



Mass transport and active area of porous Pt/Ti electrodes for the Zn-Ce redox flow battery determined from limiting current measurements[☆]



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ABSTRACT

The conversion of soluble cerium redox species in the zinc-cerium redox flow battery and other electrochemical processes can be carried out at planar and porous platinised titanium electrodes. The active area, current density, mass transfer coefficient and linear electrolyte flow velocity through these structures have a direct influence on the reaction yield and the relationship between cell potential and operational current density during charge and discharge of a flow battery. A quantitative and practical characterization of the reaction environment at these electrodes is required. The volumetric mass transfer coefficient, $k_m A_e$ has been calculated for diverse electrode structures from limiting current measurements for Ce(IV) ion reduction in a laboratory, rectangular channel flow cell. This factor can be used to predict fractional conversion and required electrode dimensions. Platinised titanium felt shows superior $k_m A_e$ values compared to other materials and is a practical, high performance electrode for the Ce(III)/Ce(IV) ion redox reaction.

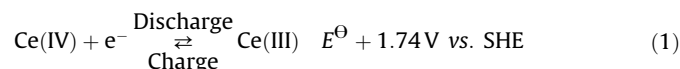
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1. Introduction

The zinc-cerium redox flow battery (Zn-Ce RFB) has been the subject of continuous development over the past decade; its progress and research challenges have been recently reviewed [1,2]. Its main advantages are a higher standard cell potential (2.48 V) and lower electrolyte toxicity than all-vanadium or Zn-Br₂ RFBs. Diverse electrode materials have been studied for both positive [3,4] and negative [5,6] electrode reactions as well as alternative electrolyte compositions [7–10]. The inhibition of hydrogen evolution as a secondary reaction, or via open-circuit corrosion, at the zinc negative electrode by electrolyte additives has also been considered [11]. In previous work [12], we have shown the contribution of thermodynamic, kinetic and ohmic components to the cell potential losses in the Zn-Ce RFB, evaluating the effect of electrolyte conductivity and interelectrode gap. Other cerium-based RFBs have been proposed, including: a Ce-Ce concentration cell [13], an undivided Zn-Ce RFB [7,14], a V-Ce

RFB [15–19], a borohydride-Ce fuel cell [20], a Pb-Ce RFB [21] and a H₂-Ce fuel cell [22–24].

Cerium-based RFBs involve reduction of Ce(IV) ions at the positive electrode during discharge, usually in aqueous methanesulfonic acid (MSA), with the reverse process during charge:



Platinised titanium (Pt/Ti) is a suitable electrode material for this reaction due to its catalytic activity for cerium conversion together with its stability to highly oxidising Ce(IV) ions [1]. The positive electrode also supports the oxygen evolution reaction (OER) as a secondary reaction, mainly during anodic Ce(III) oxidation:



This results in a lower current efficiency for reaction (1), especially at high current densities on planar electrodes or under low mass transport conditions. Porous, 3-D electrodes can reduce these limitations by decreasing the local current density and increasing the mass transport rate of Ce(IV) ions to the electrode surface. Enhanced electrolyte flow through these materials also helps prevent electrode shielding by gas bubbles and ohmic losses

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Nomenclature

List of symbols

a	Empirical constant in equation (7)
a'	Empirical constant in equation (11) (s^{-1})
A	Electrode geometrical area (cm^2)
A_e	Electrode area per unit electrode volume (cm^{-1})
A_x	Cross-sectional area of electrode ($A_x = BS$) (cm^2)
b	Empirical constant in equation (7)
b'	Empirical constant in equation (11)
B	Breadth of rectangular flow channel (cm)
c	Reactant concentration ($mol\ cm^{-3}$)
d_e	Equivalent diameter of a rectangular flow channel (cm)
D	Diffusion coefficient of an aqueous species ($cm^2\ s^{-1}$)
E	Electrode potential vs. a reference electrode (V)
E_{cell}	Cell potential (V)
F	Faraday constant ($C\ mol^{-1}$)
I	Current (A)
I_L	Limiting current due to convective-diffusion (A)
I_L'	Limiting current due to convective-diffusion at planar electrode (A)
j	Current density ($A\ cm^{-2}$)
k_m	Mass transport coefficient ($cm\ s^{-1}$)
$k_m A_e$	Volumetric mass transport coefficient (s^{-1})
L	Length of rectangular flow channel (cm)
n	Amount of an electroactive species (mol)
q	Electrical charge (C)
Q	Volumetric flow rate of electrolyte ($cm^3\ s^{-1}$)
R	Electrical resistance (Ω)
R_A	Area resistance ($\Omega\ cm^2$)
S	Channel separation between electrode and membrane (cm)
t	Time (s)
T	Temperature (K)
v	Mean linear flow velocity of electrolyte ($cm\ s^{-1}$)
V_e	Overall volume of electrode (cm^3)
z	Electron stoichiometry (Dimensionless)

