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Temperature, charging current and state of charge effects on iron-vanadium flow batteries operation

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HIGHLIGHTS

- Temperature, charging current and SOC effect on Fe-V RFB operation.
- Optimum temperature at 42 °C.
- Optimum charging/discharging current at 50 mA cm^{-2}.
- V^{2+}/V^{3+} is rate determining; k = $0.8 \cdot 10^{-5}$ cm s^{-1} at 30 °C and E_{act} = 110 kJ mol^{-1}.
- V^{2+}/V^{3+} exhibits negative asymmetry form; charge transfer coefficient 0.13 at 52 °C.

ARTICLE INFO

ABSTRACT

Reliable and low cost energy storage technologies are required in order to store electrical energy on a large scale, as the power generated from intermittent renewable resources is continuously growing. Redox flow batteries are considered as a promising technology to lead a balanced solution for the future low emissions power sector challenges. The effect of temperature, charge/discharge current and state of charge on the performance of an iron-vanadium flow battery has been investigated in this study. VCl_3 and $FeCl_2$ in HCl(aq) electrolytes have been used for the anolyte and catholyte respectively, while graphite felt has been used for the electrodes. The results reveal an optimum operating temperature of ~47 °C and an optimum charging current of 50 mA cm^{-2} when the battery is in a state of charge between 20 and 80%. The calculated voltage and coulombic efficiencies were estimated to be ~85%. Under a mean linear flow velocity of ~40 cm s^{-1}, it has been found that the process is controlled by the sluggish kinetics of the V^{2+}/V^{3+} half-reaction. The kinetic constant has been calculated equal to $0.8 \cdot 10^{-5}$ cm s^{-1} at 30 °C and $4.5 \cdot 10^{-5}$ cm s^{-1} at 47 °C, resulting in an activation energy of ~110 kJ mol^{-1}. A model based on the exchange current density values and the state of charge, has been used to calculate the charge transfer coefficient. The latter was found to decrease with respect to temperature from 0.63 at 30 °C to 0.13 at 52 °C.

1. Introduction

Energy storage is currently considered one of the major bottlenecks for the commercial implementation of renewable energy sources. At the same time, energy storage is critical for tackling the inherent limitations of renewable resources intermittent nature, which makes their integration and dispatch challenging [1,2]. Hence, a low cost, flexible, reliable and scalable energy storage technology is required to ensure the continuity of energy supply at any time.

Therefore, the ability to store energy for long at a time could help to address the issue of over-generation from solar projects in areas with high direct normal irradiance (DNI). Moreover, efficient and high density electrical energy storage is crucial to sustain the power load over wider time periods and time scales. Typically, electricity can be stored during periods of low demand, and then dispatched during periods of peak demand to reduce the peak/off peak amplitude. Long duration batteries, like flow batteries are considered a suitable option for shifting power to later in the day or when needed [3,4].

In such scenarios, redox flow batteries (RFBs) with long life-span that exhibit high efficiency and sustainability for large scale energy storage, could effectively enhance the reliability of the power grid. In a flow battery, the electrolytes are circulated between the electrochemical cell, where they are separated by an ion exchange membrane and the associated storage tank. Here, electricity is converted to

chemical energy within these electrolytes, which are composed of free-floating charged metal ions dissolved in supporting electrolytes, in an electrochemical cell during charging and vice versa during discharging. The unique property of flow batteries is their ability to independently accommodate both energy and power capacity. In this context, the energy capacity is defined by the volume of the electrolyte stored in the tanks and the concentration of redox couple species, whereas the power rating is defined by the size of electrodes and the number of cells in a stack.

Currently, the all-vanadium redox flow battery (VRB) [5], the polysulphide/bromide battery (PSB) [6] and the zinc/bromine battery (ZnBr) [7]) systems have almost reached the demonstration and commercialization stages. In VRBs the vanadium ions are dissolved in an aqueous acidic supporting electrolyte. Since the first demonstration by Skyllas-Kazacos et al. [8] who developed the VRB using V^{2+}/V^{3+} and V^{4+}/V^{5+} redox couples, several studies have been contacted in order to further investigate the effect of various electrochemical, chemical and physical variables allowing the optimization of the related system operation parameters with low capacity [9–16]. On the other hand, it became almost inevitable to search for alternatives, i.e., the complete or partial replacement of the above system constituents due to the restrictions resulting from the low solubility and stability of vanadium ion in electrolytic solutions in addition to the unpredictability of the cost of the VRB systems, due to the relatively pricey vanadium-based electrolytes and the Nafion-based membranes [17–20]. Among other elements Fe, Cr and Zn have been proposed as replacements of V ion in flow batteries as a means for charge carrier and storage [21].

