Journal of Power Sources 340 (2017) 139–149

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Evaluation of additive formulations to inhibit precipitation of positive electrolyte in vanadium battery

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HIGHLIGHTS

- Viscosity above 3.5 M V(V) electrolyte in 5.7 M H_2SO_4 increases exponentially.
- Inorganic additives performed better than organic ones to inhibit precipitation.
- Developed additive KS11prevents precipitation of 4 M V(V) electrolyte up to 50 °C.
- The developed additives inhibits precipitation of V(IV) species around 5–20 °C.

ARTICLE INFO

Article history:
Received 21 September 2016
Received in revised form
10 November 2016
Accepted 19 November 2016

Keywords:
Vanadium battery
Positive vanadium electrolyte
Scale inhibitor
Additive
V(V) precipitation

ABSTRACT

A comprehensive study has been performed to develop blended additive formulations based on organic and inorganic compounds to prevent the precipitation of supersaturated V(V) species in the Vanadium Flow Battery at high temperatures around 50 °C. It was found that organic formulations are oxidized by the strong oxidizing effect of V(V) species and are hence ineffective. The inorganic additive formulation KS11 which consists of 1 wt% of $K_3PO_4^+$ 1 wt% of SHMP appears to be very effective with a vanadium solution of composition 3.5 M V(V) in total sulphate/bisulphate concentration of 5.7 M up to a temperature of 40 °C. The phosphate ions (PO_4^{3-}) released from K_3PO_4 and PO_3^- ions from SHMP $(NaPO_3)_6$ are believed to adsorb onto the nucleating ions, thus inhibiting the precipitation of scale forming species, or adsorption onto the growing crystals, deforming and/or inhibiting further formation of vanadium crystals.

Although the electrochemical activity of 3.5 M V solutions was unaffected in the presence of the KS11, increasing vanadium concentration above 3.5 M and total sulphate/bisulphate concentration above 6 M is probably increasing the formation of electrochemically inactive complexes of vanadium-sulphate and polyvanadic species. This results in increased solution viscosity and subsequently reduces the electrochemical activity exponentially.

1. Introduction

To utilize the electricity generated from intermittent renewable energy sources such as photovoltaic (PV) or wind, large scale electricity storage systems are inevitable. Therefore, demand for large scale electricity storage systems is increasing for various applications like remote area power supply systems, telecommunication installations, offshore platforms, emergency back-up systems.

One of the mature large scale electricity storage technologies currently available is the vanadium flow battery (VFB). The VFB consists of mainly three basic components: (i) electrolytes, (ii) membranes and (iii) electrodes. The flow cell comprises positive half-cell and negative half-cell. The two half cells are separated by a membrane, which prevents cross mixing of the two different type of electrolyte (positive and negative electrolytes). An inert electrode made of highly porous carbon felt is placed in each side of the cell. The electrolytes, both positive electrolyte and negative electrolyte, are stored in two external electrolyte storage tanks. The rechargeable electrolytes are circulated through the inert porous

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http://dx.doi.org/10.1016/j.jpowsour.2016.11.071
0378-7753/

carbon felt electrodes where the electrochemical reactions occur. The V(II)/V(III) redox couple is introduced in a negative half-cell and V(IV)/V(V) redox couple in the positive half-cell to perform a reversible reaction. A schematic of the VFB is shown in Fig. 1.

The vanadium electrolyte is the most important component of the vanadium flow battery. It is basically electricity storage medium besides, the conductor of the ions. Hence, the capacity of the battery is determined by the vanadium electrolyte concentration and subsequently the volume of the electrolyte which ultimately determines the energy density of the battery. Although the energy density of the VFB is presently on the lower side but for most stationary electricity storage applications it is adequate. However, improvement in energy density of the VFB will help to lower the volume and weight of the battery that may enhance the marketability.

The precipitation of the negative electrolytes [V(II) and V(III)] at temperatures below 10 °C and positive electrolytes [V(V)] at temperatures above 40 °C currently limits the energy density of the vanadium battery to 20–25 Wh/kg when vanadium concentrations are in the range of 1.6–2.0 M. Improved stability of the vanadium electrolyte is therefore, also desirable for a wider operating temperature range.

One of the main aims of this study was to improve the stability of supersaturated V(V) solutions at higher temperatures so as to increase the energy density of the vanadium flow battery. Rahman [1] in 1998 found that the precipitation rates in vanadium solutions with vanadium concentrations of V(V) species above 3 M were significantly fast. Thermal precipitation of supersaturated V(V) solutions occurs according to the following reaction:

$$2VO_2^+ + H_2O \rightarrow V_2O_5 + 2H^+$$

Thermal precipitation of V(V) ions can thus be suppressed by increasing the concentration of sulfuric acid that increases the proton concentration, thus shifting the above equilibrium to the left. Increasing the sulfuric acid concentration will however, enhance the precipitation of V(II), V(III) and V(IV) species due to the common ion effect of the sulphate ions. In the VFB, the total sulphate concentration was therefore, set between 4 and 5 M while the maximum vanadium ion concentration was 2 M.