Greek letters

β	Limiting current enhancement factor in equation (13) (Dimensionless)
γ	Aspect ratio of flow channel (Dimensionless)
γ'	Mass transport enhancement factor (Dimensionless)
ν	Kinematic viscosity of the electrolyte ($cm^2\ s^{-1}$)
ε	Volumetric porosity (Dimensionless)
ρ	Fluid density ($g\ cm^{-3}$)

Dimensionless groups

Le	Dimensionless length of a flow channel (Dimensionless)
Re	Reynolds number (Dimensionless)
Sc	Schmidt number (Dimensionless)
Sh	Sherwood number (Dimensionless)

due to gas voidage in the electrolyte. The extended surface area of porous electrodes enables a faster conversion rate of active species.

Despite the common use of Pt/Ti mesh in cerium-based RFBs and other electrochemical reactors, no quantitative or comparative studies have been undertaken on the reaction environment at diverse Pt/Ti electrode structures for cerium ions. Here, the quantitative performance of such Pt/Ti porous electrode materials

is expressed as the volumetric mass transport coefficient $k_m A_e$ (the product of mass transport coefficient and electroactive volumetric electrode area) derived from dimensionless group analysis as a function of the electrolyte flow rate and associated flow characteristics. Assuming plug-flow and convective-diffusion control, $k_m A_e$ allows the fractional conversion of the active species, X_A , to be predicted as well as the electrode dimensions and maximum operational current for an acceptable potential loss [25]. In this way, cost-effective materials can be found and further insight into the dynamic relationship between the operational cell potential, current density and the reaction environment at the different electrode materials/structures can be provided.

The performance factor $k_m A_e$ was determined from limiting current measurements for Ce(IV) ion reduction in half-cell experiments. Few studies have considered the experimental reaction environment in RFBs from the perspective of dimensionless group analysis, which can be an important step in the scale-up of electrochemical technology [26]. Such an approach allows laboratory and pilot-scale flow cells as well as different electrode materials (including carbon felt under different degrees of compression in all-V RFBs) to be compared. As discussed in a recent review [27], the performance of Pt/Ti electrodes is also important to diverse industrial electrochemical processes reliant on anodic generation of Ce(IV). Electrode optimization is desirable to increase space-time yield and minimize electrolyte material, electrolytic cell potential and energy consumption.

2. Theoretical Considerations

2.1. Cell geometry and flow expressions

The characteristics of a rectangular flow cell required for mass transport characterization include: equivalent (hydraulic) diameter, d_e dimensionless length group, Le and the aspect ratio of the channel, γ . These are defined as:

$$d_e = \frac{2A_x}{B + S} \quad (3)$$

$$Le = \frac{d_e}{L} \quad (4)$$

$$\gamma = \frac{S}{B} \quad (5)$$

where B , S and L are the breadth, span, and length of the channel, respectively, and A_x is the cross sectional area ($A_x = BS$). The relationship between the mean linear electrolyte flow velocity, v [$cm\ s^{-1}$] and the volumetric flow rate, Q [$cm^3\ s^{-1}$] through a rectangular channel of uniform volumetric porosity, ε and cross-sectional area, A_x is given by:

$$v = \frac{Q}{\varepsilon A_x} \quad (6)$$

2.2. Dimensionless group correlations

The mass transport characteristics in a uniform cross-section, rectangular channel electrochemical flow cell can be described by the dimensionless group correlation [25,28]:

$$Sh = aRe^b Sc^{1/3} \quad (7)$$

Sh is the Sherwood number, Re is the Reynolds number, Sc is the Schmidt number and a and b are empirical constants. These

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