



## Electroactive-Zone Extension in Flow-Battery Stacks



Kyle C. Smith<sup>1,2</sup>, Victor E. Brunini<sup>1</sup>, Yajie Dong<sup>1,3</sup>, Yet-Ming Chiang, W. Craig Carter\*

Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, USA

### ARTICLE INFO

#### Article history:

Received 14 May 2014

Received in revised form 4 September 2014

Accepted 22 September 2014

Available online 30 September 2014

#### Keywords:

flow battery  
semi-solid suspension  
slurry electrode  
efficiency  
mixed-conductor

### ABSTRACT

Flowable suspensions that conduct both electrons and ions can enable the use of energy-dense electroactive species in flow batteries [M. Duduta et al., *Adv. Energy Mater.*, **1**, 511 (2011); Z. Li et al., *Phys. Chem. Chem. Phys.*, **15**, 15,833 (2013); F. Fan et al., *Nano Lett.*, **14**, 2210 (2014)]. In comparison with conventional flow batteries where electrochemical reactions are confined to a fixed current-collector region, electronically conductive flow electrodes permit electrochemical reactions to extend outside of the physical confines of the stack. We have measured and modeled how mixed-conduction enables an electroactive zone (EAZ, in which electrochemical reactions occur) that is of greater spatial extent than current collectors, the extension being termed side zone, SZ. Electrochemical reactions in SZs can reduce coulombic and energetic efficiency. Here we show that for realistic suspension properties and operating conditions, the added inefficiency is small in practice, and can be further mitigated by using appropriate operating conditions and/or materials choices. For the specific example of a non-aqueous  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  suspension, we show that EAZ extension contributes less than 1% additional efficiency loss at C/10 rates for current collectors greater than 20 mm long.

© 2014 Elsevier Ltd. All rights reserved.

### 1. Introduction

Global climate change and a desire for reduced dependence on oil are driving energy storage research that aims to electrify transportation and incorporate renewable energy sources into the power grid [1–5]. As one approach to store energy, Duduta et al. [6] demonstrated a semi-solid flow cell (SSFC) that combines the high energy-density of Li-ion batteries with the flexible and scalable architecture of flow batteries. These devices use suspension electrodes with three main functional components: (1) ion-conducting electrolytic solution, (2) electron-conducting carbon black particles, and (3) solid-state electroactive particles. These suspensions are mixed-conducting, electrochemically active, and flowable. We recently utilized this approach with lithium-polysulfide solution electrodes [7] for which greatly enhanced electrochemical activity was realized by embedding a percolating network of conductive carbon nanoparticles in the solution, and without using the usual porous current collector. Although the

viscosity of the solution is naturally increased when it is converted into a suspension, analysis has shown that pumping losses are actually *decreased* compared to pumping of lower-viscosity solution through a typical porous flow-battery current-collector [7]. Several other active materials have been investigated for use in SSFCs, including  $\text{LiFePO}_4$  [8,9],  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [10,11], and Si [12]. This approach has also been extended to store charge with electrolytic capacitance on the surfaces of suspended carbon-black particles as an electrochemical flow capacitor [13].

A flow battery's power stack is designed to exchange charge between anodic and cathodic flow-electrodes that are pumped to and from storage tanks (Fig. 1). In a conventional flow battery, electrochemical reactions are confined to the region of flow electrodes spanned by current collectors. Because electronically insulating solution is pumped *through* a stationary, porous current-collector in those devices (Fig. 1c), electronic conductivity is strictly limited to the current collector [14]. However for SSFCs (Fig. 1a,b), both the electroactive material and electron-conducting network extend throughout the flow electrode, and in theory electrochemical reactions can occur in side zones (SZs) adjacent to metallic current collectors, that represent an extension of the electroactive zone (EAZ). Though the suspension itself can be thought of as a "embedded" current collector [7], in what follows we use current collector to denote the metallic films that connect suspension to external circuitry (i.e., its conventional usage in stationary batteries).

Flow batteries can have shunt currents between electrodes in a multilayer stack [15] that lead to efficiency losses, and which

\* Corresponding author. Tel.: +1 617 253 6048.

E-mail address: [ccarter@mit.edu](mailto:ccarter@mit.edu) (W. C. Carter).

<sup>1</sup> These authors contributed equally to this work.

<sup>2</sup> Present address: Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 105 S. Matthews Ave., Urbana, IL, 61801, USA.

<sup>3</sup> Present address: NanoScience Technology Center, University of Central Florida, Orlando, FL, 32826, USA.

## Nomenclature

### List of Acronyms

CCR	current-collector region
EAZ	electroactive zone
LTO	$\text{Li}_4\text{Ti}_5\text{O}_{12}$
SSFC	semi-solid flow cell
SZ	side zone

