Ruthenium based redox flow battery for solar energy storage

Mohammed Harun Chakrabarti [a,*], Edward Pelham Lindfield Roberts [b], Chulheung Bae [b,1], Muhammad Saleem [c]

[a] Department of Chemical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia
[b] School of Chemical Engineering and Analytical Science, University of Manchester, Sackville Street, Manchester M60 1QD, UK
[c] KANUPP Institute of Nuclear Power Engineering, KNPC, P.O. Box 3183, Karachi 75400, Pakistan

ARTICLE INFO

ABSTRACT

The technical performance for the operation of a stand alone redox flow battery system for solar energy storage is presented. An undivided reactor configuration has been employed along with porous graphite felt electrodes and ruthenium acetylacetonate as electrolyte in acetonitrile solvent. Limiting current densities are determined for concentrations of 0.02 M and 0.1 M ruthenium acetylacetonate. Based on these, operating conditions for 0.02 M ruthenium acetylacetonate are determined as charging current density of 7 mA/cm^2, charge electrolyte superficial velocity of 0.0072 cm/s (through the porous electrodes), discharge current density of 2 mA/cm^2 and discharge electrolyte superficial velocity of 0.0045 cm/s. An optimum power output of 35 mW is also obtained upon discharge at 2.1 mA/cm^2. With an increase in the concentration of ruthenium species from 0.02 M to 0.1 M, the current densities and power output are higher by a factor of five approximately (at same superficial velocities) due to higher mass transport phenomenon.

Moreover at 0.02 M concentration the voltage efficiency is better for battery full of electrolytes prior to charging (52.1%) in comparison to an empty battery (40.5%) due to better mass transport phenomenon. Voltage efficiencies are higher as expected at concentrations of 0.1 M ruthenium acetylacetonate (55% when battery is full of electrolytes and 48% when empty) showing that the all-ruthenium redox flow battery has some promise for future applications in solar energy storage. Some improvements for the system are also discussed briefly.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Utility scale energy storage is of vital importance for the smooth running of the world economy. Grid scale load levelling for instance accounts between 10 MJ and 200 GJ of energy storage capacity [1]. In addition, off-grid applications such as solar or wind energy are also important because approximately 2 billion people worldwide live without electricity [1]. Hence, such energy storage devices that can store the intermittent supply of renewable energy and deliver on demand would be considered essential. Amongst a range of different technologies evaluated the redox flow battery has a strong opportunity to make a difference in the world's energy economy [1,2].

In Pakistan the local renewable energy resources are not harnessed efficiently resulting in the import of fossil fuels to cover almost all the energy requirements of the country. In addition a significant part of Pakistan lies in an arid to semi-arid region thus

being exposed to much sunshine throughout the year [3]. Solar cells are available in some parts of the country to try and harness solar energy but ineffective energy storage devices limit the application of photovoltaics to a bare minimum. Hence an efficient energy storage technology such as the redox flow battery can go far in increasing the relevance of solar energy for a country like Pakistan [4]. The significance of such work can be of benefit for other developing countries that may wish to harness renewable energy sources for storage and conversion to grid scale electricity.

The basic technology behind a redox flow battery is its ability to transform and store electrical energy as chemical energy and release it in a controlled fashion upon demand [2]. It is inherently different from other batteries in that the energy is stored in the electrolytes in contrast to energy storage in electrodes in conventional batteries. Hence, it has relatively low energy requirements for production and transportation and better efficiency than lead-acid or nickel–cadmium batteries for instance [5,6]. In fact, it has a much higher lifetime and cycle of operation than supercapacitors and other secondary batteries [7]. However, it has disadvantages associated with it such as low energy density [8,9] and high capital cost due to the extensive use of ion-exchange separators [10,11]. The estimated price of different redox flow battery technologies

* Corresponding author. Tel.: +60 37967 5206; fax: +60 37967 5319.
E-mail address: mohammedharun@um.edu.my (M.H. Chakrabarti).
[1] Present address: Energy Storage and Research, Ford Motor Company, MI 48120, USA.

Nomenclature

a	specific surface area per unit volume of electrode (m^2/m^3)
A	electrode projected area (cm^2)
C	concentration (mol/cm^3)
CE	counter electrode
C_{out}	outlet concentration (mol/cm^3)
C_0^∞	initial concentration (mol/cm^3)
Cd	cadmium
CH_3SO_3H	methanesulfonic acid
Cu	copper
E_{ch}	average battery potential during charging (V)
E_{dis}	average battery potential during discharge (V)
F	Faraday's constant (96,485 C/mol)
H_2SO_4	sulphuric acid
i	current density (A/cm^2)
i_L	limiting current density (A/cm^2)
I	current (A)
I_{ch}	constant charging current (A)
I_{dis}	constant discharging current (A)
k_m	mass transport coefficient (cm/s)

