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Improved solubility of titanium-doped polyoxovanadate charge carriers for symmetric non-aqueous redox flow batteries†

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Non-aqueous redox flow batteries constitute a promising solution for grid-scale energy storage due to the ability to achieve larger cell voltages than can be readily accessed in water. However, their widespread application is limited by low solubility of the electroactive species in organic solvents. In this work, we demonstrate that organic functionalization of titanium-substituted polyoxovanadate-alkoxide clusters increases the solubility of these assemblies over that of their homoleptic congeners by a factor of >10 in acetonitrile. Cyclic voltammetry, chronoamperometry, and charge–discharge cycling experiments are reported, assessing the electrochemical properties of these clusters relevant to their ability to serve as multielectron charge carriers for energy storage. The kinetic implications of ligand variation are assessed, demonstrating the role of ligand structure on the diffusivity and heterogeneous rates of electron transfer in mixed-metal charge carriers. Our results offer new insights into the impact of structural modifications on the physicochemical properties of these assemblies.

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Introduction

Redox flow batteries (RFBs) are electrochemical energy storage devices that interconvert chemical and electrical energy using soluble redox active species.¹ They can be classified as aqueous or non-aqueous depending upon the solvent composition. To date, the most advanced flow battery technologies leverage soluble redox couples in acidic, aqueous solutions.² However, non-aqueous RFBs (NAqRFBs) remain an intriguing alternative, as the use of organic solvents offers a wide range of working temperatures, and potentially higher energy densities due to the improved electrochemical stability window of organic solvents.³ Successful implementation of NAqRFB technologies in grid-scale energy storage is limited by lack of suitable membranes, cost and safety risks associated with organic solvents, and low solubilities of many redox-active species in polar organic solvents like acetonitrile. Additional

challenges for NAqRFBs manifest as poor round-trip voltage efficiencies owing to three major losses that result in the form of overpotentials required for charge–discharge reactions – transport, resistive, and kinetic losses.⁴ For instance, the use of organic solvents as electrolytes can result in higher ionic resistances as compared to aqueous solutions. These transport losses can impact the overall efficiency and performance of NAqRFBs and may be more pronounced as compared to their aqueous counterparts.⁵ Accordingly, charge carriers must be designed to exhibit (1) high solubility in organic solvent(s); (2) kinetically facile and reversible redox reactions; (3) a large potential window between the desired redox events; and (4) high chemical and electrochemical stability across the required oxidation states.

A popular method for the development of efficient charge carriers for applications in NAqRFBs is designing metal-based coordination complexes that exhibit at least two redox events exhibiting large (>1 V) differences in standard reduction potential. Such systems allow for symmetric flow battery design, wherein the posolyte and negolyte are comprised of the same material, preventing cross-contamination of the active species due to membrane crossover.^{6,7} One particularly intriguing class of redox-active inorganic compounds for this application are polyoxometalates (POMs). These metal oxide clusters are electrochemically robust, and display multiple redox events spread across a wide range of potentials,⁸ which makes them excellent candidates for symmetric cell design.^{9–13}

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However, their limited solubility in organic solvent(s) is a major challenge to obtain functional RFB systems due to the fact that important battery metrics, including energy conversion efficiency, volumetric energy density, and capacity, depend fundamentally on this property.^{14,15}

One strategy for improving the solubility of POMs in organic solvent invokes incorporation of organic moieties at the metal oxide surface.^{16–19} In recent years, there has been increased attention paid to the synthesis of POM-based organic–inorganic hybrids, which are generated *via* covalent grafting of organic functional groups to the surface of the POM framework.^{20,21} This technique is advantageous as it allows the attachment of specific functional groups in a predictable and reliable manner. The formation of organofunctionalized, polyoxovanadates, henceforth referred to as polyoxovanadate-alkoxide (POV-alkoxide) clusters, is a particularly popular area of research, due to the increased basicity of bridging oxide positions at the surface of the cluster.^{22–24} Zubietta and coworkers exemplified this approach through the isolation of a wide array of hexavanadium systems featuring trisalkoxy- μ -bridging groups (TRIOl^R).^{25–27} These TRIOl^R ligands are well established in the literature owing to their compatibility with a wide variety of functional groups, which allows to tune the physicochemical properties of the resultant cluster.^{26,28–30}

