Na-β-Alumina as a Separator in the Development of All-Vanadium Non-Aqueous Tubular Redox Flow Batteries: An Electrochemical and Charging-Discharging Examination Using a Prototype Tubular Redox Flow Cell

Govindan Muthuraman, Lee Boyeol, and Moon Il-Shik

Department of Chemical Engineering, Sunchon National University, Jeollanam-do, Suncheon 57922 Korea

The non-aqueous redox flow battery (N-ARFB) is in the development stages with the strong potential for high power density storage systems. In addition to the development of N-ARFBs, this study examined the applicability of a sodium beta alumina (Na-β-Al2O3) membrane in the development of a N-ARFB through an analysis of the electrochemical processes, redox active species migration, and charging/discharging at room temperature (25 ± 3°C). Through impedance analysis, the ionic conductivity of the Na-β-Al2O3 membrane was 2.97 × 10⁻² S cm⁻¹ which is slightly higher than the literature value. UV-Visible analysis showed no migration of the vanadium acetylacetonate (V(acac)₃) ion in a single compartment to another, either during the charging or discharging process. In addition, the lack of a change in the morphology of the spent membrane revealed not only stability, but also confirmed the permeation of V(acac)₃ species. The maximum applied current density for charging and discharging was 0.01 mA cm⁻² and 0.0015 mA cm⁻², respectively. The charging/discharging of V(acac)₃ enables voltage and current efficiencies of almost 16% and 11% respectively, at the state of charge of 15%. This demonstrates that the Na-β-Al2O3 membrane can be improved for use in N-ARFB after optimizing the conditions.

The charging/discharging of V(acac)₃ enables voltage and current efficiencies of almost 16% and 11% respectively, at the state of charge of 15%. This demonstrates that the Na-β-Al2O3 membrane can be improved for use in N-ARFB after optimizing the conditions.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.1461809jes]
Received. Sodium perchlorate (NaClO₄, 98.0e102.0%) was obtained from Alfa-Aesar.

Electrochemical characterizations.—Cyclic voltammetry was carried out in a tailor made glass cell with an electrolyte volume of 100 mL, furnished with two compartments separated by a piece of commercially available Na-β-Al₂O₃ membrane (Gifted from Linetech Co. Ltd, Korea) for the working and counter electrodes. A platinum mesh and Ag wire were used as counter and quasi-reference electrodes, respectively. The measurements were taken with a PARC VersaSTAT 3 instrument. The scan rate was 50 mVs⁻¹. Fig. 1 presents the prototype electrochemical cell with a Na-β-Al₂O₃ (Na-β-Al₂O₃) tube membrane (Gifted from Linetech Co. Ltd, Korea) divided cell that was used for the impedance studies using the same PARC VersaSTAT 3 instrument. Galvanostatic mode with an applied current of 1 mA (vs. OCP) using a two electrode configuration was applied with carbon as the counter and working electrodes (0.5 cm distance) with frequencies ranging from 200 kHz to 0.01 Hz. The area of the working electrode exposed to the electrolyte solution was approximately 140 cm². The ionic conductivity within the membrane was calculated using the impedance results according to the following equations:¹

\[
\sigma (S \text{ cm}^{-1}) = \frac{d}{R} \ \ [1]
\]

\[
R(\Omega \text{ cm}^2) = (R_1 - R_2) \times A \ \ [2]
\]

where \(\sigma\) and \(R\) are the ionic conductivity and area resistance of the membrane, respectively; \(d\) and \(A\) denote the thickness (cm) and area (cm²) of the membrane, respectively; and \(R_1\) and \(R_2\) represent the resistance (Ω) of the cell with and without the membrane, respectively.

