Charge coup de fouet phenomenon in soluble lead redox flow battery

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HIGHLIGHTS

- Voltage dip after initial peaking of charging voltage, and slow return to normalcy.
- Effective conductivity is obtained using a percolation model with a critical fraction.
- Voltage drop across surface deposits included in model through reduced over-potential.
- Insulating regions on electrode expand and contract with discharge/charge cycle.
- Charging Coup de fouet increases with increase in depth of discharge in previous cycle.

ARTICLE INFO

ABSTRACT

The *charge coup de fouet* phenomenon, known in the context of lead-acid battery, refers to the presence of a voltage dip shortly after charging of a fully discharged battery begins. While the attempts to relate magnitude of *coup de fouet* phenomena with the state of health of battery have appeared in the literature, the phenomena continue to be poorly understood. The soluble lead redox flow battery (SLRFB), with potential for energy storage at large scale at low cost, also displays similar features. We report in this work our modeling and experimental efforts aimed at understanding *charge coup de fouet* phenomenon in natural convection driven SLRFB. We present a model that incorporates the presence of non-conducting PbO in deposits through a percolation type model for conductivity. The associated potential drop across the deposits is incorporated in the model through reduced overpotential available for driving Butler–Volmer kinetics. The complete model with coupled natural convection induced by non-uniform concentration of Pb ions in electrolyte successfully captures *charge coup de fouet* phenomenon, and explains the measured variation of its magnitude with the depth of discharge in the previous cycle. The model explains our earlier observation that during the discharge process, a receding zone of deposits is seen only on cathode but not on anode. The approach used is applicable to electrochemical systems in which solid conducting matrix evolves to non-conducting or poorly conducting and vice-versa, with a change in composition.

1. Introduction

Coup de fouet phenomena are reported in the literature in the context of conventional lead-acid batteries. When a fully discharged battery is charged, the voltage first rises sharply in a rather short time, following which is decreases, goes through a comparatively shallow minimum, and then begins to rise slowly and steadily, as expected of charging voltage for a battery. Similarly, when a fully charged battery is discharged, the battery voltage first drops sharply in a rather short time, following which it rises, goes through a rather broad maximum, and then begins to

decrease slowly and steadily, as expected of discharging voltage for a battery. These two phenomena, shown schematically in Fig. 1, are named *charge coup de fouet* and *discharge coup de fouet* respectively. Depending on the operating conditions, magnitude of the voltage dip and voltage rise in *charge* and *discharge coup de fouet* phenomena varies in range of 10–50 mV, and lasts from a few seconds to a couple of minutes (Delaille et al., 2006; Pascoe and Anbuky, 2002). These phenomena find use in battery diagnosis through their correlation with state of health (SOH) of a battery (Bose and Laman, 2000; Pascoe and Anbuky, 2002; Pascoe et al., 2002), an indicator of its ability to perform well in charge-discharge cycles. The SOH tells a user when to replace a battery. The *coup de fouet* phenomena are also correlated to state of charge (SOC) of a battery (Pascoe and Anbuky, 1999) which indicates how
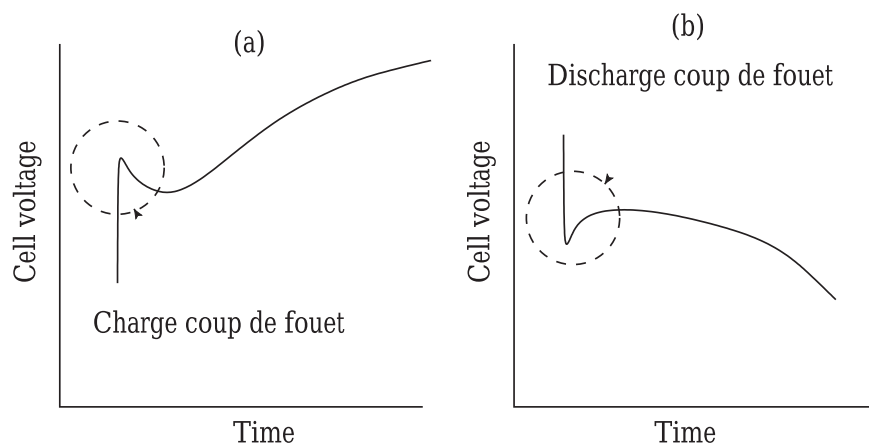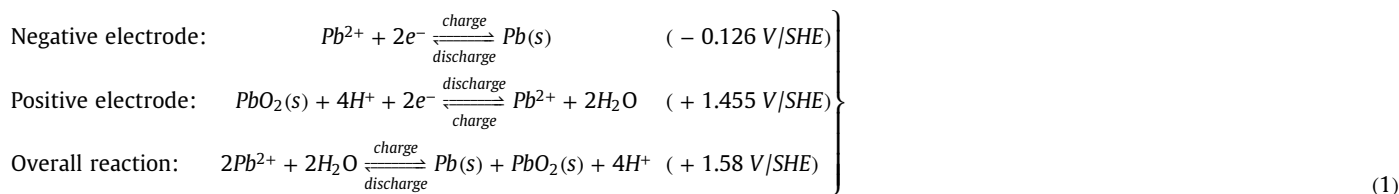
Fig. 1. Schematics of (a) *charge coup de fouet* and (b) *discharge coup de fouet* observed in conventional lead-acid battery.

much more charge can be put in it.

