Surface functionalization of polyoxovanadium clusters: Generation of highly soluble charge carriers for nonaqueous energy storage

Journal:	*ChemComm*
Manuscript ID	CC-COM-07-2019-005380.R1
Article Type:	Communication

COMMUNICATION

Surface functionalization of polyoxovanadium clusters: Generation of highly soluble charge carriers for nonaqueous energy storage

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Here, we demonstrate the effects of surface functionalization on a tunable series of nano-sized electron shuttles toward improving their function in nonaqueous energy storage. The synthesis of a series of polyoxovanadium clusters featuring bridging ether functional groups is reported, revealing the influence of bridging "R" group identity on electrochemical stability in solution. Furthermore, the presence of bridging ether moeities yields enhanced solubility in acetonitrile (up to 1.2 M), highlighting synthetic strategies for the development of organofunctionalized polyoxometalate-derived charge carriers for nonaqueous, electrochemical energy storage.

Nonaqueous redox flow batteries (NRFBs) are a promising technology for grid-scale energy storage that make use of dissolved, redox-active molecules to reversibly store energy.[1] The use of nonaqueous solvents enables active species to be selected from a diverse library of organic and inorganic molecules that are compatible with this medium, creating the potential for the identification of a more cost-effective device.[2] However, despite intense research efforts, charge carrier solubility remains a key limitation for the viability of NRFB devices. As such, research in NRFB development has turned toward the discovery of new electroactive materials featuring structural components that improve this physical property of charge carriers in organic media.

Polyoxometalates (POMs) have emerged as an exciting new class of molecules for solution-state energy storage, attracting attention due to their electrochemical stability across numerous charge states. Systems such as the $[P_2W_{18}O_{62}]^{6-}$ core, recently described by Cronin and coworkers, highlight the potential for POMs in RFB application, through the demonstration of reversible storage of up to eighteen electrons per molecule in solution.[3] However, to date, the application of POMs as charge carriers has been restricted to aqueous energy storage, owing to their limited solubility in organic solvents. While metal coordination complexes and organic charge carriers have seen steady improvements in their solubility in organic solvents through targeted synthetic adaptations,[4-7] similar molecular modifications are challenging for POM-based systems. Despite the established structural diversity of POMs, strategies for solubilizing these wholly inorganic metal-oxide clusters have been limited to counter-ion substitution, making POM solubility highly dependent on overall solution charge-state.[8]

Research in our group has broadly focused on translating the synthetic strategies employed by organic and inorganic chemists to the field of POM synthesis, toward the development of a robust, soluble, multielectron NRFB charge carrier. Toward this goal, we have identified a family of polyoxovanadate alkoxide (POV-alkoxide) clusters, $[V_6O_7(OR)_{12}]$, as a class of tuneable synthetic frameworks (Figure 1).[9-15] Their unique structure makes POV-alkoxides something of a hybrid: The robust metal-oxide core features a delocalized electronic structure which can facilitate multiple reversible redox events—characteristic of a POM; yet the organic functional groups that flank the surface of the cluster have proven to serve as handles for tuning the physicochemical properties of the series. Through a series of synthetic investigations, we have demonstrated the extent of this tunability to great effect, improving the electrochemical stability,[9] electron-transfer kinetics,[14] and solubility[11] of this family of compounds.

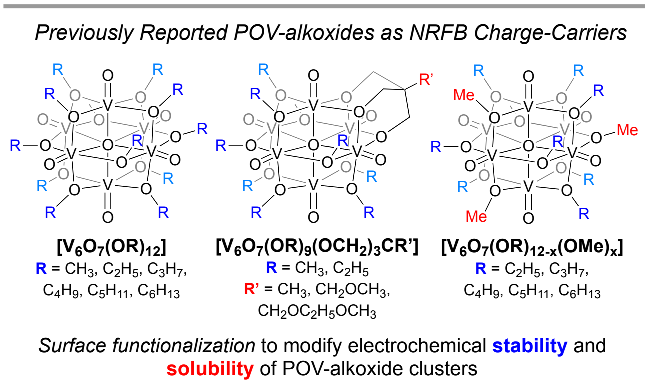

Figure 1. POV-alkoxide clusters as charge carriers for NRFBs.

