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Sustainability of vanadium redox-flow batteries: Benchmarking electrolyte synthesis procedures

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ABSTRACT

This work focuses on the assessment, in terms of effectiveness, feasibility and sustainability, of three different procedures for the synthesis of vanadium-based mixed-acid electrolytes to be used in vanadium redox-flow batteries (VRFBs). Procedures considered consisted in: a) the mere mixing of suitable vanadium precursors (Electrolyte A); b) the chemical reduction of V_2O_5 by oxalic acid (Electrolyte B); c) the electrochemical reduction of V_2O_5 using a home-made “H-shaped” electrolysis cell (Electrolyte C). VRFB properties such as energy efficiency, mean charge–discharge voltages, cycle duration as well as stability and conductivity of the electrolyte were analysed and compared with the state-of-the-art. Experimental tests carried out on a laboratory scale VRFB battery comprised: thermal stability test, cyclic voltammetry, electrochemical impedance spectroscopy measurements and charge–discharge tests. A Life Cycle Assessment of the three electrolytes is also presented for benchmarking purposes.

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Introduction

The first Vanadium Redox Flow Battery (VRFB) was conceived in 1975 at the US National Aeronautics and Space Administration (NASA) [1,2]. Nowadays, redox flow battery is considered one of the most promising technologies as electrochemical energy storage system, due to independence of energy and power rating, fast response, ambient temperature operation, and extremely long life. In particular, VRFB has an additional advantage in that it does not suffer from permanent self-discharge thanks to the use of the same element in both cell compartments. VRFB possesses the proper

technology maturity for market uptake in the next years and several VRFB systems are already demonstrated all over the world [3–8].

Although VRFB is one of the more consolidated technologies among the flow type batteries, it has great margins of technological improvements and developments for the fabrication of short-term and long-term storage devices [9]. This technology possesses an extraordinary operational flexibility, as it is suitable to operate in combination to a wide range of renewable and conventional energy application [10,11]. Because of the intrinsic intermittent nature of the renewable energy sources (RES), VRFB may represent an efficient tool for the requalification of the energy provided to the grid [12,13], to

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confirm the use of renewable energy [10,14], to enhance Smart Grid [15] and to implement Stand Alone Power Supply (SAPS) system for off-grid applications [11,14]. A recent work assesses the use of fast charging stations for Electric Vehicles in conjunction with VRFBs [16].

The main drawback of VRFB is its high capital cost, which is one of the major limitations to market uptake and widespread deployment of such systems. The high capital cost of VRFB is due to several factors such as the use of expensive vanadium precursors, costly Nafion® membranes [17–19], and the use of additional electrolyte temperature management system to prevent precipitation of vanadium compounds, when a conventional supporting pure sulphate electrolyte is used [8].

In order to break market barrier, beside the optimization of the cell and stack design [20], it is necessary to reduce the VRFB overall cost, paying great attention to the cost of vanadium electrolyte, which accounts for, approximately, 40–45% of the total cost [21]. The laboratory methods for vanadium electrolyte preparation require either the use of expensive vanadium compounds (VOSO_4 , V_2O_5 , or VCl_3) [22,23], and chemical reducing agent (typically oxalic acid or ethylene glycol), otherwise tricky multi-step processes has to be used to dissolve divanadium pentoxide (i.e. the raw material) in the supporting electrolyte. Other methodologies focus on the implementation of relatively complex processes and/or on the use of expensive stabilizing agents, to produce a conventional pure sulphate vanadium electrolyte (in which sulphuric acid is the support electrolyte) [24–27]. Pure sulphate vanadium electrolytes have lower performances with respect to a mixed acid supporting vanadium electrolyte (in which the support electrolyte is made up of sulphuric and hydrochloric acids) [23].

Life Cycle Assessment (LCA) may help to better appreciate optimal methodologies evaluating their sustainability from cradle to grave throughout the full life cycle. Few LCA studies have been performed for redox flow batteries so far and a comparison has been reported between a big size VRFB and a Lead-Acid Battery systems [28]. Strong uncertainties affects LCA analysis, since limited stages of technology maturity is possible to compare (differently from Lead-Acid Batteries, VRFBs are even today far from being a largely industrialised systems).