In the context of the development of charge carriers for NAqRFBs, our group has reported the installation of TRIOl moieties at the surface of low-valent POV-alkoxide clusters (Fig. 1).^{31–33} These synthetic modifications increase the solubility by an order of magnitude in comparison to the homoleptic con-

gener. In this work, we report the functionalization of the surface of titanium-substituted POV-alkoxide clusters with the same solubility-enhancing TRIOl ligands. Interest in these synthetic targets results from prior work from our laboratory, establishing that incorporation of titanium ions within the Lindqvist core results in widening of the redox window of the charge carrier by ~ 1 V. However, the poor solubility of the methoxide-substituted derivative of the heterometallic assembly (<0.05 M) motivates additional structural modifications to increase the energy density of this system.³⁴ Our results summarize the synthesis of two new TRIOl-substituted TiPOV-alkoxide clusters, as well as their solubilities and performance as charge carriers in NAqRFBs. This synthetic modification improves the solubility of these clusters by an order of magnitude. Collectively, the understanding gained from these investigations informs strategies for improved energy densities in NAqRFBs.

Experimental

General considerations

Unless otherwise noted, all manipulations were carried out in the absence of water and oxygen in a UniLab MBraun inert atmosphere glovebox under a dinitrogen atmosphere. The glassware was oven dried for a minimum of 4 hours and cooled in an evacuated antechamber prior to use in the drybox. Anhydrous methanol was purchased from Sigma-Aldrich and stored over activated 4 Å molecular sieves purchased from Fisher Scientific. All other solvents were dried and deoxygenated on a Glass Contour System (Pure Process Technology, LLC) and stored over activated 3 Å molecular sieves purchased from Fisher Scientific. $\text{Ti}(\text{O}^i\text{Pr})_4$ was purchased from Sigma Aldrich and used as received. Tetrabutylammonium hexafluorophosphate ($[\text{tBu}_4\text{N}][\text{PF}_6]$) was purchased from Sigma-Aldrich. $[\text{tBu}_4\text{N}][\text{PF}_6]$ was recrystallized thrice using hot ethanol, and stored under dynamic vacuum for a minimum of two days prior to use. $\text{VO}(\text{OCH}_3)_3$,³⁵ $[\text{Ti}_2\text{V}_4\text{O}_5(\text{OCH}_3)_{14}]$,³⁶ $\text{CH}_3\text{C}(\text{OCH}_2)_3\text{CCH}_2\text{OCH}_3$,³⁷ and $\text{CH}_3\text{C}(\text{OCH}_2)_3\text{CCH}_2\text{OC}_2\text{H}_4\text{OCH}_3$ ³⁷ were synthesized according to previously reported methods.

^1H NMR spectra were recorded at 500 MHz on Bruker DPX-500 spectrometer locked on the signal of deuterated solvents. All chemical shifts were reported relative to the peak of residual ^1H signal in deuterated solvents.³⁸ CD_3CN and CDCl_3 were purchased from Cambridge Isotope Laboratories and used as received. Electronic absorption measurements were recorded at room temperature in acetonitrile (MeCN) in a sealed 1 cm quartz cuvette with an Agilent Cary 60 UV/Vis spectrophotometer. Infrared spectra were recorded on a Shimadzu IRAffinity-1 Fourier Transform Infrared spectrophotometer and are reported in wavenumbers (cm^{-1}).

Modified procedure for the preparation of protected ligand precursor (PLP)

The synthesis of PLP has been modified from prior reports.^{31,39} The preparation of PLP was conducted outside of

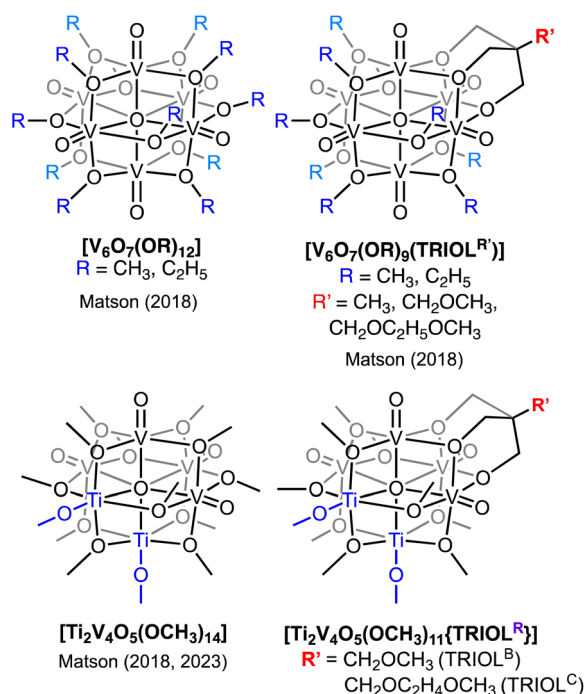


Fig. 1 Overview of the use of tridentate ligands to enhance the solubility, and thus theoretical energy density, of POV-alkoxide clusters as charge carriers for NAqRFBs.