Charge-discharge cycling.—The charge-discharge tests were conducted using a prototype tubular (made using Teflon material) Na-β-Al₂O₃-divided flow cell assembly with 0.1 M V(acac)₃ and 0.1 M TBAP or NaClO₄ in AN solution at 0.5 cm gap between the membrane and electrodes. (B) Nyquist plot showing the effect of the electrolyte (a) 0.1 M NaClO₄ and (b) 0.1 M TBAP on Na-β-Al₂O₃ membrane in a 0.01 M V(acac)₃ solution in AN.

Analysis.—The migration of the V(acac)₃ via Na-β-Al₂O₃ was measured primarily during charging and discharging separately by UV-visible spectroscopy using a Scinco s-3100 spectrophotometer. A 5 ml sample withdrawn from the cathodic (charging) or anodic (discharging) compartment at the desired time interval and analyzed by UV-visible spectroscopy to identify the migrated concentration of vanadium ions using a plot of standard vanadium concentrations. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) of a used Na-β-Al₂O₃ piece taken from a tailor made electrolysis setup was performed using a Zeiss EVO-MA10, and the membrane surface morphologies were investigated.

Results and Discussion

Na-β-Al₂O₃ membrane suitability by electrochemical analysis.—To check the suitability of Na-β-Al₂O₃ in the N-ARFB system, resistance analysis was performed by electrochemical impedance analysis (EIS) and the results are shown in Fig. 2. The Nyquist plot was obtained for 0.01 M V(acac)₃ in the presence of 0.1 M NaClO₄ solution under vacuum. Prior to use, the electrodes and membranes were conditioned, as described previously, by soaking in a 0.1 M electrolyte solution for at least 4 h.¹⁰
in AN with (Fig. 2A curve a) and without (Fig. 2A curve b) the Na-β-Al2O3 membrane. The difference in solution resistance (derived by an instant fit with an error % below 15) between with and without a membrane was 5.383 Ω cm2, which is considered to be the Na-β-Al2O3 membrane resistance (Eq. 2). By combining the thickness of the membrane with the obtained membrane resistance, an ionic conductivity of 2.97 × 10−2 S cm−1 was derived using Eq. 1. The obtained ionic conductivity is comparable to the literature value (1.2 × 10−2 S cm−1) obtained in biphenyl and dimethoxyethane-dissolved sodium. EIS of V(acac)3 dissolved in a 0.1 M TBAP electrolyte in AN was compared to determine the suitability of the Na-β-Al2O3 membrane, as shown in Fig. 2B. The Na-β-Al2O3 membrane in a 0.1 TBAP supporting electrolyte showed a slightly elongated semicircle with an increased resistance (Fig. 2B curve b) of 12.881 Ω cm2, which suggests that the charge carrier could be via a standard vacancy mechanism or correlated movement of interstitial Na+ ions25 or the charge balance might have occurred by size exclusion. At the same time, the cell potential between the divided (by Na-β-Al2O3) and undivided cell containing the 0.1 M NaClO4 supporting electrolyte in AN showed a noticeable difference. The cell potential for the undivided cell reached 8 V by an applied current density of 1.7 mA cm−2 with a potential range of approximately 4 V for charging/discharging in N-ARFB. On the other hand, electrolysis in non-aqueous or ionic liquid medium leads to a high cell potential at the applied current density, galvanostatic mode, of below 10 mA cm−2.26,27 This could be due to the attainment of a solvent polarization limit. The present results obtained using the Na-β-Al2O3 membrane strongly correlated with not only the results of galvanostatic mode electrolysis in the non-aqueous medium electrolysis potential, but also many polymeric membranes in N-ARFB system worked in this applied current density region (0.004 to 0.01 mA cm−2).28–30

