

Shunt currents are an important factor which must be considered when designing a stack for flow batteries. They lead to a reduction of the coulombic efficiency and can cause furthermore a critical warming of the electrolyte. Shunt currents inevitably appear at bypass connections of the hydraulic system between the single cells of a stack.

In this work the shunt currents of a five-celled mini stack of a vanadium flow battery with external hydraulic system and their effects are investigated directly. The external hydraulic system allows the implementation of current sensors for direct measurement of the shunt currents; moreover, the single bypass channels can be interrupted by clamping the tube couplings and with it the shunt currents between the cells when the pumps are off. Thus the shares of losses by cross contamination and by shunt currents are quantified separately by charge conservation measurements.

The experimentally gained data are compared to a shunt current model based on a equivalent circuit diagram and the linear equation system derived from it. Experiments and model data are in good agreement. The effects of shunt currents for different flow frame geometries and number of cells in a stack are simulated and presented in this work.

1. Introduction

Flow batteries, especially the vanadium system, are regarded as a promising storage technology for the realization of large-scale battery storage systems. The energy converter unit, which is built up from a large number of electro-chemical cells connected in series, forms the main component of this battery. The quality of the design of this converter unit, i.e. the attainable power and efficiency at given material input, is an important parameter for the associated costs (€/kW). An important part of the dimensioning concerns the hydraulic system. It supplies every cell with electrolyte, however, constitutes at the same time an electric connection between the cells through which parasitic currents can flow, the so-called shunt currents.

The problem of shunt currents plays an important role for the designing of stacks for flow batteries. Shunt currents reduce the coulombic efficiency of a flow battery by causing an internal self-discharge: they enable an undesirable run of the discharge reactions at simultaneous ion shift through the bypass connections (that unfavourably close the circuit). Driven by the potential difference between the cells of a stack (and between stacks themselves) currents flow over the conducting electrolyte connections between them, over the electric resistances they constitute, respectively. Cross section, length and state of charge (via viscosity and conductivity) of the fluent electrolyte determine at the same time the hydraulic like the electric resistance of this bypass connections. For example, smaller cross section and longer length of

* Corresponding author.
E-mail address: fink@muc.zae-bayern.de (H. Fink).

http://dx.doi.org/10.1016/j.jpowsour.2015.03.057
0378-7753/

Nomenclature

A	anolyte
C	catholyte
I_loss	total loss currents from cross-contamination and shunt currents
IP	shunt current through primary channel
IS	shunt current through secondary channel
I_Stack	external current through stack
IZ	current through cell
n	index for position in circuit
OCP	open circuit potential (also denoted as U0)
RP	resistance of primary channels
RS	resistance of secondary channels
RZ	cell resistance
SOC	state of charge
UP	potential at primary channel position
US	potential at secondary channel position
U_Stack	stack potential
ΔU	cell potential deflection
σ	electrolyte conductivity

the connection lead to higher resistances and thus reduce the extent of the shunt currents. Ideally little hydraulic resistances are combined with high electric resistances. These opposite trends require a tradeoff, that can only be optimized with detailed understanding of the underlying processes.

There are several publications concerning shunt currents, mostly focused on creating a model for their description rather than experimental investigations. Early work has been done by NASA [1,2], calculating the manifestation of shunt currents in flow battery stacks and investigating the conflict of shunt losses vs. pumping losses. A report about shunt currents in a vanadium flow battery stack has been given by Ref. [3]. Shunt currents are not limited to single stacks, but also an important loss mechanism in battery systems consisting of several stacks; this matter was modelled by Ref. [4] and more recently by Refs. [5] and [6]. A model for thermal implications of shunt currents especially during stand by periods was published in Ref. [7]. When it comes to quantification of shunt currents, most studies fall back on models and did not measure the losses (shunt currents, self-discharge) directly. Moreover, the models often show only shunt currents in a few chosen configurations and no comprehensive correlations.