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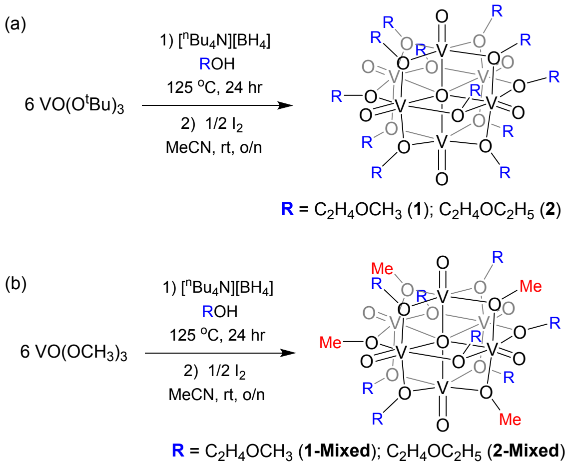
Electronic Supplementary Information (ESI) available: See DOI: 10.1039/



Scheme 1. Synthesis of (a) homoleptic ether-bridged POVs **1** and **2** (b) mixed ether-bridged POV-alkoxides **1-Mixed** and **2-Mixed**.

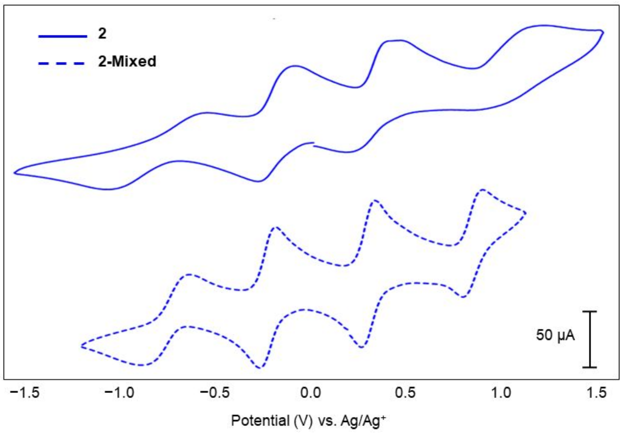


Figure 2. Cyclic voltammograms (CVs) of homoleptic complex **2** and heteroleptic **2-Mixed** in MeCN with [^{n}Bu$_4$N][PF$_4$] supporting electrolyte.

Recently, we have identified the function of appended ether moieties to yield significant improvements in the solubility POV-alkoxides, discovering that installation of a tris-alkoxy ether functional group to a single face of the cluster improves the solubility from 0.05 M to 0.6 M without changing the redox properties of the system (Figure 1).[11] Given the significant improvement in solubility that results from incorporation of this single ether moiety to the POV-alkoxide framework, we hypothesized that generation of a cluster featuring *several* ether functional groups would yield a particularly soluble POM-derived, NRFB charge carrier. To develop such a redoxmer, we targeted ether substitutions directly at the bridging-alkoxide position, generating the homoleptic clusters [$V_6O_7(OC_2H_4OCH_3)_{12}$] (**1**) and [$V_6O_7(OC_2H_4OC_2H_5)_{12}$] (**2**). Unlike the tris-alkoxy ether functionalized POV-alkoxide clusters, wherein a the ether ligand is synthesized separately,[11] complexes **1** and **2** incorporate ether-moieties directly at bridging-alkoxide positions from commercially available, industrial solvents (Scheme 1). Characterization of **1** and **2** was performed via electrospray ionization mass spectrometry (ESI-MS), ^{1}H NMR, and electronic absorption spectroscopy, supporting formation of the desired clusters (Figure S1-S3). In the case of complex **1**, X-ray analysis unambiguously confirms the structure of the charge carrier (Figure S4, Table S1).

Complexes **1** and **2** are isolated as viscous oils at room temperature, and exhibit good miscibility with acetonitrile. To quantify their solvent compatibility, we measured the solubilities of each cluster in acetonitrile with 0.1 M [^{n}Bu$_4$N][PF$_6$], thus modeling the environment of an NRFB cell (Figures S5-S6). The solubilities of complexes **1** and **2** were determined to be 0.934 and 0.923 M, respectively (Table 1), marking the highest achieved nonaqueous solubility for POM-based charge carriers reported to date.

