Short communication

Tackling capacity fading in vanadium flow batteries with amphoteric membranes

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HIGHLIGHTS

- Effective transport of vanadium ions is determined in an operating vanadium flow cell.
- Analysis over one charge-discharge cycle allows prediction of extended cycling.
- Engineering approaches to mitigate capacity fading can be conclusively explained.
- Electrolyte imbalance effects strongly depend on the type of membrane used.
- Amphoteric membranes show more balanced vanadium transfer and less capacity fading.

GRAPHICAL ABSTRACT
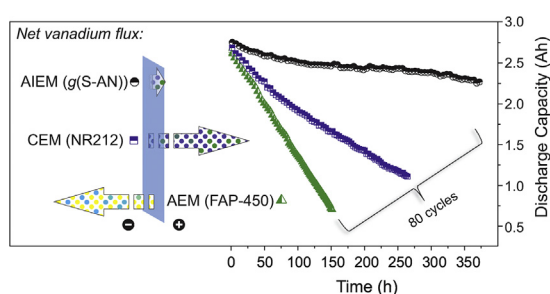
ARTICLE INFO

ABSTRACT

Capacity fading and poor electrolyte utilization caused by electrolyte imbalance effects are major drawbacks for the commercialization of vanadium flow batteries (VFB). The influence of membrane type (cationic, anionic, amphoteric) on these effects is studied by determining the excess and net flux of each vanadium ion in an operating VFB assembled with a cation exchange membrane (CEM), Nafion® NR212, an anion exchange membrane (AEM), Fumatech FAP-450, and an amphoteric ion exchange membrane (AIEM) synthesized in-house. It is shown that the net vanadium flux, accompanied by water transport, is directed towards the positive side for the CEM and towards the negative side for the AEM. The content of cation and anion exchange groups in the AIEM is adjusted via radiation grafting to balance the vanadium flux between the two electrolyte sides. With the AIEM the net vanadium flux is significantly reduced and capacity fading due to electrolyte imbalances can be largely eliminated. The membrane's influence on electrolyte imbalance effects is characterized and quantified in one single charge-discharge cycle by analyzing the content of the four different vanadium species in the two electrolytes. The experimental data recorded herewith conclusively explains the electrolyte composition after 80 cycles.

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1. Introduction

Vanadium flow batteries (VFB) receive increasing attention for grid-scale storage of electric energy [1,2]. However, the technology needs to move further towards the aggressive cost target for grid-

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scale electricity storage of \$100 kWh^{-1} [3]. The ion exchange membrane is a crucial component: the material can account for the major share of hardware investment cost [4,5], and it governs ohmic and coulombic losses and influences capacity fading induced by electrolyte imbalance, which has so far been resolved with periodical electrolyte rebalancing [6]. For this and other approaches of symptom fighting, concurrent loss of efficiency and electrolyte utilization is unavoidable. Therefore, amphoteric membranes were utilized in order to combine the high conductivity imparted by cation exchange groups with the barrier function of anion exchange groups, yielding high voltaic as well as coulombic efficiency [7–9]. Early work of Mohammadi and Skyllas-Kazakos demonstrated lower volume imbalances for an operating cell assembled with an amphoteric membrane [10]. At that time, the capacity retention effect of amphoteric membranes was assigned to a less pronounced water transport. By following the V(IV) and V(V) concentrations in an operating VFB, Luo et al. showed that this capacity fading results from imbalanced vanadium transport [11]. In this work, a straightforward method is introduced to determine the effective rate of transfer of each vanadium ion across the membrane, the associated electrolyte imbalance and capacity fading in an operating VFB. The vanadium transport across an amphoteric ion exchange membrane (AIEM) was compared to that across the cation exchange membrane (CEM) Nafion® NR212 (DuPont) and the anion exchange membrane (AEM) FAP-450 (Fumatech) to highlight the fundamental importance of the nature of the fixed charges to control vanadium species transport in ion exchange membranes for tackling capacity fading and maintaining electrolyte utilization in VFBs over extended cycling periods.

2. Experimental

2.1. Synthesis of AIEM

Amphoteric ion exchange membranes were prepared by pre-irradiation induced graft copolymerization of styrene (S) and acrylonitrile (AN) into ethylene-tetrafluoroethylene (ETFE) base film (TEFZEL 100LZ, DuPont) of 25 μm thickness, followed by amidoximation of AN groups and sulfonation of styrene units. The synthetic procedure is described in detail in Refs. [9,12]. The membranes used in this study had a graft level of 36% and a molar ratio of S:AN of 1:1 in the grafts.