the glovebox. A 1000 mL round-bottomed flask was charged with ground pentaerythritol (50 g, 367 mmol) and *p*-toluene-sulfonic acid monohydrate (0.9 g, 5.2 mmol) and a stir bar. The flask was placed under an atmosphere of argon and equipped with a reflux condenser. Subsequently, toluene (500 mL) was added. The reaction was refluxed for 1 h, after which triethyl orthoacetate (75 mL, 409 mmol) was added. The resulting suspension was refluxed until the solution turned clear, with no solid residue visible (~48 h). 1.1 mL of triethyl amine was added to the flask, and the solution was filtered while hot. The solution was concentrated under reduced pressure to obtain PLP as a white crystalline solid. Characterization of the obtained product was performed *via* ^1H NMR spectroscopy and matched with the reported spectrum (ESI, Fig. S1†).

Synthesis of $[\text{Ti}_2\text{V}_4\text{O}_5(\text{OCH}_3)_{11}(\text{OCH}_2)_3\text{CCH}_2\text{OCH}_3]$ ($\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$)

$\text{VO}(\text{OCH}_3)_3$ (0.25 g, 1.56 mmol), titanium isopropoxide (0.22 g, 0.78 mmol), and PL^{b} (0.14 g, 0.78 mmol) were combined in the Teflon liner of a 50 mL stainless steel autoclave reactor and dissolved in methanol (25 mL). The reactor was sealed and heated to 150 °C for 48 h. Initial workup of the cluster was performed outside of the glovebox under ambient conditions. After cooling the reaction vessel to room temperature, the crude mixture was passed through a syringe filter to remove any solid remains and the volatiles were removed under reduced pressure. The dark brown residue was dried under reduced pressure on the Schlenk line for 4 hours and transferred back to the glovebox for further purification. The product was extracted with diethyl ether (3 × 10 mL) and filtered over silica to recover a brown filtrate. Volatiles were again removed under vacuum inside the glovebox to yield a dark brown oil. The obtained oil was again dissolved in diethyl ether (~20 mL) and the contents were filtered over silica inside the glovebox. The resulting product was dried under reduced pressure to yield $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ as a dark brown oil. Yield: 0.14 g, 0.16 mmol, 21%. FT-IR (ATR, cm^{-1}): 1125 ($\text{O}_t\text{-CH}_3$), 1017 ($\text{O}_b\text{-CH}_3$), 976 (V=O). UV-Vis (CH_3CN , 21 °C) $\lambda = 418$ nm ($\epsilon = 656 \text{ M}^{-1} \text{ cm}^{-1}$), 1000 nm ($\epsilon = 121 \text{ M}^{-1} \text{ cm}^{-1}$). Elemental analysis for $\text{C}_{17}\text{H}_{44}\text{O}_{20}\text{Ti}_2\text{V}_4$ ($M_{\text{W}} = 889.56 \text{ g mol}^{-1}$): calc. C, 24.98; H, 5.38; N, 0.00. Found, C, 25.03; H, 5.07; N: 0.08.

Synthesis of $[\text{Ti}_2\text{V}_4\text{O}_5(\text{OCH}_3)_{11}(\text{OCH}_2)_3\text{CCH}_2\text{OC}_2\text{H}_4\text{OCH}_3]$ ($\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$)

$\text{VO}(\text{OCH}_3)_3$ (0.25 g, 1.56 mmol), titanium isopropoxide (0.22 g, 0.78 mmol), and PL^{c} (0.18 g, 0.78 mmol) were combined in the Teflon liner of a 50 mL stainless steel autoclave reactor and dissolved in methanol (25 mL). The reactor was sealed and heated to 150 °C for 48 h. Initial workup of the cluster was performed outside of the glovebox under ambient conditions. After cooling the reaction vessel to room temperature, the crude mixture was passed through a syringe filter to remove any solid remains and the volatiles were removed under reduced pressure. The dark brown residue was dried over the