Critical for NRFB application is that the redox-active molecule be stable across each of the charge states accessed during battery cycling. Cyclic voltammograms (CV) of neutral **1** and **2**, measured in acetonitrile, reveal four redox events over a ~2 V window and an open circuit potential at ~0 V (Figure 2, Table 1). As in the case of the previously reported alkyl-bridged POV series,[13, 14] modification of the bridging R groups yields no significant shifts in $E_{1/2}$ values for each of the redox events of **1** and **2**. Bulk electrolysis was used to probe the accessibility and stability of the “fully charged” di-anionic and di-cationic charge states of **1** and **2**. In the case of complex **1**, monitoring of the charged solutions by CV revealed electrochemical stability in the di-anionic state, however bulk oxidation to +1.5 V yields cluster decomposition (Figure S7a). In the case of complex **2**, despite apparent reversibility in the CV, neither the di-anionic nor the di-cationic charge states were electrochemically accessible (Figure S7b).

Pleased with the solubility improvements observed for complexes **1** and **2**, but disappointed by their electrochemical instability, we sought to further modify the POV surface to develop a system with optimal physicochemical properties. We have previously reported a series of polyoxovanadate-alkoxide clusters bearing a mixture of alkoxide ligands, of the form [$V_6O_7(OR)_{12-x}(OCH_3)_x$], where R = C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, and “x” is variable within a single product.[14] Though technically impure, the stability, kinetics, and solubilities of these mixed-POV-

Table 1. Solubility and electrochemical parameters of all complexes.

Complex	Solubility (M)	$[V^{IV}_6]^{2-}$ / $[V^V_1V^{IV}_5]^{-}$ [a]	$[V^V_1V^{IV}_5]^{-}$ / $[V^V_2V^{IV}_4]^0$ [a]	$[V^V_2V^{IV}_4]^0$ / $[V^V_3V^{IV}_3]^{+}$ [a]	$[V^V_3V^{IV}_3]^{+}$ / $[V^V_4V^{IV}_2]^{2+}$ [a]
1	0.934	−0.74 (1.09)	−0.16 (1.01)	0.34 (0.98)	1.06 (0.22)
2	0.923	−0.70 (1.18)	−0.17 (1.03)	0.34 (1.00)	1.15 (0.14)
1-Mixed	1.174	−0.67 (1.12)	−0.17 (1.04)	0.31 (1.09)	0.82 (0.32)
2-Mixed	0.956	−0.67 (1.10)	−0.19 (0.95)	0.31 (0.98)	0.85 (0.87)

[a] Standard potentials (measured *vs.* Ag/Ag$^+$) identified using cyclic voltammetry at 100 mV s^{-1} of 1 mM solutions of each complex with 0.1 M [^{n}Bu$_4$N][PF$_6$] supporting electrolyte in acetonitrile. Values in parentheses indicate ratios of the cathodic to anodic peak heights (i_c/i_a).

alkoxide solutions are categorically improved over their homoleptic congeners. We therefore targeted the synthesis of mixed ether/methoxide clusters $[V_6O_7(OC_2H_4OCH_3)_{12-x}(OCH_3)_x]$ (**1-Mixed**) and $[V_6O_7(OC_2H_4OC_2H_5)_{12-x}(OCH_3)_x]$ (**2-Mixed**), hypothesizing that the improvements in physicochemical properties observed for the mixed-aliphatic alkoxide species could be similarly imparted to the ether-bridged POV clusters. Indeed, **1-Mixed** and **2-Mixed** could be generated following similar procedures to those used for the mixed-alkoxide solutions,[14] with ESI-MS analysis revealing the expected normal distribution of products (Figure S8). Further characterization of **1-Mixed** and **2-Mixed** via ^{1}H NMR and electronic absorption spectroscopies matches that anticipated for the heteroleptic products (Figure S3 and S9).

Like their homoleptic analogues, **1-Mixed** and **2-Mixed** present as oils at room temperature. Solubilities of **1-Mixed** and **2-Mixed** were measured to be 1.174 and 0.956 M, respectively (Table 1, Figures S10-S11). As was the case for the mixed-alkoxide POV series,[14] both **1-Mixed** and **2-Mixed** possess enhanced solubilities over their homoleptic congeners **1** and **2.** We attribute this to reduced symmetry of the clusters which inhibits ordered packing of the molecules.

The CVs of **1-Mixed** and **2-Mixed** again reveal a set of four, evenly-spaced one-electron redox events, with similar $E_{1/2}$ values to the homoleptic clusters **1** and **2** (Figure 2, Table 1). Despite being a mixture of compounds, the CVs of **1-Mixed** and **2-Mixed** display electrochemical behavior that would be expected of a pure solution, in line with our observations for the mixed-aliphatic alkoxide clusters.[14] Similarly, the diffusion coefficients (D_0) and heterogeneous electron transfer constants (k_0) for both **1-Mixed** and **2-Mixed** exceed those of the homoleptic clusters by nearly an order of magnitude (Table S2).