l	thickness of the porous electrode (cm)
n	number of electrons transferred per mole of reactants
P	power output of the electrochemical battery (W)
Pb	lead
PbO_2	lead oxide
Q	volumetric flow rate of electrolyte through each electrode (cm^3/s)
R	resistance (Ω)
R.E	reference electrode
$Ru(acac)_3$	ruthenium acetylacetonate
t	time (s)
t_{ch}	total time for charging electrolytes (s)
t_{dis}	total time for discharging electrolytes (s)
$TEABF_4$	tetraethyl ammonium tetrafluoroborate
u	mean linear flow velocity approaching the electrode (cm/s)
UPVC	unplasticized polyvinyl chloride
V	total volume of electrolyte reacted (m^3)
WE	working electrode
ϕ_V	voltage efficiency (%)

---

are comparable and lie in the range \$110–320 per kW h and \$1100–4500 per kW [8]. A redox flow battery must not be mistaken with a reversible fuel battery, which is used to either produce electricity from hydrogen fuel or vice versa [8].

Due to the high capital cost associated with ion-exchange separators and possible problems due to cross contamination [12], the need for an undivided flow through configuration arose [13]. Flow through redox systems have been gaining popularity mainly since the last decade [14–22]. Among them, the Pb–PbO_2–CH_3SO_3H, Cu–PbO_2–H_2SO_4 and Cd–chloranil systems were studied in some detail and reported to give high efficiencies for large numbers of charge/discharge cycles. However, a ruthenium based electrolyte proposed about 20 years back [23] has gone unstudied in the recent literature. It was reported to have low energy efficiencies using a divided flow by electrochemical reactor but some recent experiments using an H-type glass battery gave very good results [24]. Hence it required further investigation to verify its suitability for solar energy storage.

Previous studies have indicated the potential use of ruthenium acetylacetonate in a redox flow battery where the electrolyte can be mixed in the discharged state [24,25]. The main reason for selecting the ruthenium system is because it exhibits fast kinetics for both oxidation and reduction with no other solution species taking part in the electrochemical reaction [23]. Furthermore, ruthenium acetylacetonate has a relatively high solubility in acetonitrile, is commercially available and exhibits three redox states in solution [25] so that a single discharged species can be used. The purpose of this investigation is an attempt to determine suitable charging and discharging parameters of operation for the ruthenium based undivided redox flow battery for solar energy storage applications. Dilute concentrations are selected mainly to minimise costs (since the chemical is expensive [24]).

2. Materials and methods

The following subsections describe the equipment, chemicals and design of electrochemical reactor for redox flow battery purposes. The main chemical in use is $Ru(acac)_3$ and the instrumentation for the purposes of determining charge/discharge performance of the undivided redox flow battery reactor is also described in brief.

2.1. Reactor design

The undivided electrochemical reactor was designed using PTFE, stainless steel and silicone rubber gasket materials (Fig. 1). The approximate dimensions of the reactor were 18 cm × 14 cm × 7 cm. The void internal volume of the reactor was about 642 cm^3. As the organometallic chemicals and acetonitrile conventionally used for charge/discharge tests are corrosive to both UPVC and Perspex, PTFE was used as the main construction material. A porous graphite felt electrode (SIGRATHERM® GFA 10) was used having dimensions of 7 cm × 7 cm × 1 cm with an active (flow through) area of 5 cm × 5 cm. An expanded view of the reactor components is shown in Fig. 1 [10,13].

The stainless steel current feeder (3 mm thick) was insulated using 45 stopping off lacquer (H.S. Walsh and Sons) on the parts of its surface that were not in direct contact with the graphite felt electrode (Fig. 1). The graphite felt electrodes were attached to the current feeder using flow frames E and plastic bolts and nuts. A polypropylene retaining mesh was used as before to prevent electrical shorting and to provide better contact between the felt and the current feeder. A relatively large inter-electrode gap of 10 mm was needed for the incorporation of a PTFE block that was attached to the current feeder below the felt to prevent solution from flowing between the felt and the current feeder. This ensured optimum usage of the electrode flow area, but also increased the electrode gap. Although this meant that the resistance of the electrochemical reactor would increase, it also ensured a more uniform electrolyte flow. The current feeder had a flow window of 5 cm × 5 cm that was fitted with a stainless steel mesh. The porous electrode projected flow area was thus 25 cm^2. A vent was fitted at the top of frame D to enable release of any trapped or electro-generated gases. Flow calming regions were incorporated as shown in Fig. 2 to allow for laminar flow through the electrodes [13]. Once assembled, the electrochemical reactor was used as an undivided redox flow battery (Fig. 2).

2.2. Equipment and chemicals

Ruthenium acetylacetonate [$Ru(acac)_3$, 97% purity, Aldrich] was used for the preparation of the active organic electrolytes using acetonitrile as solvent (99.9% pure, Aldrich). Supporting electrolyte