The cell potential variation may have also been influenced by the reversibility of the redox active species under the given electrolytic conditions. In the N-ARFB system, tetra ethylammonium tetrafluoroborate (TEAB) showed the maximum suitability, particularly on reversibility, than the other electrolytes due to the small radii and high limiting oxidation potential.31 In the present work, the cyclic voltammetry (CV) behavior of V(acac)3 using the Na-β-Al2O3 membrane-divided electrochemical cell in 0.1 M tetra butylammonium perchlorate (TBAP) and NaClO4 in AN at the glassy carbon (GC) electrode were compared, as shown in Fig. 3. In the 0.1 M TBAP electrolyte, a redox peak at approximately −1.50 V and −1.34 V vs. Ag/Ag+ was observed (Fig. 3 curve a), which was approximately 100 mV higher than the value reported for V(III) to V(II) reduction.32 Other redox peaks at approximately 0.85 V and 0.69 V vs. Ag/Ag+ was approximately 100 mV higher than the values reported for V(III) to V(IV) and an additional reduction peak at −0.66 V vs. Ag/Ag+ related to intermediate vanadium species.32,33 In contrast, the CV behavior of V(acac)3 in the 0.1 M NaClO4 electrolyte showed only two redox couples related to V(III) to V(II) (−1.40 V and −1.24 V vs. Ag/Ag+) and V(III) to V(IV) (0.76 V and 0.58 V vs. Ag/Ag+) (Fig. 3 curve b) with intermediate vanadium (−0.73 V) formation (Fig. 3 curve b). Note that highly reversible redox couples were recorded for V(acac)3 in the presence of tetraethylammonium hexafluoro phosphate (TEAPF6) or TEAB supporting electrolyte in AN on a GC electrode.33 On the other hand, the two vanadium redox couples exhibited quasi-reversible behavior under these given conditions, particularly in the TBAP and NaClO4-supporting electrolytes. In addition, the V(acac)3 redox behavior varied according to the supporting electrolyte used,31 which means that V(acac)3 shows sluggish electron transfer in the both the TBAP and NaClO4 supporting electrolytes, which might have influenced the cell potential variations. Importantly, the redox peak potentials in the presence of the NaClO4 supporting electrolyte was 100 mV less than the TBAP supporting electrolyte, either in the oxidation or reduction region, support that the NaClO4 supporting electrolyte facilitates the V(acac)3 redox process.

**Vanadium migration analysis.**—In many polymeric membrane-divided RFB systems, capacitive decay is a major setback of the cell performance4,10,34 due to the permeation of redox active species that leads to self-decay. In the present study, the migration of V(acac)3 through Na-β-Al2O3 was monitored during charging and discharging by UV-visible spectroscopy at defined electrolysis time intervals, as shown in Fig. 4. The V(acac)3 or V(acac)2 absorbance occurs at approximately 650 and 800 nm, respectively,35 which was used to determine its concentration in the cell during charging or discharging (Fig. 4A curve a). During charging, the cathodic compartment containing a 0.1 M NaClO4 solution in AN showed no peaks (expected the V(acac)3 ion migration from the anodic half-cell), which are related to vanadium ions (Fig. 4A curve b). This was confirmed by the different charging timings (inset figure in Fig. 4A), where no change in the UV-visible absorbance peak was observed until 4 h charging. In a similar manner, V(acac)2 migration was monitored during discharging (cathodic to anodic half-cell) (Fig. 4B), where also no peak related to the vanadium species was observed (Fig. 4B curve b) in the anodic half-cell and with discharging timings up to 4 h (inset figure of Fig. 4B), which confirms that the Na-β-Al2O3 will minimize the capacitive decay through the migration of redox active species, here vanadium. Furthermore, SEM analysis of the Na-β-Al2O3 before (Fig. 5a) and after (Fig. 5b) the charging/discharging experiments showed no prominent change in the membrane surface. EDS analysis of the before and after experiments, particularly for the Na ion atomic % showed a slight increase (4.69%) compared to the before electrolysis sample (4.56%), which suggests that Na+ ions are not leaching out. The slight increase in the Na ion % could be due the use of NaClO4 as an electrolyte, which might have helped the Na ions become intact or remain in the membrane. Overall, Na-β-Al2O3 can be used as a membrane in N-ARFB with a suitable electrolyte.