Bulk electrolysis along with CV monitoring was used to determine the accessibility and stability of the di-anionic and di-cationic charge states for both **1-Mixed** and **2-Mixed** (Figure S13). For **1-Mixed**, analysis revealed similar electrochemical responses to highly oxidizing as reducing conditions as the homoleptic cluster **1**. For **2-Mixed**, both the di-anionic and di-cationic charge states can be electrochemically accessed, with CV monitoring of charged solutions revealing only a small change following reduction (namely, a slight loss of i_p for the redox event at $E_{1/2} = -0.67$ V). This is an improvement in stability over complex **2**.

The electrochemical behavior of the ether-bridged POVs observed by CV and bulk electrolysis is somewhat perplexing. While we anticipated that **1-Mixed** and **2-Mixed** might have improved electrochemical properties compared to their homoleptic equivalents, we did not expect that **1** and **2** would possess such diminished redox behavior. Even the heteroleptic complex, **1-Mixed**, exhibits relatively poor redox stability, resulting in irreversibility of the [**1-Mixed**]$^+$/[**1-Mixed**]$^{2+}$ couple at fast scan rates. Given that **1**, **1-Mixed**, and **2** possess analogous chain lengths to the previously published complexes $[V_6O_7(OC_4H_9)_{12}]$, $[V_6O_7(OC_4H_9)_{12-x}(OCH_3)_x]$, and $[V_6O_7(OC_5H_{11})_{12}]$, respectively, all of which demonstrate rapid diffusion kinetics,[13, 14] it cannot be assumed that the poor behavior of the ether-bridged complexes is a result of their size.

For the homoleptic POV-alkoxide series, we observed improved redox stability upon incorporation of additional CH_2 units within the bridging alkoxides.[9] This improvement has been credited to the positive inductive effect imparted to the cluster by the additional electron-releasing carbon atom.[9, 16] Given the diminished redox profiles and electrochemical instability of the ether-bridged POVs, we hypothesize that the addition of oxygen to the bridging-R groups has the opposite influence—that the electronegative oxygen atom has a negative inductive effect, which in turn destabilizes the cluster core. This may explain why the electrochemical properties of **1** and **2** are weakened compared to **1-Mixed** and **2-Mixed**, clusters that possess fewer bridging-ethers moieties. As for the improved electrochemical stability of **2-Mixed** compared to **1-Mixed**, this likely results from the combination of several structural factors. Firstly, the bridging ether groups of **2-Mixed**, $-OC_2H_4OC_2H_5$, have one additional carbon center compared to those in **1-Mixed** ($-OC_2H_4OCH_3$). This may serve to slightly offset the negative inductive effect imparted by the oxygen atom. It is also possible that the terminal methoxy group of the $-OC_2H_4OCH_3$ moiety is more reactive than the terminal ethoxy of $-OC_2H_4OC_2H_5$, contributing to the instability of **1-Mixed**. Lastly, we observe that for **2-Mixed** there is a relatively greater number of substituted methyl units and overall broader distribution of products when compared to **1-Mixed** (Figure S8). While for **1-Mixed**, x varies from 0-4, and is centered on x = 2, in **2-Mixed**, x varies from 0-6 and is centered on x = 3. The overall reduction in number of destabilizing ether units in **2-Mixed** may influence its improved electrochemical performance.

Next, we pursued further analysis of the electrochemical performance of **2-Mixed** under NRFB conditions. The accessibility of five charge states indicates that **2-Mixed** can be used as both the posolyte and negolyte in an NRFB cell, storing two electrons at each electrode. To assess the charge-discharge characteristics of **2-Mixed** in such a charging schematic, a two-compartment H-cell was assembled as an approximation of the conditions in a flow system. The H-cell was divided by a microporous frit (1.6 µm), with each compartment containing high surface area carbon electrodes and identical solutions of **2-Mixed** (1 mM) with $[^nBu_4N][PF_6]$ (0.1 M) in acetonitrile (5 mL). Galvanostatic cycling of the cell was performed to 60 % state of charge (SOC), with charging and discharging currents of 0.1 mA and voltage cutoffs of 2.5 and 0.1 V.

