



# Effect of surface transport properties on the performance of carbon plastic electrodes for flow battery applications



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## ABSTRACT

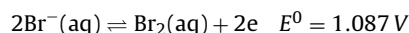
Due to their high electrical conductivity and corrosion resistance, carbon nanotube (MWNT)-high density polyethylene (HDPE) composites are potential candidates to replace traditional activated carbon electrodes for the next generation of fuel-cells, super capacitors and flow batteries. Electrochemical impedance spectroscopy (EIS) is employed to separate the surface conduction from bulk conduction in 15% HDPE-MWNT and 19% carbon black (CB)-HDPE composites for zinc-bromine flow battery electrodes. While exhibiting superior bulk conductivity, the interfacial conductivity of MWNT-filled composites is lower than that of CB-filled composites. High resolution conductive atomic force microscopy (C-AFM) imaging and current-voltage (I-V) spectroscopy were employed to investigate the sub-surface electronic transport of the composite. Unlike the CB-composite, the fraction of conducting MWNTs near the surface is very low compared to their volume fraction. In addition, the non-linear I-V curves reveal the presence of a tunneling junction between the tip and the polymer-coated MWNTs. The tunneling resistance is as high as 1 GΩ, which strongly affects the electronic/electrochemical transfer at the interface of the electrolyte and the surface of the composite, which is evident in the voltammetric and EIS observations.

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## 1. Introduction

With the growing desire of governments to increase the fraction of electricity supplied from renewable sources, there is an increasing concern over the ability to manage intermittency from sources such as wind and solar power. The use of large scale, grid-connected energy storage is seen as a potential solution to this problem, if storage costs can be reduced. Of the multitude of potential storage solutions [1], batteries have received the most attention, and flow batteries in particular have great promise. Flow batteries operate by flowing an electrolyte over electrodes that remain chemically unchanged during the charge and discharge cycles. The most well known and developed of the flow batteries is the vanadium redox battery [2], in which the multiple oxidation states of vanadium are used for both analyte and catholyte. One of the advantages of pure flow batteries is that their capacity is only limited by the volume of stored electrolyte. However the vanadium redox battery suffers from low specific energy and specific power [3] and the stability of

the electrolyte at elevated temperatures is also of concern [4]. The zinc-bromine battery is also a flow battery, but differs in that during charge, zinc metal is plated on the anode, and bromine is generated at the cathode, resulting in a maximum charge/discharge capacity according to the mass of zinc deposited during charge. The half-cell reactions are:



Each cell is composed of two electrode surfaces and two electrolyte flow streams separated by a microporous membrane. The electrochemical reactions take place in a system, which includes cell stack, electrolyte storage tank and electrolyte circulation system. During charge, elemental bromine is formed at the positive electrode while zinc is deposited at the negative electrode. During discharge, zinc and bromide ions are formed at the respective electrodes. The microporous separator between the electrode surfaces impedes diffusion of bromine to the zinc deposit, which reduces direct chemical reaction and the associated self-discharge of the cell. Because of the corrosive nature of bromine, the electrodes are generally constructed using polymeric materials such as high-density polyethylene (HDPE) made conductive through the use of carbon black (CB) [5], or more recently, multi-walled carbon

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nanotubes (MWNT). As the overpotential of the bromine reaction on carbon-filled plastic (CP) is higher than on carbon [6] a high surface area carbon is usually bonded to the carbon plastic substrate on the positive (bromine) electrode. The zinc-bromine battery has undergone major development, characterization, and field testing efforts, and is now commercially available from at least two manufactures. There is a general consensus that the technology is suitable for some utility applications, particularly load-levelling and other applications requiring high efficiency and high energy density. These applications also require longer lifetimes from the electrode materials. The aim of this study is to understand the electrical properties of these CP electrodes in the zinc-bromine battery environment. We measure surface conductivity using atomic force microscopy (C-AFM) to analyse the conductivity at the micron scale and sub-surface conduction using I-V curves. Additionally we use electrochemical impedance spectroscopy (EIS) and cyclic voltammetry to understand the effect of surface conductivity on the electrochemical properties of the composite samples. We demonstrate that a combination of techniques reveals the cause of unexpected electrochemical behavior, and that C-AFM can explain the origins of the observed bulk behavior.

## 2. Materials & Methods

Carbon electrodes for zinc-bromine batteries have been based on carbon-filled polyethylene, because of their durability [7,8]. The electrodes were manufactured using methods described by Bolstad and Miles [9], and Cathro [10]. Two composite materials have been studied - high density polyethylene admixed with carbon black (HDPE-CB) and high density polyethylene admixed with multiwalled carbon nanotubes (HDPE-MWNT).

