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Enhanced VRB electrochemical performance using tungsten as an electrolyte additive

Moonsu Kim, Hyeonseok Yoo, Gibaek Lee*, Jinsub Choi*

Nano & Energy Materials Lab, Department of Chemistry and Chemical Engineering, Inha University, 22212 Incheon, South Korea

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ABSTRACT

In this study, we investigated the addition of a tungsten catalyst into the electrolyte of a vanadium redox flow battery (VRBs) and measured the cell performance with respect to the concentration of the W^{6+} precursor. The VRBs showed a clear improvement in electrochemical performance because of the deposition of tungsten on the electrode. The presence of tungsten allowed the ionization of tungsten in the electrolyte during battery cycling. The optimized concentration of the tungsten additive was examined using electrochemical methods, which showed that the efficiency of the VRBs improved by 2–3% after the addition of 3 mM tungsten to the electrolyte. In particular, the performance of VRB cells in an anolyte containing a W^{6+} catalyst was significantly enhanced at high current rates.

1. Introduction

Globally, renewable energy sources such as solar energy, wind energy, and tidal power [1–4] are being developed to solve problems caused by the consumption of fossil fuels, such as environmental pollution. However, these natural power sources are technically complex and expensive and suffer from an inherent imbalance in energy production and consumption [5,6]. Thus, large-scale energy storage solutions that can store the surplus electrical energy during periods of low demand and then supply that energy during periods of high demand have been extensively studied. Recently, high-performance Li-ion batteries, fuel cells, and air batteries have been suggested as potential solutions [7–11]. In particular, the redox flow battery is widely known as a large-scale energy storage system (ESS). Vanadium redox flow batteries (VRBs), which use the redox reactions of vanadium ions, have received considerable attention because of their long cycle lives, low self-discharge behavior, easy maintenance, high energy efficiency, and environmental friendliness [12–15]. In addition, VRBs have relatively high cell potentials, which arises from the combination of the redox reactions of vanadium ion and the reduced degradation in cell performance compared to other ESS devices because there is less cell cross-contamination. However, the performance of cells at high current densities must be improved before VRBs can be commercially applied.

A recently reported problem concerning VRBs is the low energy density that results from 1) the limited vanadium solubility and concentration, 2) the evolution of hydrogen or oxygen during cycling, and 3) the poor reversibility of the kinetics at the electrode [16–19]. Regarding the solubility, the electrolyte has a variable temperature window that depends on the supporting acid electrolyte containing the vanadium ions. If the temperature goes beyond the bounds of the operating window, a V_2O_5 solid phase forms (see Eq. (1)) [20].

$$VO_2^+(aq) + \frac{1}{2}H_2O(l) \leftrightarrow \frac{1}{2}V_2O_5(s) + H^+(aq) \quad (1)$$

To avoid this problem, the inclusion of additives to the electrolyte or a supporting acid electrolyte, such as hydrochloric acid, nitric acid, or a mixture of acids, is necessary [16,17,21]. Concerning the evolution of hydrogen or oxygen, the generation of these species causes a change in the conductivity and ion concentration; thus, the hydrogen evolution reaction (HER) affects the activation of vanadium [22]. Therefore, to improve the VRB performance, the hydrogen or oxygen evolution reactions must be prevented by applying a low current density ($<50\,mA\,cm^{-2}$) or by using inhibitor catalysts such as Bi, Sb, Zn, Ag, Ca, or Mg. [23]. Thirdly, to overcome the poor kinetic reversibility of the electrode materials, catalysts are often used. For example, metal oxide catalysts such as WO_3/super active carbon (SAC), Mn_3O_4, TiO_2, Nb_2O_5, and PbO_2 [24–29] are acid resistant, and their use in VRBs can result in an improvement in the cell performance. However, because metal oxide catalysts generally have lower conductivities than metal catalysts, their applications are limited. Furthermore,

* Corresponding authors.
E-mail addresses: gibaek@inha.ac.kr (G. Lee), jinsub@inha.ac.kr (J. Choi).

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