



A study of different carbon composite materials for the negative half-cell reaction of the zinc cerium hybrid redox flow cell



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ABSTRACT

An investigation into the suitability of several carbon composites materials as substrates for the negative electrode in the zinc–cerium redox flow cell has been carried out. The zinc deposition process was carried out in a methanesulfonic acid electrolyte over the temperature range between 25 °C and 60 °C. Elevated temperatures increased the kinetics of the zinc deposition and dissolution reactions and also shifted the onset (nucleation) potential at more positive values. Galvanostatic charge/discharge cycles were performed in order to test the performance of these composite materials under a variety of operating conditions. For all the materials, the highest charge/discharge coulombic efficiencies (~95%) were found at elevated temperatures. Yet, the voltage efficiencies were found to be higher at lower temperatures (viz. 25 °C). Increased methanesulfonic acid concentrations promoted the hydrogen evolution reaction which in turn led to lower coulombic efficiencies. Three of the composite carbon materials tested (viz. PVE, PVDF, HDPE-1) were found to be robust with no surface deterioration or loss in efficiency observed over 250 cycles. Scanning electron microscopy revealed the formation of zinc clusters/grains on all the substrates tested whilst dendritic and granular growth was also present on some of the carbon samples.

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1. Introduction

Energy storage is the most dominant factor in economic development with the widespread use of chemical fuels like gasoline and natural gas. In the majority of the developed countries, excess power generation and transmission are underused every year due to insufficient energy storage leading to problems like reduced reliability, raised volatility in prices, and threatened security [1]. Currently for large energy storage applications, only pumped hydro and compressed gas are cost effective. Pumped storage hydro-electricity is the largest type of grid energy storage available and constitutes more than 99% of bulk storage worldwide [2]. However, these technologies are limited by geography and are not flexible [3].

One alternative technology for grid-scale storage is large-scale flow batteries. The electrochemical energy storage devices such as solid state batteries, supercapacitors and flow batteries are amongst the leading electricity energy storage (EES) technologies for the future because of their lower operating cost, flexibility and scale-ability. These relatively new technologies are able to store

large quantities of energy and have the potential to increase the flexibility of power systems and improve the response to the rising demand in energy as well as minimizing environmental damage. The energy density of the flow battery can be determined independently of the battery power because it is related to the electrolyte concentration and volume whereas the power output is related to the reactor size. Various classes of flow battery systems exist including the classic redox flow battery (RFB), in which all electroactive species are dissolved in the electrolyte. These batteries do not require any special terrain and compared to the conventional batteries (Pb–acid) they are easier and less costly to maintain. The discharge time of a RFB at full power can be varied, as required, from several minutes to many days.

Early research on the redox flow battery (RFB) was carried out in the 1970s by the National Aeronautics and Space Administration (NASA) [4] and the Energy Development Associates (EDA) [5]. Since then, numerous other redox flow battery technologies have been developed, such as the all vanadium battery [6,7], the soluble lead–acid [8,9], the zinc–cerium [10], the zinc–nickel [11], the cadmium–chloranil [12], the vanadium–cerium [13] the zinc–air [14] and the copper–lead dioxide [15] systems.

The zinc/cerium cell is a new redox flow technology that has been developed in the last decade [16–19]. Its great advantage is its high open circuit cell voltage ($E_{cell} = 2.4$ V). This high cell potential (c.f. 1.4 V for the all-vanadium battery open circuit voltage)

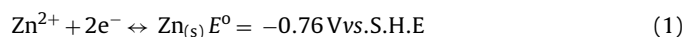
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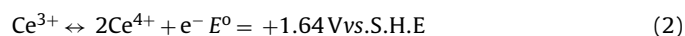
Table 1
Properties of carbon composite materials used in the study.

Electrode	Comment	Supplier
BMA5 (PVDF)	Polyvinylidene difluoride, 3–5 mm thickness Thermal conductivity through plane: $20 \text{ W m}^{-1} \text{ K}^{-1}$ Permeability coefficient: $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ Bulk density: 2.1 g m^{-3}	SGL Carbon GmbH [27]
PE20	20 w% Polyvinylidene difluoride, cured, 1 mm thickness Thermal conductivity through plane: $14 \text{ W m}^{-1} \text{ K}^{-1}$ Permeability coefficient: $7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ Bulk density: 1.85 g m^{-3}	SGL Carbon GmbH [27]
Entegris (PVE)	Polyvinyl ester, 3–5 mm thickness Thermal conductivity through plane: $18.5 \text{ W m}^{-1} \text{ K}^{-1}$ Specific heat through plane: $8 \times 10^{-1} \text{ J g}^{-1} \text{ K}^{-1}$	Entegris Inc. [28]
HDPE-1	Uncured high density polyethylene, 1 mm thickness Thermal conductivity through plane: $20 \text{ W m}^{-1} \text{ K}^{-1}$ Permeability coefficient: $8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ Bulk density: 1.97 g m^{-3}	SGL Carbon GmbH [27]
HDPE-2 BAC2	High density polyethylene, 3–5 mm thickness Conductive polymer–acid–cure version (10–20% carbon)	GE Bac2 Ltd. [29]
Glassy carbon	3–5 mm thickness Non-graphitizing carbon, 3–5 mm thickness Density: 1.45 g m^{-3}	Alfa Aesar