The voltage trace of H-cell testing with **2-Mixed** reveals several short plateaus at varying potentials during both charging and discharging (Figure S15). This stands in contrast with the well-defined redox processes observed in the CV of **2-Mixed**, which would suggest two distinct charging and discharging plateaus should be observed.[9] We attribute the perturbed appearance of the voltage trace to the delocalization of electron density within the cluster core, a phenomenon likewise observed for previously characterized POM-based charge carriers.[17-19] Coulombic efficiencies remained >95 % throughout each of the thirty cycles, though a steady capacity fade is also observed (Figure S15; from 0.59 to 0.44 mAh over 30 cycles). Analysis of the catholyte and anolyte solutions following charge-discharge using CV indicates partial decomposition of **2-Mixed** localized to the oxidative half-cell (Figure S16). The decomposition is likely a cause for the observed progressive capacity loss.

Preliminary testing at the full cell level was conducted using solutions of **2-Mixed** (20 mM) with $[^{n}Bu_4N][PF_6]$ (0.1 M) in acetonitrile (5 mL) separated by 20 sheets of Tonen (E20MMS) separator. Solutions were flowed at 2.5 mL/min over a 5 cm^2 carbon electrode with galvanostatic charging and discharging at 10 mA. Initial testing using voltage cutoffs of 2.5 and 0.05 V, analogous to H-cell testing parameters, revealed a similar voltage trace to that observed for static cycling (Figures S17-S18). However, coulombic efficiencies are markedly lower, and steadily decline over 20 cycles (Figure S19; from 88% to 85%). CV analysis of the electrolyte solutions following cycling reveals decomposition in both the anolyte and catholyte, the probable cause for the downward trend in both coulombic efficiency and electrochemical yield. Likely this decomposition occurs only in the oxidized solution (anolyte), but species crossover results in the progressive depletion of charge carriers in both solutions. Still, given the observed degradation in both the preliminary H-cell and flow-cell experiments, higher concentration flow-cell testing was not pursued.

Understanding the physical and electrochemical effects that result from the inclusion of bridging alkoxide ligands that contain ether functional groups is essential for the future of POV-based charge carriers, as these moieties are established to yield improved solubility in acetonitrile.[4, 7, 11] Here, we report that the identity and quantity of ether functional groups have significant influence on the electrochemical properties of the system. While previous work has demonstrated that functionalization with a tris-alkoxy ether-moeity, as in $[V_6O_7(OC_2H_5)_9(OCH_2)_3CH_2OC_2H_4OCH_3]$, yields no reduction in electrochemical performance,[11] in this work we see significant losses in reversibility upon ether functionalization at the bridging-position. This indicates that ether moieties can be included in the POV scaffold, so long as they are sufficiently removed from the hexavanadium core. Or, possibly, the results with $[V_6O_7(OC_2H_5)_9(OCH_2)_3CH_2OC_2H_4OCH_3]$ suggest that the presence of a single ether moiety is not sufficient to cause disruption of the redox properties of the system. Current efforts in our laboratory are exploring these hypotheses. In sum, the insights reported here highlight avenues for future research into designing soluble and stable POV-based charge carriers.

Conflicts of interest

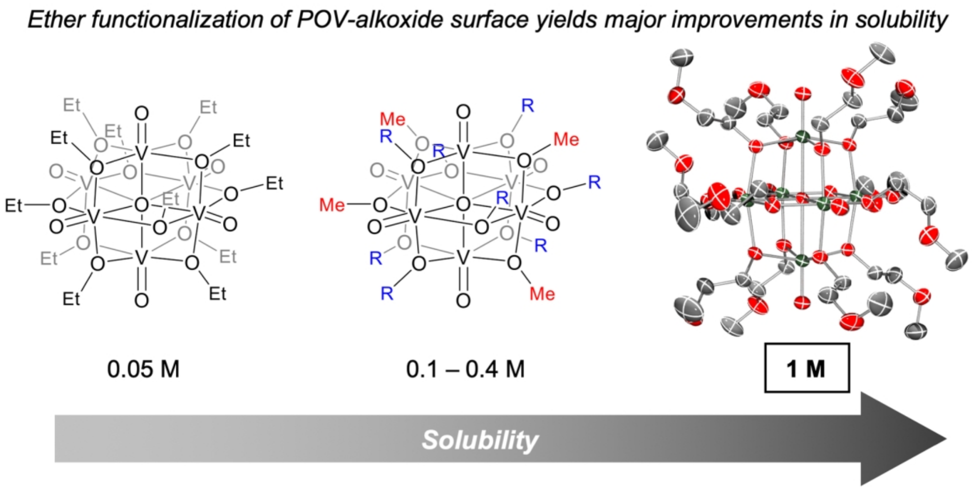
There are no conflicts to declare.