**Charging/discharging analysis.**—Fig. 6A shows the typical charge (V3+ oxidation-reduction) and discharge (V4+ reduction-V3+ oxidation) potential limits with time at a Na-β-Al2O3 tubular membrane-divided prototype electrochemical cell using a graphite electrode pair in AN electrolyte. The charging potential (upper limit) at first cycle reached 2.2 V and remained relatively constant up to 4 hr. From then, the discharge process was initiated with different cell potentials around 0.85 V and ended at 0.3 V in 4 hr. without a prominent discharging plateau. Similar charging discharging trend with increase in upper potential limits up to 3.5 V was observed in the first six cycles and remain constant in remaining all cycles. The interesting point here is the cell potential limits. The upper and lower limits reached 3.6 V and 0.85 V, respectively, which may be due to...
the ohmic or IR resistance of the electrochemical cell due to the electrolyte, electrode, and membrane resistance. V(acac)$_3$ at the H-type cell showed a charging and discharging potential of 2.75 V and 0.4 V, respectively, where the discharge potential difference was affected by the electrode distance. Similar H-type cells used for the Mn(acac)$_3$ and Cr(acac)$_3$ redox flow battery in AN showed a huge potential difference between charging and discharging, including ohmic and IR resistance, according to electrode distance. Another possibility could be the dissociation of the V(acac)$_3$ complex to V(acac)$_2$ or the formation of a V(V) oxidation state or vanadium crossover. A recent study of V(acac)$_3$ in AN with a zero gap (electrodes to membrane) showed a minimized charging and discharging potential of almost 0.2 V showing that the charging discharging potential difference is due mainly to the electrode distance. In addition, the membrane thickness affects the charging discharging cell potential and columbic efficiency reduction by 15%. As shown in Fig. 2 and Fig. 4, the lower membrane resistance and no crossover of V(acac)$_3$ leads to an electrode distance or electrode for a high charging discharging.

Figure 4. (A) UV-Visible absorption spectra of 0.01 M V(acac)$_3$ in AN (a) and solution of cathodic half-cell after 1 h charging process (b). The inset shows the absorbance of cathodic half-cell solution during different charging timings (B) UV-Visible spectrum of the anodic half-cell solution (0.1 M NaClO$_4$ in AN) after the 1 h discharging process (cathodic half-cell contains 0.01 M V(acac)$_3 + 0.1$ M NaClO$_4$ in AN). The inset shows the absorbance of the anodic half-cell solution during different discharging timings. Conditions: Carbon felt electrodes with a geometric surface area of 2 cm$^2$; applied current density of 0.01 mA cm$^{-2}$; 250 mL (each half-cell) of electrolyte.

Figure 5. SEM images of Na-β-Al$_2$O$_3$ before (a) and after (b) charging/discharging experiments for N-ARFB. Conditions: Carbon felt electrodes with a geometric surface area of 2 cm$^2$; applied current density of 0.01 mA cm$^{-2}$; 250 mL (each half-cell) of 0.01 M V(acac)$_3$ in AN.

Figure 6. (A) Charge-Discharge curve and (B) Charge-Discharge capacity of 0.01 M V(acac)$_3$ in 0.1 M NaClO$_4$ in AN solution with charge and discharge current densities of 0.01 mA cm$^{-2}$ and 0.0015 mA cm$^{-2}$. 15% state of charge.
potential difference. Further, no capacity decay was found while charging and discharging using the prototype tubular cell (Fig. 6B), though the capacity values found less (4.5 mA h g⁻¹), confirms no crossover of V(acac)₃ ions through Na-β-Al₂O₃ membrane. The calculated voltage and current efficiency for the above second cycle were approximately 16% and 11%, respectively, at the 15% state of charge. Some current loss might occur by complex dissociation and electrode distance but these can be rectified under optimized conditions.