Along this course, the Fe/V redox flow battery has been also proposed as one potential candidate for low cost and long life battery for large scale energy storage. As a result the Fe/V redox flow battery has been the subject of a few theoretical [22] and experimental studies [23,24]. However, although these studies have added great values in understanding the electrochemical properties of the battery, however, the studies were mainly focused on the chemical and/or physical processes which are requisites for the development of cell/stack design [22,25–27]. This is also the case for the two ongoing studies [28,29], where efficiency, capacity and energy density were investigated at various temperatures. However, no studies have been published on the correlation between the performance/efficiency of the energy storage system and electrical measurements and the equilibrium kinetics under various states of charge (see Table 1).

In this study the effect of temperature, charging current and state of charge on iron-vanadium flow batteries operation has been investigated, due to their strong potential for practical application and commercialization in large scale energy storage systems. Battery charging and discharging experiments were conducted upon application of different currents in the range between 28 and 73 mA cm^{-2}, at temperatures from 30 °C up to 52 °C and under various states of charge. Furthermore, a method to estimate the kinetic constant and the charge transfer coefficient values, in absence of diffusion limitations, is proposed. The model is based on the kinetic rate expression of a two-way electrochemical reaction as a function of the concentration and reaction order and also, on the exchange current density values calculated by the polarization curves under various operating conditions of the battery system. It provides a means for estimating the kinetic constant and the charge transfer coefficient of the rate determining half-reaction utilizing the data generated at equilibrium conditions (I_o). The results can be used to optimize the performance of the Fe-V flow battery under various conditions.

2. Experimental

2.1. Experimental setup

The experimental bench scale setup, designed and fabricated in-house, is shown in Fig. 1. It is consisted of two electrolyte tanks, the electrochemical cell, the gas feed unit and the electrochemical analysis system.

Two concentric glass cylinders assembled with two Teflon taps, at the top and the bottom, have been used as jacketed tank for each electrolyte. Thermostated water is used in the outer chamber of the tank to adjust and maintain the temperature of the electrolytes, which flow in the internal tank chamber, to the desired level. The tanks were configured in order to prevent the unwilling oxidation of the reduced species (Fe or V) in the electrolytes by oxygen in air. A type-K thermocouple was installed in each tank to monitor the electrolyte's temperature. Both electrolyte solutions were pumped at an equal mean linear flow velocity past the electrode surface of ~40 cm s^{-1} to the corresponding sides of the electrochemical cell and then they were circulated back to the tanks. The above mentioned mean velocity has been selected in order to avoid mass transfer limitation phenomena at high temperatures.

A Teflon-frame electrochemical cell with two electrochemical-grade graphite rods (6 mm diameter) for the electrical connections has been designed and fabricated in the cell configuration to study the electrochemical behavior. The cell has been designed to host membrane-

Table 1
Used symbols.

Latin symbols	
I	Charging/discharging current
i	Charging/discharging current density
I_o	Exchange current
i_o	Exchange current density
J_{ch}, J_{dis}	Charging and discharging current used in differential voltage efficiency measurement
j_{ch}, j_{dis}	Charging and discharging current density used in differential voltage efficiency measurement
T	System temperature
SOC	State of charge
k^o	Kinetic constant
Q	Reaction quotient
E^{eq}	Open circuit voltage/voltage at equilibrium
E^o	Standard potential difference
η	Overpotential, E-OCV-IR
$\varepsilon_v, \varepsilon_c, \varepsilon_E$	Voltage, coulombic and energy efficiency
F	Faraday constant

Greek symbols	
α	Charge transfer coefficient
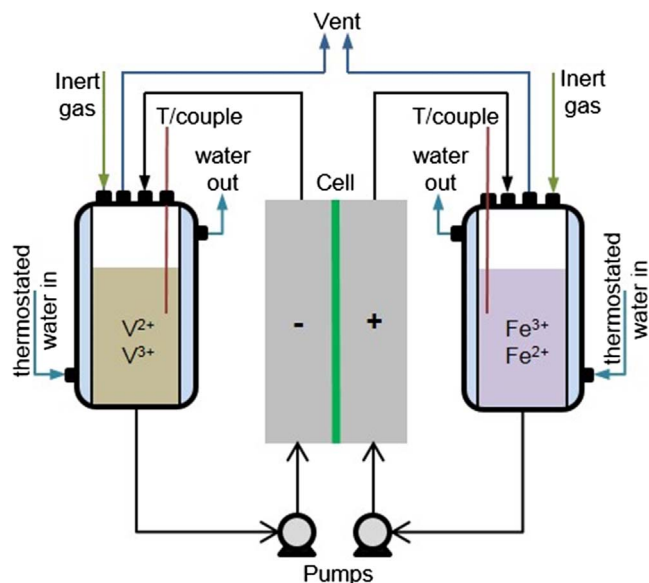
Fig. 1. Flow battery experimental setup.