In this work, three preparation methods of mixed acid vanadium electrolytes for VRFB are compared in terms of effectiveness, feasibility and sustainability. The first method consists in the mere mixing of suitable vanadium precursors affording Electrolyte A. The second method requires the chemical reduction of V_2O_5 by oxalic acid and produces Electrolyte B. The third method, yielding Electrolyte C, consists in the electrochemical reduction of V_2O_5 using a home-made “H-shaped” electrolysis cell. The electrolyte properties (i.e. stability, energy density, etc.) were analysed in function of the electrolyte production methods. To this purpose, thermal stability tests as well as Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements were performed. The performances of laboratory scale VRFB using the three different electrolyte produced were evaluated by means of several consecutive charge–discharge cycles. The environmental sustainability study performed by the Life Cycle Assessment (LCA) allow to benchmark the three methodologies.

Experimental

Materials

V_2O_5 (provided from Duferco Energia spa, 99.95%), $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ (Sigma–Aldrich, 97%), VCl_3 (Sigma–Aldrich, 99.999%), HCl (Sigma–Aldrich, 37%_{w/w}, $d = 1.20 \text{ g/mL}$), H_2SO_4 (Sigma–Aldrich, 98%_{w/w}, $d = 1.84 \text{ g/mL}$) and $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Sigma–Aldrich, 99.6%) were used as received.

General procedure for preparation of electrolyte A

In a 2.0 L graduated round flask, 55.5 mL (1.0 mol) of H_2SO_4 was added to 450.0 mL of deionized water at 298 K. The dissolution of the concentrated acid in deionized water is strongly exothermic and, then, after letting the sulphuric acid solution to cool down to 298 K, 164.2 mL (2.0 mol) of HCl was added. Then, 205.155 g (1.0 mol) of $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ and 162.165 g (1.0 mol) of VCl_3 were added to the mixed acid solution and deionized water was poured to the flask to reach the total volume of 1.0 L. The as-prepared electrolyte solution was magnetically stirred for 3 h, obtaining the $\text{V}^{3+}/\text{VO}^{2+}$ working electrolyte with a $[\text{V}^{3+}]/[\text{VO}^{2+}]$ ratio equal to 1.0. UV–Vis: $[\text{V}^{3+}] = 1.06 \text{ M}$; $[\text{VO}^{2+}] = 1.03 \text{ M}$. Potentiometric precipitation titration: $[\text{Cl}^-] = 4.97 \text{ M}$.

General procedure for preparation of electrolyte B

In a 2.0 L graduated round flask, 111.0 mL (2.0 mol) of H_2SO_4 was added to 450.0 mL of deionized water at 298 K. After cooling of sulphuric acid solution, 410.5 mL (5.0 mol) of HCl was added for the preparation of the mixed acid electrolyte support. Then, 126.63 g (1.0 mol) of oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), and 182.80 g (1.0 mol) of vanadium pentoxide (V_2O_5) were added and deionized water was poured to reach the total volume of 910 mL. The reaction mixture was magnetically stirred for 96 h, during which 90 mL of water were produced. After reaction, the electrolyte was filtered by means of a 50 μm glass frit to remove a gelatinous precipitate which formed during reaction. After filtration, the as-obtained VO^{2+} solution (Electrolyte D) was electrolysed in a flow cell to reduce half of the V(IV) to V(III) . Each half-cell reservoir was filled with 125 mL of the electrolyte which was cyclically pumped into the corresponding half-cell by dual head peristaltic pump with a flow rate corresponding to an electrode face velocity of 2 cm s^{-1} . Each electrolyte solution was charged galvanostatically at a current density of 20 mA cm^{-2} until the cell potential reached the value of 1.9 V, in order to produce V^{3+} and VO_2^+ in the negative and the positive compartment, respectively. At the end of the electrolysis, 125 mL of the catholyte was mixed with 125 mL of fresh Electrolyte D (containing VO^{2+} in $\text{H}_2\text{SO}_4/\text{HCl}$) obtaining a working electrolyte having a $[\text{V}^{3+}]/[\text{VO}^{2+}]$ ratio equal to 1 referred to as Electrolyte B. UV–Vis: $[\text{V}^{3+}] = 0.99 \text{ M}$; $[\text{VO}^{2+}] = 1.03 \text{ M}$. Potentiometric precipitation titration: $[\text{Cl}^-] = 4.93 \text{ M}$.

General procedure for preparation of electrolyte C

This process consisted in the dissolution assisted by an electrochemical reduction of divanadium pentoxide in mixed acid solution. The electrolysis cell was a home-made H-shaped cell having half-cell compartments with a volume of 2.0 L

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