Conclusions

The Na-β-Al₂O₃ tubular membrane was applied successfully to the all-vanadium N-ARFB system through a prototype RFB cell. EIS confirmed that the ionic conductivity of the Na-β-Al₂O₃ membrane in the presence of 0.1 M NaClO₄ in AN was 2.97 × 10⁻² S cm⁻¹, which assisted in the development of a N-ARFB. The redox couples, V⁵⁺/V⁴⁺ and V³⁺/V²⁺, are quasi-reversible under the given conditions. UV-visible analysis during the charging and discharging of V(acac)₃ confirmed that the lack of crossover through the Na-β-Al₂O₃ membrane can minimize the capacity loss. In addition, no definite change in the Na-β-Al₂O₃ membrane confirmed its stability toward long term operation. The high charging and discharging potential difference might be related to the electrode distance and quasi-reversible redox couples of V⁵⁺/V⁴⁺ and V³⁺/V²⁺, respectively, under the given conditions. The charging discharging cycle with approximately 16% voltage efficiency and 11% current efficiency at the 15% state of charge highlight the potential of the Na-β-Al₂O₃ membrane.

Acknowledgment

This study was supported by the National Research Foundation of Korea (NRF) funded by Ministry of Engineering Science and Technology (MEST) from the Korean government (grant No. NRF-2017R1A2A1A05001484).