Schlenk line for 4 hours and transferred back to the glovebox for further purification. The product was extracted with diethyl ether (3 × 10 mL) and filtered over silica. Volatiles were again removed under vacuum inside the glovebox to yield a dark brown oil. The obtained oil was dissolved in diethyl ether (~20 mL) and the contents were filtered over silica inside the glovebox. The resulting product was dried under reduced pressure to yield $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$ as a dark brown oil. Yield: 0.17 g, 0.19 mmol, 26%. FT-IR (ATR, cm^{-1}): 1125 ($\text{O}_t\text{-CH}_3$), 1018 ($\text{O}_b\text{-CH}_3$), 972 (V=O). UV-Vis (CH_3CN , 21 °C) $\lambda = 392$ nm ($\epsilon = 877 \text{ M}^{-1} \text{ cm}^{-1}$), 1000 nm ($\epsilon = 122 \text{ M}^{-1} \text{ cm}^{-1}$). Elemental analysis for $\text{C}_{19}\text{H}_{48}\text{O}_{21}\text{Ti}_2\text{V}_4$ ($M_{\text{W}} = 933.62 \text{ g mol}^{-1}$): calc., C, 26.37; H, 5.56; N, 0.00. Found, C, 26.79; H, 5.46; N, -0.027.

Cyclic voltammetry

Cyclic voltammetry (CV) was performed using a three-electrode setup inside a nitrogen filled glove box (MBraun, USA) using a Bio-Logic SP 150 potentiostat/galvanostat and the EC-Lab software suite. The concentrations of Ti_2V_4 ($[\text{Ti}_2\text{V}_4\text{O}_5(\text{OCH}_3)_{14}]$), $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$, and $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$ were kept at 5 mM and 100 mM supporting electrolyte ($[\text{Bu}_4\text{N}][\text{PF}_6]$) was used. CVs were recorded using a 3 mm diameter glassy carbon working electrode (CH Instruments, USA), a Pt wire auxiliary electrode (CH Instruments, USA), and a $\text{Ag}|\text{Ag}^+$ non-aqueous reference electrode with 0.01 M AgNO_3 in 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ in MeCN (BASi, USA). CVs were iR compensated *via* positive feedback at 95% with solution resistance measurements collected at 100 kHz using the ZIR tool included within the EC-Lab software. The remaining 5% of uncompensated resistance was accounted for by manual correction.⁴⁰

Bulk electrolysis

Bulk electrolysis experiments were performed in a H-cell with a glass frit separator (porosity = 10–16 μm , Pine Research, USA) using a Bio-Logic SP 150 potentiostat/galvanostat. An active species concentration of 5 mM was used. The working electrode compartment contained 5 mL of the active species with 0.1 M supporting electrolyte ($[\text{Bu}_4\text{N}][\text{PF}_6]$) in MeCN and counter electrode compartment consisted of 5 mL of 0.1 M electrolyte ($[\text{Bu}_4\text{N}][\text{PF}_6]$) in MeCN. A Pt mesh working electrode and a Pt wire counter electrode were used. Bulk electrolysis experiments were carried out using chronoamperometry techniques available in EC lab software suite at constant potentials, selected from CV experiments.

Solubility measurements

A 0.1 M concentration of $[\text{Bu}_4\text{N}][\text{PF}_6]$ was used in all samples to simulate the electrochemical conditions of the cells studied in this work. All samples were referenced against a baseline of 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ in MeCN. To establish a calibration curve, 10 mM stock solutions were prepared by combining the supporting electrolyte (0.194 g $[\text{Bu}_4\text{N}][\text{PF}_6]$), the appropriate TiPOV-alkoxide cluster (*e.g.* 0.043 g of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$; 0.046 g of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$) and 5 mL of solvent in a vial and stirring until completely dissolved. Additionally, a stock solution of 0.1 M

[¹³⁷Bu₄N][PF₆] was prepared by combining 0.581 g [¹³⁷Bu₄N][PF₆], in 15 mL of MeCN. In a cuvette, 0.3 mL of the cluster stock solution was added and was subsequently diluted with 2.7 mL of the 0.1 M [¹³⁷Bu₄N][PF₆] stock solution. This process was repeated 4 times to obtain solutions with the following concentrations: 1.0 mM, 0.8 mM, 0.6 mM, 0.4 mM, and 0.2 mM. The electronic absorption spectra (UV-Vis) of these samples were recorded, and their absorbances at 415 nm were plotted against the sample's concentration to obtain a calibration based on the Beer–Lambert equation.