2.2. Ion exchange capacity

The cation exchange capacity (CEC) and anion exchange capacity (AEC) were measured by pH-titration (Metrohm Titrinio 702 SM and 877) with potassium hydroxide and hydrochloric acid, respectively. The detailed procedure is reported elsewhere [9].

2.3. Operando vanadium concentration analysis

The accumulation and consumption rate of each vanadium ion during charging and discharging was calculated from the volume change of anolyte/catholyte and the concentration change of vanadium species in the electrolytes (cf. Supporting Information, page 2). The concentration of V(II), V(III) and V(IV) was measured by the immediate titration of 300 μL samples of the positive and negative electrolyte, which were periodically taken from the operating cell over one cycle. The positive electrolyte sample was subsequently analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian VISTA AX) to determine the V(V) concentration from the difference of the total vanadium concentration and the V(IV) concentration.

2.4. Redox flow cell test

The membranes equilibrated in the electrolyte were assembled with SGL® Sigracell GFD4.6 EA carbon felt electrodes (30% compression, heat treated [13]) in a 25 cm^2 cell and cycled at room temperature and a constant current of 40 mA cm^{-2} between 0.8 V and 1.7 V as limiting voltage (redox flow test system: Scribner Model 857). A vanadium electrolyte with a concentration of 1 M vanadium and 2.1 M sulfuric acid (Oxkem, Reading, UK) was used.

3. Results and discussion

3.1. Investigated membranes

The electrolyte imbalance effect caused by an AEM, CEM and AIEMs was investigated with the representative membranes FAP-450 (AEM), Nafion® NR212 (CEM) and the grafted AIEM g(S-AN). All three membranes are suitable for VFB applications (Table 1). With increasing amount of anion exchange groups, the permeance of highly charged cations is disfavored due to coulombic repulsion. As a consequence, cells assembled with AEMs exhibit high coulombic efficiency and the vanadium transfer is significantly decreased compared to the use of CEMs [14,15]. AIEMs have been suggested to combine the high conductivity associated with proton exchange groups with the increased vanadium barrier caused by anion exchange groups [8,9,16]. The grafted AIEM g(S-AN) exhibits an improved selectivity of a factor of 4 and 2 compared to NR212 and FAP-450, respectively.

The ion exchange capacities of FAP-450, NR212 and g(S-AN) (cf. Table 1) represent the fixed charges in the membrane. The influence of the type of membrane on vanadium ion transport in the VFB was studied by analyzing the change in the electrolyte composition in an operating redox flow cell.

3.2. Electrolyte imbalance effects over a single cycle

In an ideal charge-discharge process, the conversion rate of each vanadium ion is given by the cell current. At a charging current of 1 A (40 mA cm^{-2}), V(III) and V(IV) undergo electrochemical reduction and oxidation, respectively, at a rate of 37.3 mmol h^{-1}. In reality, deviations from this rate are caused by vanadium crossover and side reactions, such as oxygen reduction and hydrogen evolution on the negative side. Vanadium ions crossing the membrane reduce the SOC of the permeate side, consequently the observed conversion rate is higher during discharging and lower during charging compared to the faradaic rate. These deviations evidence not only the overall rate of self-discharge but also the contribution of each vanadium ion (Fig. 1). To maintain the initial capacity of the system, the amount and the average valence of transferred vanadium between the negative and the positive side and between the charging and discharging process has to be balanced.

Table 1
Performance relevant parameters of tested membranes. The selectivity is calculated according to $\alpha = \frac{R \cdot T}{F} \cdot \frac{1}{R_\Omega \cdot i_x}$, where R and F are the ideal gas and Faraday constant, respectively and T is taken as 298 K ([17], cf. Supporting Information page 1). AEC and CEC are anion exchange capacity and cation exchange capacity, respectively.

Property	Unit	FAP-450	g(S-AN)	NR212
Area resistance R_Ω	[Ω cm^2]	0.66 ± 0.04	0.52 ± 0.05	0.30 ± 0.03
Permeance i_x	[mA cm^{-2}]	0.19 ± 0.14	0.14 ± 0.10	0.80 ± 0.09
Selectivity α	[-]	204 ± 6	352 ± 10	107 ± 1
Thickness (H$_2$O-swollen)	[μm]	59 ± 2	41 ± 3	57 ± 1
CEC	[mmol g^{-1}]	0.01 ± 0.03	0.82 ± 0.02	0.94 ± 0.08
AEC	[mmol g^{-1}]	2.90 ± 0.07	0.61 ± 0.03	0.00 ± 0.01