has naturally a direct impact on the amount of power that can be delivered at a specified current density. The energy density of the system is reported to be between 20 Wh L^{-1} and 41 Wh L^{-1} [10] $\{8 \times 10^{-1} \text{ mol dm}^{-3} \text{ Ce(III) carbonate assuming a potential of } 2.4 \text{ V will give } (96485 \times 2.4) \times 0.8/3600 = 51.45 \text{ Wh L}^{-1} \times 0.8 \text{ (viz. at } 80\% \text{ discharge)} = 41.17 \text{ Wh L}^{-1}\}$. The flow cell in its basic form consists of a single cell pair with a cation exchange membrane separating the anode and the cathode. During the charge–discharge cycle of the zinc–cerium flow cell the electrodeposition of zinc takes place at the negative side:



The positive half-cell reaction is:



Methanesulfonic acid (MSA) is used as the supporting electrolyte, as it allows zinc electroactive species to dissolve in concentration larger than 2.0 mol dm^{-3} . The solubility of Ce(III) in MSA is 10 times greater than in sulfuric acid [20]. Methanesulfonic acid has also been reported to minimise the decomposition of water into hydrogen and oxygen while also helping with the zinc deposition process [21]. Furthermore, the use of this organic acid as the background electrolyte is sustainable as it is less harmful to the environment than other acids used in flow batteries such as sulfuric acid due to its low vapour pressure, absence of volatile organic compounds, low oxygen demand for degradation. MSA is favoured in this particular application, as zinc dendrites can be suppressed and so avoid potential short circuit during zinc electrodeposition [22].

In this paper, we concentrate solely on the negative electrode side of the zinc–cerium RFB cell. The zinc deposition and dissolution reactions are investigated on a number of carbon electrodes through cyclic voltammetry, steady state and rotating disk electrode studies and galvanostatic charge–discharge cycles. Parameters such as temperature, flow velocity, zinc and acid concentrations were varied and their impact on the performance of the zinc deposition/dissolution process at the carbon composite electrodes examined.

2. Experimental

The carbon composite samples used for the zinc half-cell reaction are listed in Table 1. Apart from the glassy carbon electrode,

the remainder of the composite materials were manufactured using thermoplastic (polyvinylidene difluoride: PVDF, high density polyethylene: HDPE) or thermosetting resins (epoxies and vinyl esters: PVE). A detailed study on the effect of vinyl ester resins on expanded graphite has been given by Fu [23] while the electrical properties of the polyvinylidene difluoride were investigated by Cunningham [24], Del Rio [25] and Chunhui [26]. The key material properties of such electrodes include chemical resistance, electrical conductivity, compactness and also mechanical strength. The electrical resistance of the carbon composite materials was reported to be between $5.0 \times 10^{-1} \Omega \text{ cm}$ and $8.0 \times 10^{-1} \Omega \text{ cm}$ [27–29].

For the electrochemical studies, these materials were cut into cylinders of suitable diameter (7 mm \rightarrow surface area = 0.38 cm^2) which could be mounted using electrically conducting paint (silver conducting paint (RS 186–36000) onto an Oxford Electrodes® rotating disc electrode set up and sealed with a glue resin (Loctite 3430 A&B Hysol®) so as to prevent any unwanted contact of the solution with the support. The carbon materials were at the same level as the electrode support creating an infinite flat surface. The surface of the carbon composites was rinsed with ethanol prior to use and dried in an air stream. Care was also taken to ensure that the samples did not suffer any mechanical damage to the exposed surface.

The glassy carbon electrode was used for comparing the electrochemical behaviour with those from the composite materials (viz. galvanic cycles and zinc deposit morphologies). A standard 3-electrode configuration was employed with a platinum gauze acting as the counter electrode, while the reference electrode was a Hg|Hg₂SO₄|K₂SO₄ (sat.) (Russell pH Ltd.). This has a standard potential of 0.64 V vs. S.H.E. The electrolyte was contained in a jacketed cell which enabled its temperature to be controlled ($\pm 1^\circ \text{C}$) by means of a thermostated water bath (Gallenkamp thermostirrer 95). All solutions were prepared using Milli-Q deionised water (resistivity $18.2 \text{ M}\Omega \text{ cm}$) using methanesulfonic acid (70%, BASF) and ZnO (99.5%, Fisher Chemicals).

The cyclic voltammograms and galvanic cycles were carried out using either an EG & G M100A Potentiostat/Galvanostat controlled by custom written software in LabVIEW or the 1286 Electrochemical Interface, Solatron Instruments, Schlumberger Ltd., controlled by the Corrware® software (Corrware electrochemistry, Schriber Associates, Inc. [30]). Both systems were also employed for examining charge and discharge efficiencies for the zinc half-cell reaction. The morphology of the zinc electrodeposits was

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