Acknowledgements

The authors would like to thank Timothy R. Cook for helpful discussions. E. M. M. and L. E. V. would like to thank the University of Rochester for funding supporting this research, as well as the National Science Foundation (MRI-1725028). L. E. V. is supported by the National Science Foundation Graduate Research Fellowship Program (DGE-1419118). The efforts of T. M. A. and H D. P. III were was generously supported by program manager Dr. Imre Gyuk through the U.S. Department of Energy, Office of Electricity Delivery and Energy Reliability. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

References

1. K. Gong, Q. Fang, S. Gu, S. F. Y. Li and Y. Yan, *En. & Environ. Sci.*, 2015, **8**, 3515-3530.
2. R. Dmello, J. D. Milshtein, F. R. Brushett and K. C. Smith, *J. Power Sources*, 2016, **330**, 261-272.
3. J.-J. Chen, M. D. Symes and L. Cronin, *Nat. Chem.*, 2018, **10**, 1042-1047.
4. J. A. Suttil, J. F. Kucharyson, I. L. Escalante-Garcia, P. J. Cabrera, B. R. James, R. F. Savinell, M. S. Sanford and L. T. Thompson, *J. Mater. Chem. A*, 2015, **3**, 7929-7938.
5. P. J. Cabrera, X. Yang, J. A. Suttil, R. E. M. Brooner, L. T. Thompson and M. S. Sanford, *Inorg. Chem.*, 2015, **54**, 10214-10223.
6. C. S. Sevov, S. L. Fisher, L. T. Thompson and M. S. Sanford, *J. Am. Chem. Soc.*, 2016, **138**, 15378-15384.
7. J. D. Milshtein, A. P. Kaur, M. D. Casselman, J. A. Kowalski, S. Modekrutti, P. L. Zhang, N. Harsha Attanayake, C. F. Elliott, S. R. Parkin, C. Risko, F. R. Brushett and S. A. Odom, *En. & Environ. Sci.*, 2016, **9**, 3531-3543.
8. J.-J. J. Chen and M. A. Barteau, *Ind. & Eng. Chem. Res.*, 2016, **55**, 9857-9864.
9. L. E. VanGelder, A. M. Kosswattaarachchi, P. L. Forrestel, T. R. Cook and E. M. Matson, *Chem. Sci.*, 2018, **9**, 1692-1699.
10. L. E. VanGelder and Ellen M. Matson, *J. Mater. Chem. A*, 2018, **6**, 13874-13882.
11. L. E. VanGelder, B. E. Petel, O. Nachtigall, G. Martinez, W. W. Brennessel and E. M. Matson, *ChemSusChem*, 2018, **11**, 4139-4149.
12. B. Schurr, O. Nachtigall, L. E. VanGelder, W. W. Brennessel and E. M. Matson, *J. Coord. Chem.*, 2019, **7**, 1267-1286.
13. A. M. Kosswattaarachchi, L. E. VanGelder, O. Nachtigall, J. P. Hazelnis, W. W. Brennessel, E. M. Matson and T. R. Cook, *J. Electrochem. Soc.*, 2019, **166**, A464-A472.
14. L. E. VanGelder, E. Schreiber and E. M. Matson, *J. Mater. Chem. A*, 2019, **7**, 4893-4902.
15. L. E. VanGelder, T. R. Cook and E. M. Matson, *Comments on Inorg. Chem.*, 2019, **39**, 51-89.
16. C. Daniel and H. Hartl, *J. Am. Chem. Soc.*, 2005, **127**, 13978-13987.
17. J. Friedl, M. V. Holland-Cunz, F. Cording, F. L. Pfanschilling, C. Wills, W. McFarlane, B. Schricker, R. Fleck, H. Wolfschmidt and U. Stimming, *En. & Environ. Sci.*, 2018, **11**, 3010-3018.
18. H. D. Pratt, N. S. Hudak, X. Fang and T. M. Anderson, *J. Power Sources*, 2013, **236**, 259-264.
19. H. D. Pratt, W. R. Pratt, X. Fang, N. S. Hudak and T. M. Anderson, *Electrochem. Acta*, 2014, **138**, 210-214.



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