Electrochimica Acta 204 (2016) 1–8

Contents lists available at ScienceDirect

Electrochimica Acta

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

Mathematical modeling and experiments of a half-cell redox flow lithium ion battery system

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ARTICLE INFO

Article history:
Received 22 October 2015
Received in revised form 31 January 2016
Accepted 11 March 2016
Available online 18 March 2016

Keywords:
Renewable energy
Energy storage
Charge conservation
Nernst equation
Mass balance

ABSTRACT

A mathematical model for an anodic half-cell redox-flow lithium-ion battery is derived and complemented with experiments. In short, the model considers conservation of charge and species – two redox shuttle molecules and their ionic counterparts – coupled with electrochemical reactions in the battery and conservation of species coupled with chemical reactions in the tank. Based on quantitative arguments, it is postulated that such a model is sufficient to capture the behavior of the system. This is confirmed by calibrating and validating the model with a training and test set from the experiments respectively – overall, good agreement is found. In particular, the model is able to capture the two distinct charge and discharge regimes that occur in the system as well as the dependence of the overall battery performance on the chemical reactions taking place in the tank.

1. Introduction

The redox flow Li-ion battery (RFLB) is a recently proposed concept for energy storage that seeks to exploit the high energy density of Li-ion batteries with the safety and flexibility of redox flow systems [1–3]. As a Li-ion battery, the RFLB employs Li-salts as electrolytes and stores/releases the energy via exchange of Li-ions between two Li-storage materials. Like a flow battery, the electrolyte is not confined to the electrodes, but rather stored in external tanks and pumped through the electrodes. Unlike a traditional flow battery such as the Vanadium-redox flow battery [4], the liquid electrolytes are not the means to store the energy in a RFLB; instead, the energy is stored in tanks with solid Li-storage materials similar or identical to those in conventional Li-ion batteries. The transfer of Li-ions from the cell to the tank or vice versa is facilitated by redox *shuttle* molecules in the flowing electrolyte. During charge or discharge, these shuttle molecules are oxidized/reduced at the electrodes.

For the battery chemistry that we are considering here, the following reactions take place at the positive electrode of a RFLB:

$$M1^+ + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} M1 \tag{1}$$

$$M2^+ + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} M2 \tag{2}$$

With the flowing electrolyte, the oxidized/reduced shuttle molecules enter the tank and react there with the present Li-storage material, e.g., TiO_2:

$$xLi^+ + TiO_2 + xM1 \rightarrow Li_xTiO_2 + xM1^+ \tag{3}$$

$$Li_xTiO_2 + xM2^+ \rightarrow xLi^+ + TiO_2 + xM2 \tag{4}$$

In 2006, Wang et al. [5] demonstrated that a Li-storage material can be reversibly delithiated/lithiated in the presence of shuttle molecules without being attached to the current collector – referred to as redox targeting. Based on the concept of redox targeting reactions at both the electrodes, Huang et al. [2] proposed the RFLB as a novel energy storage technology. As a proof-of-concept, they built a cathodic half-cell of RFLB that employed $LiFePO_4$ as the storage material, ferrocene derivatives as the shuttle molecules and a lithium foil as the counter electrode. (In this context, "half-cell" refers to the fact that the only one electrode of the cell is operated with pumped electrolyte and shuttle molecules.) Further, TiO_2 was found to be a suitable storage material for the anodic half-cell of the RFLB, and bis(pentamethylcyclopentadienyl) cobalt and cobaltocene as a corresponding pair of required shuttle molecules [3]. The reversible delithiation/lithiation of TiO_2 in the presence of shuttle molecules was demonstrated in a glass cell without pumping of the electrolyte.

Alongside experimental design and material research, mathematical modeling and simulations have come to play an important

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http://dx.doi.org/10.1016/j.electacta.2016.03.072
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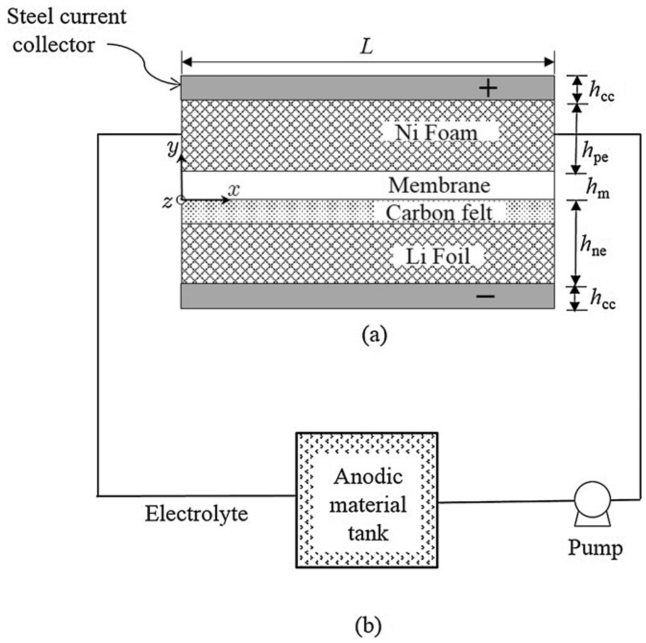

Fig. 1. A schematic of the half-cell RFLB system (N.B. $h_{ne} = h_{cf} + h_{Li}$).