Three saturated solutions for each solvent were prepared by stirring an excess of Ti-POV in 5 mL of 0.1 M electrolyte ([¹³⁷Bu₄N][PF₆]) solution for a minimum of 24 hours. These solutions were passed through a syringe filter (EZFlow Syringe Filter, diameter = 25 mm, pore size = 0.22 μm) to remove undissolved TiPOV-alkoxide. 10 μL aliquots of each solution were removed and diluted such that the absorbance of the sample fell between 0.1 and 1.0. The absorbance of each diluted sample at appropriate wavelength (Ti₂V₄TRIOl^B = 422 nm; Ti₂V₄TRIOl^C = 415 nm) was recorded, and the concentration of the diluted sample was determined using the Beer's law equation from the corresponding calibration curve. The concentration of each saturated solution was then calculated from the concentration of the diluted sample. See ESI† for figures and details pertaining to the solubility calculations performed for each Ti-substituted POV-alkoxide cluster reported.

Charge–discharge experiments

Charge–discharge testing was conducted in a nitrogen filled glove box using a glass H-cell separated by a microporous glass frit (P5, 1.6 μm, Adams and Chittenden, USA) and a Bio-Logic SP 300 potentiostat/galvanostat. The electrolyte solutions used in charge–discharge experiments were 5 mM Ti-POV in 0.1 M electrolyte ([¹³⁷Bu₄N][PF₆]) in MeCN. Each compartment of the H-cell was filled with 5 mL of electrolyte solution. Two graphite felt electrodes (1 × 1 × 0.5 cm, Fuel Cell Store, USA) were placed in the posolyte and negolyte chambers. For the symmetrically unbalanced cycling experiment, the volume of the negolyte was increased to 10 mL, whereas the posolyte was maintained at 5 mL. Electrodes were attached to Pt wire current collectors submerged in the electrolyte solutions (~0.5 cm). Graphite felt electrodes were soaked in electrolyte solutions for 24 hours before each experiment. A sequential galvanostatic–potentiostatic charge–discharge method was adopted using a charging current of 0.2 mA until the potential reached 1.9 V.⁴¹ Subsequently, the potential was held at 1.9 V until the current dropped to 0.02 mA. Similarly, a discharging current of 0.2 mA was applied until a cut-off potential of 1.4 V was reached, followed by a potentiostatic discharge at 1.4 V until the current reached a value of 0.02 mA. For the duration of the charge–discharge experiments, both half cells were stirred at ~1000 rpm.

For the polarity reversal experiments, purely galvanostatic mode of charge–discharge was followed. A (dis)charging current of 0.2 mA was utilized throughout. The cell was

allowed to operate for 4 consecutive cycles with potential cut-offs for charging and discharging as 1.9 V and 1.4 V, respectively. Subsequently, the polarity of the electrochemical was reversed by applying the charging and discharging potential cut-offs as −1.4 V and −1.9 V, respectively. These conditions were maintained for 4 cycles, after which the conditions were reverted to the original value. Both half cells were stirred at ~1000 rpm for the entire duration of the experiment.

Results and discussion

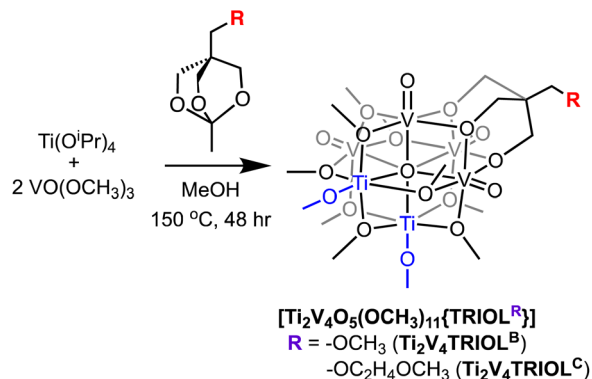
Organic functionalization of [Ti₂V₄O₅(OCH₃)₁₄]

Our group has demonstrated that installation of a TRIOL ligand featuring ether functional groups at the surface of POV-alkoxide clusters can enhance the solubility of the assembly in MeCN.³¹ In this work, we extend this finding to a Ti-doped POV-alkoxide cluster, [Ti₂V₄O₅(OCH₃)₁₄] (Ti₂V₄), which possess large cell voltage windows (ΔE_{1/2} ~ 1.7 V and 2.6 V for the inner and outer redox couples, respectively). Synthetic insights from our published preparation of TRIOL-functionalized dititanium POV-alkoxides were invoked.³²

