**A simple model for vanadium precipitation in vanadium redox flow batteries**

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**Highlights**

* Optimization of vanadium redox flow battery
* Impact of precipitation on electrochemical performance
* Half-cell modelling

**1. Introduction**

The future of the energy grid will require an ever-larger capacity of energy storage. Among all the technological solutions available, the redox flow batteries are ones of the most attractive as they deal a large operation scale, a good efficiency and a large design flexibility [1]. The common and most popular redox flow battery is the all-vanadium redox flow battery, which uses the same element in both cell compartments. This system avoids the contamination risk due to crossover, which occurs with the long-run use. This device leads to ideal sustainability and practical unbounded lifetime.

However, the all liquid vanadium redox flow batteries are limited by the solubility of vanadium in water (from 2 to 4 M of VOSO4 in 2M acid sulfuric [2]). The vanadium ions solubility limits the energy density ca. 15 Wh/kg [1]. This energy density is quite low in contrast with the specific energy of Li-ion batteries (close to 100 Wh/kg [3]). Hence, operating points at high vanadium concentrations are essential to obtain higher energy density. Consequently, high concentration of vanadium results in large risk of precipitation of vanadium salts in the cell.

Numerous models have already been introduced to describe the liquid vanadium redox flow batteries [4–8] but without taking into account the precipitation phenomenon. This work exhibits a 2D transient model which takes into account solubility. In addition an experimental study of flow cells is introduced in order to validate the model.

**2. Methods**

The model solves usual mass, momentum and energy conservation equations. The Butler-Volmer law describes the electrochemical kinetic of the vanadium. The dissolution/precipitation of the vanadium salts is modelled with first order kinetic law and Fick’s equation. We have assumed a pseudo-homogeneous system to solve the equation set.

To validate this model, the oxidation of vanadium (IV) to vanadium (V) is studied in a half-flow-cell made of PMMA, with carbon felt electrodes. The inlet solution of VOSO4 and 3M sulfuric acid could be recycled or the cell could be fed by clean solution. Potentiometric measurement have been performed and compared with the model results. At specific time, the solution of vanadium at the outlet of the flow cell is sampled and the vanadium ions are quantified using UV-visible spectrophotometry for the vanadium (IV) and potentiometric titration with Mohr salt for the vanadium (V).

**3. Conclusions**

This model allows a better understanding of the impact of the vanadium precipitation on the battery operation at high vanadium concentration and could provide strategies for redox flow battery optimization.

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