A comprehensive investigation was thus undertaken by Rahman [1] to stabilise supersaturated V(V) solutions of concentration above 3 M by using various antiscalant. The main focus of the study was on increasing the induction times of vanadium solution (V(V) species) in different total concentrations of sulphate/bisulphate and at various temperatures using precipitation inhibitors.

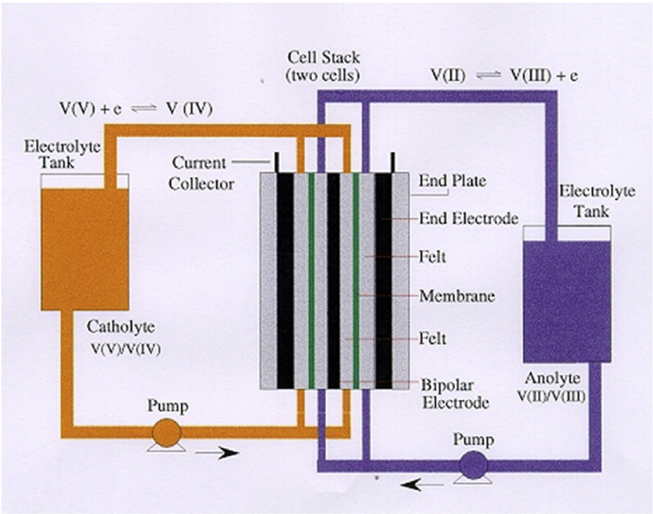

Fig. 1. Main components of vanadium flow battery [1].

The addition of scale control chemicals to prevent the formation of scale in a variety of applications such as cooling towers, boilers, desalination plants, oil wells etc. is well known. Presently methods of inhibiting scale formation using chemicals in the water treatment industry are known as threshold agents. The addition of less than stoichiometric amounts of specific polyphosphates or polyphosphonates to supersaturated solutions of brines has been shown to inhibit the precipitation for substantial periods of time (Rice and Partridge [2]; Buehrer and Reitemeier [3]).

The specific mechanism of minimization of scale formation by threshold activity is not fully understood but it is strongly believed that a common feature of threshold agents is sequestration or the capability of forming stable complexes with polyvalent cations thus preventing precipitation. Supersaturated solutions of brines are evidently stabilised by threshold agents in some manner involving alteration and distortion in crystal morphology at the time of nucleation and/or subsequent inhibition during growth rate (Spiegler and Laird [4]).

Logan and Walker [5] are of the opinion that additives may act to stifle formation of scale by one of the following routes: (i) additives may change the precipitating salt's chemical potential by affecting complex formation and adsorption; (ii) they may adsorb onto the precipitating ions, thus inhibiting the scale formation at nucleation step; (iii) they may adsorb onto the surface of growing crystals, thus distorting and/or preventing further crystal formation. It is possible that precipitation is minimized through more than one of the above routes. However, it is well known and fully established that once supersaturation occurs in any aqueous system, *precipitation is inevitable,* regardless of the merits of all known or available threshold agents or blended formulations.

Therefore, if the induction time for the onset of precipitation can be increased sufficiently, it would be possible to increase the energy density of vanadium flow battery by employing supersaturated vanadium solution in the presence of appropriate additives or blended formulation which inhibits precipitation. Skyllas-Kazacos and co-workers initially proposed the use of stabilizing agents for inhibiting precipitation in supersaturated vanadium solutions in 1994 (Skyllas-Kazacos [6,7]). Rahman [1] extended the work on screening various inhibitors to prevent the precipitation of concentrated V(V) electrolytes, while sodium hexa-metaphosphate and potassium sulphate were reported to inhibit precipitation of supersaturated V(IV) electrolyte by Skyllas-Kazacos et al. [8]. Recently a number of researchers have diverted their attention towards the vanadium battery particularly on the investigation of additives to stabilise the supersaturated vanadium electrolytes.

Li et al. [9] investigated organic additives such as fructose, mannitol, glucose, d-sorbitol to inhibit the precipitation of positive electrolyte. They stated that d-sorbitol exhibits the best electrochemical performance. In terms of energy efficiency, d-sorbitol demonstrated a slightly higher average value of 81.8% compared to 79.8% for the electrolyte without additives. Wu et al. [10] employed organic additives such as inositol and phytic acid to improve the stability and electrochemical reversibility of positive vanadium electrolyte. They reported that the thermal stability of V(V) electrolyte was found to be improved by both additives. Effects of organic inhibitors containing NH_2 and SO_3H on electrochemical behaviour of VFB were reported by He et al. [11]. They found that amino-methyl-sulfonic acid (AMSA) and methanesulfonic acid (MSA) can inhibit the precipitation of V(V) solutions at higher temperatures. However, in our opinion, it appears that a significant improvement in stability could not be achieved