To access the desired ether-functionalized TiPOV-alkoxide clusters, we first generated the alkoxyether-substituted pentaerythritol derivatives through a modified procedure. Briefly, protection of three hydroxyl substituents of pentaerythritol was accomplished by addition of triethylorthoacetate to generate the protected ligand precursor (PLP), CH₃C(OCH₂)₃CCH₂OH.³⁹ The remaining −OH group of PLP was functionalized according to the previously established protocols by our group to yield CH₃C(OCH₂)₃CCH₂OCH₃ (PL^b) and CH₃C(OCH₂)₃CCH₂OC₂H₄OCH₃ (PL^c).³¹

Following successful synthesis and characterization of the ligands PL^b and PL^c, we sought to generate the TRIOL-functionalized derivatives of Ti-POVs. We hypothesized that the innate acidity of the solvothermal syntheses, combined with the reducing nature of methanol at elevated temperatures, would preclude the requirement of an additional ligand deprotection step. Indeed, the methoxyether substituted TRIOL-functionalized TiPOV-alkoxide cluster, [Ti₂V₄O₅(OCH₃)₁₁(OCH₂)₃CCH₂OCH₃] (Ti₂V₄TRIOl^B), was produced in moderate yield *via* solvothermal treatment of the ligand precursor, PL^b (1 equiv.), Ti(OⁱPr)₄ (1 equiv.) and VO(OCH₃)₃ (2 equiv.) in methanol (Scheme 1, see Experimental section for more details). The crude reaction mixture presents as a dark brown liquid with solid precipitate at the bottom of the autoclave. Analysis of each of the phases using cyclic voltammetry (CV) suggests that the desired product is found in the liquid phase; analysis of the filtrate reveals four reversible redox events, consistent with the electrochemical profiles previously reported for TiPOV-alkoxide clusters (Fig. S2†).

Following work-up, further characterization of the complex was performed *via* infrared (IR) and electronic absorption spectroscopies. In the IR spectra of Ti₂V₄TRIOl^B, two absorption features are observed at ~975 cm^{−1} and ~1020 cm^{−1}, which correspond to ν(V=O_t) (O_t = terminal oxo) and ν(O_b–



Scheme 1 Synthesis of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ and $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$.

CH_3) (O_{b} = bridging oxo), respectively (Fig. S3†). Additionally, a transition at 1125 cm^{-1} is observed, consistent with the $\nu(\text{O}_{\text{t}}-\text{CH}_3)$ of the terminal alkoxide ligands bound to the heterometallic titanium centres. Analysis of the electronic absorption spectrum of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ reveals broad feature around 420 nm, assigned as an electron transfer event between $\text{V}^{\text{IV}}(\text{d}^1)$ and $\text{Ti}^{\text{IV}}(\text{d}^0)$ ions within the heterometallic clusters.⁴² The canonical intervalence charge transfer (IVCT) band characteristic of electron transfer between $\text{V}^{\text{IV}}(\text{d}^1)$ centres and $\text{V}^{\text{V}}(\text{d}^0)$ centres was absent suggesting that the cluster possess an iso-valent V^{IV} electron configuration. This is analogous to the observations made for the neutral, homoleptic cluster Ti_2V_4 .³⁶ This oxidation state distribution is further confirmed by the presence of a weak shoulder around 630 nm, a feature observed in both Ti_2V_4 and the di-anionic hexavanadium cluster, $[\text{V}_6\text{O}_7(\text{OCH}_3)_{12}]^{2-}$.⁴³ Bulk purity of the sample was assessed *via* elemental analysis (see Experimental section for details).

Single crystal X-ray diffraction was performed on crystals of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ serendipitously grown from the crude reaction mixture, providing an opportunity to unambiguously determine the identity of the product. The refined data reveals the expected heterometallic Lindqvist structure, in which three bridging-methoxide ligands defining a single face of the assembly are replaced by the tridentate TRIOL^B ligand (Fig. 2 and Table S1†). Analogous to the reported TRIOL-substituted TiPOV-alkoxide clusters, the tridentate ligand is coordinated exclusively at bridging positions located between two vanadium centres.³² The overall cluster geometry closely resembles that of the homoleptic compound Ti_2V_4 , with the two titanium centres located *cis* to one another, linked by a bridging-methoxide unit. Both Ti^{IV} centres possess pseudo-octahedral coordination geometries and short $\text{Ti}-\text{O}_{\text{m}}$ bonds ($\sim 1.76 \text{ \AA}$) (O_{m} = oxygen atom of the terminal methoxide ligand). The $\text{Ti}-\text{O}_{\text{c}}$ (O_{c} = central μ^6 -oxygen atom) bond distance of the cluster is relatively short (~ 2.133 and $\sim 2.086 \text{ \AA}$) compared to the $\text{V}_{\text{t}}-\text{O}_{\text{c}}$ bond lengths in each cluster ($\sim 2.464 \text{ \AA}$; V_{t} = vanadium centre located *trans* to the two titanium centres). As in the case of Ti_2V_4 and other reported TRIOL-substituted TiPOV-alkoxide clusters, the affinity of the titanium ions for