Fig. 2. Experimental setup of the half-cell RFLB system.

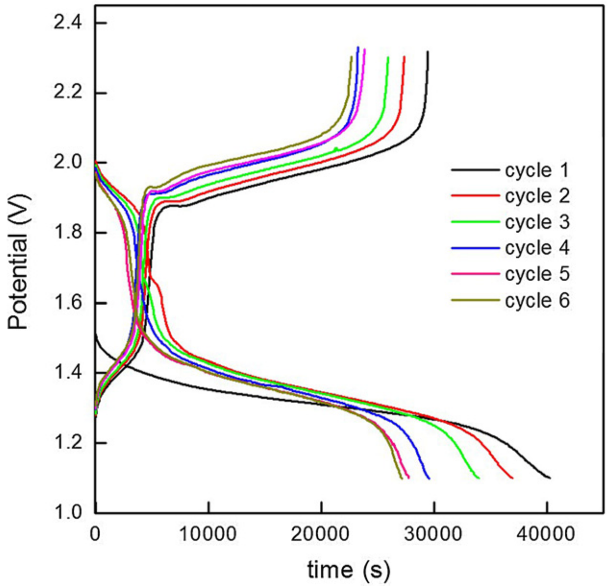

Fig. 3. Galvanostatic charge/discharge curves for six cycles.

part in research and development of the flow batteries. This has resulted into appearance of several flow battery models in the last few years, in particular for all-vanadium redox flow batteries (VRFBs) [6–26]. Most of these models have been developed based on the fundamental conservation principles to describe the macroscopic physicochemical phenomena taking place in the system.

Towards fabricating a full-cell RFLB, the aim of this paper is twofold: first, to design and operate a flow cell for the anodic half-cell of the RFLB, as shown schematically in Fig. 1; and second, to derive a mathematical model based on arguments and assumptions of the inherent physical phenomena. In brief, the model solves for macroscopic conservation of shuttle molecules in both the cell and the tank, one-dimensional conservation of charge in the cell and electrochemical and chemical reactions in the cell and tank respectively. Four parameters pertaining to the reactions are identified and calibrated with a training set from the experiments; the model is then validated with a test set. We proceed to analyze the key characteristics – the macroscopic behavior, the two voltage regimes, and the dual role of the tank for both storage and reactions – of the half-cell RFLB and finish with conclusions and a discussion of model extensions towards a full cell and stack.

2. Experimental

A half-cell RFLB system comprising the electrochemical cell and the tank was assembled as shown in Fig. 2. Overall, the electrochemical cell comprises the following layers (from bottom to top in Fig. 1a): a stainless steel end plate, a lithium foil, a carbon felt spacer filled with electrolyte, a lithiated nafion membrane, a porous flow-through electrode made of nickel foam with an active area of $2 \times 2\,\mathrm{cm}^2$, and a stainless steel end plate. Dimensions of all the cell components can be found in Table 1.

The electrolyte for the carbon felt (negative electrode) as well as for the nickel foam (positive electrode) was a mixture of dehydrated propylene carbonate and anhydrous lithium perchlorate; in addition, the electrolyte at the positive electrode contained the shuttle molecules bis(pentamethylcyclopentadienyl) cobalt and cobaltocene – each at concentration of 5 mM. For convenience, we will refer to the former as M1 and the latter as M2 and to their oxidized forms as $M1^+$ and $M2^+$ respectively. The electrolyte in the positive electrode containing the shuttle molecules is pumped through the nickel foam by a peristaltic pump that connects with the tank as shown in Fig. 1b.

The two shuttle molecules (M1 and M2), $LiClO_4$ and PC were purchased from Sigma-Aldrich and the TiO_2 powder was from Degussa (P25). All the chemicals were used as received without any pretreatment.

A cylindrical glass bottle of radius 0.01 m and length 0.05 m was employed as tank. In the tank, a 15 mg tablet (equivalently 62.5 mM) of TiO_2 was placed.

In the charge/discharge experiments, a constant current of 200 μA in the voltage range of 1.1 to 2.3 V was passed through the cell. A total of six charge/discharge curves were measured over a period of 98 hours with a decrease of cell performance of around 30% between the first and last curve (see Fig. 3). The drop in the cell performance can be attributed to imperfect filtering of the electrolyte through TiO_2. The TiO_2 may gradually lose reactivity with trapped dead electrolyte causing the capacity loss. For the purpose