Berndt and Voss (1965) has studied *charge coup de fouet* in conventional lead-acid battery, and suggested that a peak in potential could arise from insulating $PbSO_4$ formed on discharge products in lead-acid battery. Delaille et al. (2006) have contested the above explanation. According to them, end-of-discharge does not correspond to complete coverage of electrode by an insulating layer of $PbSO_4$. The authors instead proposed mass transport limitations to be the reason for *charge coup de fouet*. No mathematical model appears to have captured the peak associated with *charge coup de fouet* yet.

The recently proposed membraneless soluble lead-acid redox flow battery (SLRFB) with only one electrolyte flow loop (Hazza et al., 2004, 2005; Li et al., 2009; Pletcher and Wills, 2004, 2005; Pletcher et al., 2008ab) is a promising candidate for large scale storage of energy, as it can potentially offer a number of advantages over the other widely used redox flow batteries (Verde et al., 2013; Nandanwar and Kumar, 2014). The active species Pb^{2+} in SLRFB comes from lead methanesulfonate salt [$(CH_3SO_3)_2Pb$: PbMS] dissolved in aqueous solution of methanesulfonic acid [CH_3SO_3H: MSA]. The redox reactions involved are:

review of the current understanding of SLRFB, as this is needed for model development. This is followed by sections covering experimental details, model development, and results.

2. Current state of understanding of SLRFB

The continued investigations on SLRFB over the last ten years have brought up a number of their characteristics which need to be explained by models. Hazza et al. (2004) experimented with 10 cm × 10 cm electrodes with inter-electrode separation of 1.2 cm and found anode to be the limiting one. Collins et al. (2010) reported that charging in the first cycle occurs at a nearly constant voltage, followed by two step charging in the subsequent cycles. Beck and Bhn (1975) suggested that reduction of PbO_2 during discharge leads to its electro-dissolution and also formation of an insoluble deposit which oxidizes more readily than Pb^{2+} ions in the next charge cycle to form PbO_2 deposits. The second cycle charging therefore starts at a lower voltage. Pletcher and Wills (2005) carried out EDAX analysis of insolubles on anode and found Pb and O in ratio close to 1:1, suggesting PbO as insolubles. Oury et al. (2012) carried out mass change

Negative electrode: $Pb^{2+} + 2e^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} Pb(s)$ $(-0.126 \; V/SHE)$

Positive electrode: $PbO_2(s) + 4H^+ + 2e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} Pb^{2+} + 2H_2O$ $(+1.455 \; V/SHE)$

Overall reaction: $2Pb^{2+} + 2H_2O \underset{discharge}{\overset{charge}{\rightleftharpoons}} Pb(s) + PbO_2(s) + 4H^+$ $(+1.58 \; V/SHE)$

(1)

In charge cycle, lead ions are deposited from electrolyte on cathode and anode in the form of Pb and PbO_2 respectively. The same are redissolved as Pb^{2+} ions in discharge cycle. The electrode reactions involved in soluble lead battery appear much simpler than those involved in the conventional lead-acid battery. The measurements however show similar *charge coup de fouet* and *discharge coup de fouet* phenomena (Verde et al., 2013).

In this work, we investigate *charge coup de fouet* in SLRFB experimentally, and develop a quantitative model to understand it. The latter is necessary as the existing models do not capture it. The experiments are carried out in a standard rectangular cell, with no external flow, but in the presence of induced natural convection, explained in latter sections. We begin in the next section with a

investigations at anode using quartz crystal micro-balance to confirm the presence of solid state reaction on anode, and suggested formation of non-stoichiometric PbO_x. The authors suggested that such non-stoichiometric compounds may come from modification of intermediate compound $Pb(OH)_2$ formed during PbO_2 to Pb^{2+} conversion. These findings provided basis for Shah et al. (2010) to propose the following side reaction at anode to run concurrently to the main reactions given by Eq. (1):

$$PbO + H_2O \underset{discharge}{\overset{charge}{\rightleftharpoons}} PbO_2 + 2e^- + 2H^+.$$

(2)
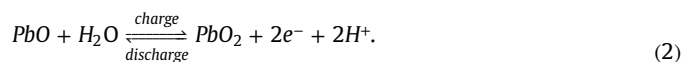
Shah et al. (2010) developed the first model for SLRFB. The model considered Nernst-Planck equations to govern transport of