ORCID

Moon Il-Shik  https://orcid.org/0000-0002-8191-9662

References

1. S.-H. Shin, S.-Y. Yun, and S.-H. Moon, RSC Adv., 3, 9095 (2013).
2. K. Gong, Q. Fang, S. Gu, S. F. Y. Li, and Y. Yan, Energ. Environ. Sci., 8, 3515 (2015).
3. L. Su, M. Ferrandon, J. A. Kowalski, J. T. Vaughey, and F. R. Brushett, J. Electrochem. Soc., 161, A1905 (2014).
4. M. O. Bamgbopa and S. Almheiri, J. Power Sources, 342, 371 (2017).
5. L. Su, R. M. Darling, K. G. Gallagher, W. Xie, J. L. Thelen, A. F. Baile, J. L. Barton, K. J. Cheng, N. P. Balsara, J. S. Moore, and F. R. Brushett, J. Electrochem. Soc., 163, A5253 (2016).
6. S. E. Doris, A. L. Ward, A. Baskin, P. D. Frischmann, N. Gavvalapalli, E. Chénard, C. S. Sevov, D. Prendergast, J. S. Moore, and B. A. Helms, Angew. Chem. Int. Ed., 56, 1595 (2017).
7. A. E. S. Sleighbolome, A. A. Shinkle, Y. Li, and L. T. Thompson, Electrochem. Commun., 11, 2312 (2009).
8. J. Mun, M.-J. Lee, J.-W. Park, D.-J. Oh, D.-Y. Lee, and S.-G. Doo, Electrochem. Solid St., 15, A80 (2012).
9. K. S. Chakrabarti, R. A. W. Dryfe, and E. P. L. Roberts, Electrocim. Acta, 52, 2189 (2007).
10. I. L. Escalante-Garcia, J. S. Wanrigh, L. T. Thompson, and R. F. Savinell, J. Electrochem. Soc., 162, A363 (2015).
11. S. Maurya, S.-H. Shim, K.-W. Sung, and S.-H. Moon, J. Power Sources, 255, 325 (2014).
12. D.-H. Kim, S.-J. Seo, M.-J. Lee, J.-S. Park, S.-H. Moon, Y.-S. Kang, Y.-W. Choi, and M.-S. Kang, J. Membrane Sci., 454, 44 (2014).
13. S.-H. Shin, Y. Kim, S.-H. Yun, S. Maurya, and S.-H. Moon, J. Power Sources, 296, 245 (2015).
14. G. Nagarjuna, J. Hui, K. J. Cheng, T. Lichtenstein, M. Shen, J. S. Moore, and J. Rodriguez-Lopez, J. Am. Chem. Soc., 136, 16309 (2014).
15. J. Winsberg, T. Hagemann, S. Muench, C. Friebe, B. Haupler, T. Janoschka, S. Morgenstern, M. D. Hager, and U. S. Schubert, Chem.Mater., 28, 3401 (2016).
16. B. Zhu, Z. Hong, N. Milne, C. M. Doherty, L. Zou, Y. S. Lin, A. J. Hill, X. Gu, and M. Duke, J. Membrane Sci., 433, 126 (2014).
17. B. Zhu, D. T. Myat, J.-W. Shim, Y.-H. Na, I.-S. Moon, G. Connor, S. Maeda, G. Morris, S. Gray, and M. Duke, J. Membrane Sci., 475, 167 (2015).
18. M. Govindan, B. Zhu, M. Duke, S. Gray, and L. S. Moon, J. Ind. Eng. Chem., 52, 28 (2017).
19. R. Yang, Z. Xu, S. Yang, I. Michos, L.-F. Li, A. P. Angelopoulos, and J. Dong, J. Membrane Sci., 450, 12 (2014).
20. K. B. Hueso, M. Armand, and T. Rojo, Energ. Environ. Sci., 6, 734 (2013).
21. X. Lu, G. Li, J. Y. Kim, J. P. Lemmon, V. L. Sprenkle, and Z. Yang, J. Power Sources, 215, 288 (2012).
22. X. Lu, G. Li, J. Y. Kim, D. Mei, J. P. Lemmon, V. L. Sprenkle, and J. Liu, Nat. Commun., 5, 4578 (2014).
23. Y. Pan, S. Chou, H. K. Liu, and S. X. Dou, Natl. Sci. Rev., nws037 (2017).
24. N.-S. He, F. Pan, Z. Zhang, Q. Wang, H. Li, X. Huang, and L. Chen, Nat. Commun., 8, 14629 (2017).
25. S. P. Butee, K. R. Kambale, and M. Firodiya, Process. Appl. Ceram., 10, 67 (2016).
26. O. Kargina, B. MacDougall, Y. M. Kargin, and L. Wang, J. Electrochem. Soc., 144, 3715 (1997).
27. L. Palombi, Electrochim. Acta, 56, 7442 (2011).
28. A. A. Shinkle, A. E. S. Sleighbolome, L. T. Thompson, and C. W. Monroe, J. Appl. Electrochem., 41, 1191 (2011).
29. M.-S. Park, N.-J. Lee, S.-W. Lee, K. J. Kim, D.-J. Oh, and Y.-J. Kim, ACS Appl. Mater. Inter., 6, 10729 (2014).
30. J.-H. Kim, K. J. Kim, M.-S. Park, N. J. Lee, U. Hwang, H. Kim, and Y.-J. Kim, Electrochem. Commun., 13, 997 (2011).
31. K. Gong, Q. Fang, S. Gu, S. F. Y. Li, and Y. Yan, Environ. Sci., 8, 3515 (2015).
32. T. L. Riechel, L. J. De Hayes, and D. T. Sawyer, Inorg. Chem., 15, 1900 (1996).
33. M. A. Nawi and T. L. Riechel, Inorg. Chem., 21, 2268 (1982).
34. Y. Ashraf Gandomi, D. Aaron, and M. Mench, Membranes, 7, 29 (2017).
35. W. Linert, E. Herlinger, P. Margl, and R. Boˇcka, J. Coord. Chem., 28, 1 (1993).
36. E. Garriga, G. Micera, and D. Sanna, Inorg. Chim. Acta, 359, 4470 (2006).
37. D. Zhang, Q. Liu, X. Shi, and Y. Li, J. Power Sources, 203, 201 (2012).
38. A. E. S. Sleighbolome, A. A. Shinkle, Q. Liu, Y. Li, C. W. Monroe, and L. T. Thompson, J. Power Sources, 196, 5742 (2011).
39. J. D. Saraidaridis, B. M. Bartlett, and C. W. Monroe, J. Electrochem. Soc., 163, A1239 (2016).