Aim of this work is to compile a detailed understanding of shunt currents in a stack of a vanadium flow battery and to derive a complete presentation of shunt current effects for different flow frame geometries and numbers of cells. Therefore, a specific experimental setup was built, consisting of a five-celled mini stack with an external hydraulic system. This external hydraulic system, realized by tubing connections between the cells, allows a direct measurement of the particular shunt currents as well as their interruption. Single cell potentials are monitored at different operating states and the shares of losses by shunt currents and by cross contamination are quantified separately by charge conservation measurements.

The experimentally gained data are compared to a shunt current model. This model is based, like most models found in literature, on an equivalent circuit. Thereof derived linear equation system was implemented in a *Mathematica* algorithm that allows a dynamic and flexible calculation of implications for various stacks (number of single cells, nature of flow channels) with regard to the shunt currents occurring in them and the expected coulombic efficiencies. The work concludes with a comprehensive sensitivity analysis and the evaluation of the consequences of shunt currents at cell level and as an outlook for stacks of different sizes.

2. Experiment and model

2.1. Experimental setup

The investigated stack consists of five cells. The hydraulic connections between the cells are realized by a tube coupling system which lies accessibly outside the flow frames, see Fig. 1. Tube lengths and consequently connecting resistances can thereby be varied. More important is the possibility to switch off shunt currents by clamping the flexible tubing (when pumps are off).

The cells consist of: activated graphite felts (GFD5, SGL Carbon; activated at 400 °C for 20 h), graphite foils as bipolar plates (TF6, SGL Carbon), Nafion membranes (N117, DuPont), copper plates as current collectors, flow frames and end frames of PVC. The Nafion membranes were pretreated firstly with a hydrogen peroxide solution (3%, boiling for 1 h), secondly a sulphuric acid solution (1 mol/L, boiling for 1 h) and rinsed thirdly with deionized water after each step.

A standard vanadium-electrolyte solution (1.6 mol/L of vanadium in 2 mol/L of sulphuric acid, GfE) was used (250 ml per half cell). This electrolyte was delivered with state of charge (SOC) of −50% or a 1:1 mixture of V(III)- and V(IV)-ions, respectively. An initial charging was conducted prior to the experiments. The SOC was determined via the open circuit potential (OCP) of a small cell preceding to the stack. Here, the SOC of 20, 50 and 80% correspond to the OCP of 1.34, 1.41 and 1.49 V, respectively.

Potential and current of the stack are controlled by a potentiostat/galvanostat (PGStat302N, Metrohm). Single cell voltages are monitored by a second (multi) potentiostat/galvanostat (SP-240, Bio-Logic). The shunt currents are measured contactless via current sensors (CYCT04-LTA20 mA, Chen Yang Technologies); the respective points of measurement are variable. The current sensors have a measuring range from ± 20 mA with an accuracy of ± 0.1 mA.

For measurement of conductivity of electrolyte solutions (anolyte and catholyte) at different SOC a suitable measuring electrode (SG78, Mettler Toledo) was used.

All experiments were conducted at room temperature (about 20–25 °C).

2.2. Model of shunt currents

In the electric equivalent circuit diagram of a stack the single

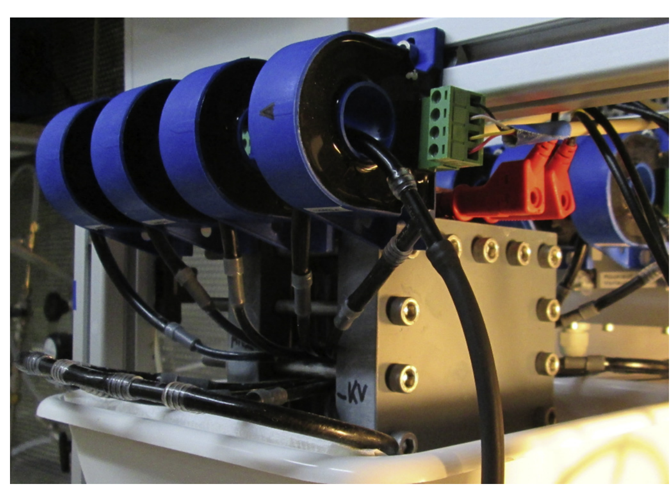

Fig. 1. Picture of the experimental setup shows: current sensors, external fluid system and mini stack.