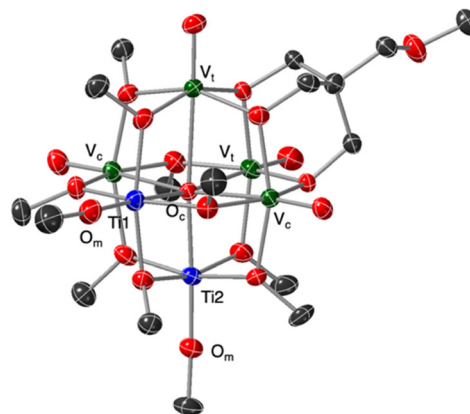


Fig. 2 Molecular structure of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ shown with 40% probability ellipsoids. Hydrogen atoms and solvent molecules are removed for clarity. Key: blue ellipsoids: Ti; green ellipsoids: V; red ellipsoids: O; grey ellipsoids: C.

the μ^6 -oxo seemingly pulls the oxygen atom out of its central position in the cluster, as evidenced by elongated $\text{V}_{\text{t}}-\text{O}_{\text{c}}$ bond distances.^{32,36}

The redox properties of an analytically pure sample of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ were analyzed *via* CV. Electrochemical analysis was performed in MeCN with tetrabutylammonium hexafluorophosphate ($[\text{nBu}_4\text{N}][\text{PF}_6]$) as the supporting electrolyte in order to draw comparisons between the redox profile of the title compound and similar assemblies reported previously by our laboratory. Four quasi-reversible electrochemical events are observed, with half wave potentials analogous to both the homoleptic cluster Ti_2V_4 and other TRIOL-substituted TiPOV-alkoxide clusters (Fig. 3 and Table 1).^{32,44}

Electronic absorption spectroscopy was used to confirm the oxidation state distribution of transition metal ions in the oxidized and reduced forms of the $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$, generated *via* bulk electrolysis (Fig. 4).^{42,43} The oxidation processes ($E_{1/2} = 0.15, 0.64 \text{ V vs. Ag}^{+|0}$ in Ti_2V_4) are assigned to successive, one-electron vanadium-based processes ($\text{V}^{\text{IV}} \rightarrow \text{V}^{\text{V}} + \text{e}^-$), while the two reductive events ($E_{1/2} = -1.58, -2.1 \text{ V vs. Ag}^{+|0}$ in Ti_2V_4) are assigned to the reduction processes localized at one of the two titanium ions in the Lindqvist core ($\text{Ti}^{\text{IV}} + \text{e}^- \rightarrow \text{Ti}^{\text{III}}$). Accordingly, we hypothesized that the two reduction events in the voltammogram of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ ($E_{1/2} = -1.53 \text{ V}, -2.11 \text{ V}$) correspond to sequential $\text{Ti}^{\text{IV}}/\text{Ti}^{\text{III}}$ redox couples, whereas the observed series of oxidation events ($E_{1/2} = +0.22 \text{ V}, +0.70 \text{ V}$) are assigned to the $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$ couples.

Spectroelectrochemical characterization of mono-reduced and mono-oxidized forms of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ confirms our assignments of these redox processes. The electronic absorption spectrum of the mono-reduced cluster, $[\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}]^{1-}$, possesses a weak absorption around 630 nm ($\epsilon = 140 \text{ M}^{-1} \text{ cm}^{-1}$), consistent with a V_4^{IV} electronic configuration. The absorption feature at 422 nm which corresponds to the intervalence charge transfer (IVCT) between V^{IV} and Ti^{IV} ions is reduced in intensity from that of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$, ($\epsilon = 656 \text{ M}^{-1} \text{ cm}^{-1}$ to 625