### 2.1. HDPE-CB

This material is made via extrusion of a mixture of high density polyethylene, with carbon black (CB - Ketjen Black), fumed silica and glass fiber as described by Arnold [8]. The composite electrode contains (19%) of carbon black (CB), 16% glass fiber and 1% of fumed silica. Electrode samples were made by heat pressing the composite to a thickness of 1.0 mm.

### 2.2. HDPE-MWNT

This material was provided by Redflow and consists of HDPE with ~15% multiwalled carbon nanotubes. Electrodes were produced via compression molding of the pre-compounded pellets into sheets of approximately 1.0 mm thickness.

### 2.3. Electrochemical Analysis

Electrochemical analyses were undertaken in an electrolyte of composition 2.25 M ZnBr<sub>2</sub>, 0.5 M ZnCl<sub>2</sub>, 0.8 M N-ethyl N-methyl pyrrolidinium bromide (MEP) as bromine sequestering agent [11]. HDPE-carbon and platinum electrodes were tested using cyclic voltammetry and electrochemical impedance spectroscopy. Cyclic voltammetry was carried out using a Voltalab 50 instrument, with a platinum wire auxiliary electrode and a silver-silver chloride (Ag/AgCl) reference electrode. The electrochemical impedance of each electrode was measured using an electrochemical analyser (Bio-logic Science SP-300 instrument, Grenoble, France) and assembled in an Inphaze 3-terminal cell (Inphaze Pty Ltd, Australia). A sinusoidal excitation voltage of 5 mV was swept across a frequency range of 1 Hz to 4 MHz, superimposed on a potentiostatic bias of -0.95 V or -1 V vs a Ag/AgCl reference electrode. Zplot and Zview software (Scribner Associates, North Carolina, USA)

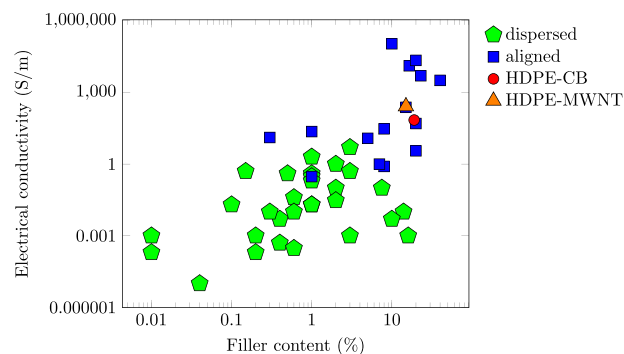


Fig. 1. Measured electrical conductivity of composite electrodes

were used to construct Bode and Nyquist plots as well as fit the impedance data to simplified electrical equivalent models.

XPS spectra were obtained for both composite materials using an Escalab 250Xi photoelectron spectrometer with a monochromated Al K $\alpha$  energy of 1486.68 eV.

### 2.4. Bulk Conduction

The macroscopic electrical conductivity measurements were carried out using the Van Der Pauw (VDP) 4 wires method [12]. Copper wires were used as the contacting electrode and silver paint was used to improve the electrical contact with the composite surface. The contacts were found to be Ohmic (the I–V curves were linear) and thus the Van Der Pauw/Hall-effect analysis can be used.

## 3. Results

### 3.1. Bulk Conduction by macroscopic Hall-effect measurements

The results show that despite the lower volume content of MWNTs (15%), the MWNT-based filler composite presents the highest electrical conductivity of 260 S/m. This value is four times higher than the electrical conductivity of the CB-composite (~70 S/m). The reasons behind the enhanced conductivity of MWNT-composite with respect to the CB-composite are mainly 1) the high intrinsic electrical conductivity of MWNTs, that can reach 10<sup>7</sup>–10<sup>8</sup> S/m, 2) in dispersed MWNT-polymer composites, the high conduction is often attributed to low tunneling junction resistance at point contacts between the MWNTs, 3) from CS-AFM images one can see a certain alignment of MWNTs, probably due to the manufacturing process and 4) the low percolation threshold. Indeed, because of the high aspect ratio of MWNTs, the percolation threshold (the minimum volume fraction of fillers necessary to form a continuous current path within the composite) is low (even lower than 0.01%). However, for spherical fillers (or in the case of CB nanoparticles), the percolation threshold is higher, ~15%.

In Fig. 1 we report the state of the art of the electrical conductivity in case of aligned and unaligned (dispersed) MWNT-polymer composites. The value of electrical conductivity of the compression molded HDPE-MWNT samples here is higher than what is reported in the case of dispersed MWNT-composites.

### 3.2. Electrochemical measurements

On the basis that the bulk conductivity of the MWNT composite is greater than the CB composite, it would be expected that electrochemical deposition of zinc would be facilitated on the former. This was studied using cyclic voltammetry at 100 mV/s in a 2.25 M ZnBr<sub>2</sub>, 0.5 M ZnCl<sub>2</sub> and 0.8 M MEP zinc-bromide electrolyte. The results are shown in Fig. 2.

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