### List of Symbols

$A$	channel cross-sectional area, $\text{m}^2$
$c_{s,max}$	maximum concentration of intercalated Li in solid, mol/L
$\Delta t$	elapsed time, s
$F$	Faraday's constant, C/mol
$\gamma$	volumetric capacitance of electroactive material, $\text{F}/\text{m}^3$
$H$	SZ heat generation, W-hr
$I$	applied current, A
$I_{SZ}$	SZ current, A
$L$	current collector length, m
$n$	C-rate pre-factor, 1/hr
$\phi_{cell}$	cell voltage, V
$\phi_{eq}$	equilibrium potential, V
$\bar{\phi}_{eq}$	average equilibrium potential, V
$\phi_p$	plateau voltage, V
$\phi_s$	solid-phase potential, V
$\phi_{s,0}$	initial SZ potential, V
$Q$	SZ capacity, A-hr
$\rho$	electroactive material volumetric loading fraction, -
$\rho_{s/cc}$	suspension/current-collector specific contact resistance, $\Omega\text{-m}^2$
$R_{SZ}$	SZ resistance, $\Omega$
$\sigma_{cc}$	current collector electronic conductivity, S/m
$\sigma_s$	suspension electronic conductivity, S/m
$t$	time, s
$x_{Li}$	intercalated-Li fraction, -

aredriven by total conductivity (i.e., the sum of electronic and ionic conductivity) [7] (Fig. 1b). Though shunt currents and EAZ extension both generate efficiency losses, these processes differ in two ways. EAZ extension can occur in a single flow electrode, while shunt currents occur between multiple electrodes that share flow pathways. Also, EAZ extension can occur only in flow electrodes that are mixed conducting (i.e., having simultaneous electronic and ionic conductivity), while shunt currents can occur in both electronically insulating solutions [16,17] and electronically conductive suspensions [7] (Fig. 1b,c). EAZ extension is a source of inefficiency because cell polarization is induced by the potential drop (between the SZ and the region between current collectors) that drives electrochemical reactions in SZs. But as we show later, the capacity that is (dis) charged from SZs can be controlled. In particular, we use the dependence of SZ capacity on operational, design, and material parameters to inform the design of suspensions and cell architectures that mitigate efficiency losses. We note that carbon-black suspensions have previously been polarized in other cell geometries, and enhanced capacitance relative to graphite slurries was attributed to electroactive surface area [18]. If suspensions have finite electronic conductivity, suspension far from the polarizing electrode will not be electroactive. To our knowledge no systematic study has quantified the spatial extent of the electroactive zone and how the electroactive zone's size is affected by the electronic conductivity of suspensions.

Flow *itself* can reduce efficiency below the values expected from conventional batteries (i.e., those not designed to flow). In

particular, mechanical energy is required to pump suspension that results in round-trip inefficiency [6,19]. Also, the particular flow-mode employed [7,20] (e.g., continuous or intermittent, pulsed flow) and velocity-profile shape [9,20] affect electrochemical efficiency, and general strategies have been predicted to minimize inefficiencies due to these mechanisms [20]. In this work, inefficiencies due to EAZ extension were isolated from the effects of bulk flow by cycling under conditions where the suspension electrode was stationary. This is not simply an idealized configuration; it also reflects one preferred mode of SSFC operation (called the intermittent mode) in which the suspension is rapidly injected into the region between current collectors (termed the current-collector region or CCR), and then held stationary while being electrochemically (dis) charged.

Slurries have been used in electrochemical systems for a variety of purposes in the past, including in zinc/air batteries [21–23], copper etching and recovery [24], coal oxidation [25], electrocatalysis [26], photoelectrochemical cells [27], and capacitive deionization [28]. The properties of these various slurries are not the same. In particular, zinc/air slurries contain suspended zinc particles that do not form an electronically conductive network. As a result, stationary, meshed current-collectors have been used to increase the effective area in contact with the slurry [22], and zinc slurries have been fluidized with liquid electrolyte to increase reaction rates [23]. In contrast, carbon black slurries (which is the class of slurries that the present semi-solid suspensions belong to) exhibit a connected three-dimensional structure that enables electron transfer throughout the entire slurry [7,24]. Under stirred or flowing conditions these suspensions transition from a network with persistent contact among particles and between particles and current collectors to a regime of intermittent contact [10,29–31]. The present study is restricted to non-flowing conditions where semi-solid suspensions exhibit persistent contact.

In this paper, we used a semi-solid flow cell-configuration with a non-aqueous,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -carbon suspension as a model system to study EAZ extension. A polymer flow-cell body with a metallized conductor of variable length was used to quantify the scaling of SZ capacity with current-collector length under various electrochemical operating conditions. We show that EAZ extension proceeds according to two distinct modes, as though either a potentiostat or galvanostat were placed at the SZ's edge. We used a simple analytical model to quantify the scaling of energy losses with associated driving forces and present strategies to minimize energy losses resulting from EAZ extension.

The paper is organized as follows. Section 2 describes the cell design, materials, and computational model. Section 3.1 compares experimental and simulated results to elucidate the charge transfer processes that drive EAZ extension. Section 3.2 shows the variation of SZ capacity as a function of cycling conditions and current-collector lengths. Section 3.3 demonstrates the existence of passive and active modes of EAZ extension. Section 3.4 introduces analytical models for energy-loss scaling and presents mitigation strategies for EAZ extension.

## 2. Methodology

### 2.1. Cell Design

EAZ extension results in a measured capacity that differs from the theoretical capacity between the current collectors by the capacity of the two SZs at the terminating ends. We experimentally varied the current-collector lengths ( $L_{cc}$  = 6, 12, 24, 36, and 47 mm) and cycled the cells at several C-rates (C/5.5, C/11 and C/22), the capacity by which C-rate is defined being the theoretical capacity between the current collectors (i.e., in the CCR). The experimental setup is shown in Fig. 2. We note that the geometry of the inlets

Download English Version:

<https://daneshyari.com/en/article/185086>

Download Persian Version:

<https://daneshyari.com/article/185086>

[Daneshyari.com](https://daneshyari.com)