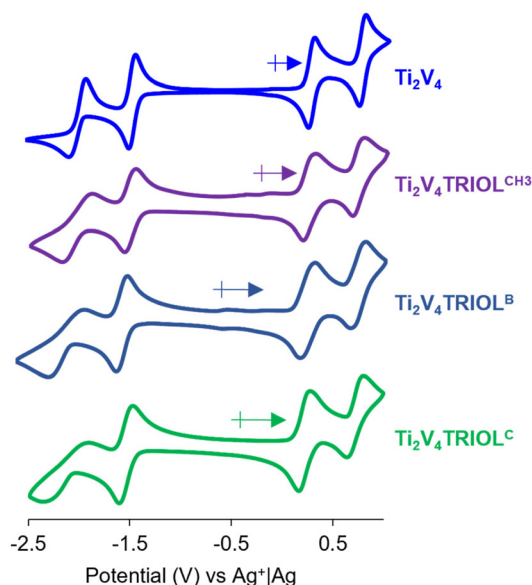


Fig. 3 Cyclic voltammograms of Ti_2V_4 , $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{CH}_3}$, $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ and $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$ recorded in acetonitrile with 0.1 M $[\text{tBu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte. Scan rate = 100 mV s^{-1} . Arrows indicate open circuit potential and sweep direction.

$\text{M}^{-1} \text{cm}^{-1}$) consistent with reduction of a single titanium centre. The electronic absorption spectrum of the mono-oxidized form of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ exhibit intense absorption features at 388 nm ($\epsilon = 4428 \text{ M}^{-1} \text{cm}^{-1}$) and around 1000 nm ($\epsilon = 478 \text{ M}^{-1} \text{cm}^{-1}$). It should be noted that this feature is not a discrete peak due to the operable wavelength window of the instrument and the true λ_{max} can be $\geq 1000 \text{ nm}$. The transition at lower energies is assigned to an IVCT event between V^{IV} and V^{V} metal centres, consistent with the oxidation event occurring at vanadium. The durability of complex $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ across the +1 and -1 charge states was assessed by monitoring the charged solutions using CV at room temperature (Fig. S4†). Over the course of one week, no evidence of degradation of the charge carrier was noted, indicating that $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ is stable across at least a 1.73 V potential range at room temperature. The outer redox events observed in the CV of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ ($E_{1/2} = -2.11 \text{ V}$, $+0.70 \text{ V vs. Ag}^{+|0}$) result in the formation of redoxmers that are not stable (see bulk electrolysis experiments in

Fig. S19†); as such we limit battery analysis to the inner electrochemical processes ($E_{1/2} = -1.53 \text{ V}$, $+0.22 \text{ V vs. Ag}^{+|0}$).

Next, we targeted the synthesis of a TiPOV-alkoxide cluster bearing a longer-chain alkoxyether functional group, $[\text{Ti}_2\text{V}_4\text{O}_5(\text{OCH}_3)_{11}(\text{OCH}_2)_3\text{CCH}_2\text{OC}_2\text{H}_4\text{OCH}_3]$ ($\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$). Successful synthesis was accomplished *via* analogous reaction conditions and work-up to that described for $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$. Complex $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$ was isolated as a viscous brown oil. Characterization of the product *via* infrared spectroscopy was used to confirm the formation of the desired Lindqvist species; two absorption bands are observed at $\sim 975 \text{ cm}^{-1}$ and $\sim 1020 \text{ cm}^{-1}$, corresponding to $\nu(\text{V}=\text{O}_t)$ (O_t = terminal oxo) and $\nu(\text{O}_b-\text{CH}_3)$ (O_b = bridging oxo), with an additional feature at 1125 cm^{-1} assigned to the $\nu(\text{O}_t-\text{CH}_3)$ of the terminal alkoxide ligand bound to titanium (Fig. S3†). Bulk purity of the cluster was assessed *via* elemental analysis (see Experimental section for details).

Electrochemical analysis of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$ was performed *via* CV; the resultant voltammogram is similar to that observed for the parent cluster Ti_2V_4 and complex $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ (Fig. 3). Both bulk electrolysis afforded complete conversion of the cluster assembly to its mono-oxidized and mono-reduced charge-states, respectively (Fig. 4). Characterization of the oxidized and reduced forms of the cluster *via* electronic absorption spectroscopy revealed analogous changes in the spectroscopic profile to that observed for $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$. The spectrum of the oxidized assembly possesses strong transitions at 388 nm ($\epsilon = 3805 \text{ M}^{-1} \text{cm}^{-1}$) and 1000 nm ($\epsilon = 453 \text{ M}^{-1} \text{cm}^{-1}$), consistent with an oxidation localized to the vanadium centres of the TiPOV-alkoxide cluster. In contrast, a sample of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$ subjected to reducing potentials indicates that cluster reduction is localized to a titanium centre, as indicated by a reduction in the molar absorptivity of the $\text{V}^{\text{IV}} \rightarrow \text{Ti}^{\text{IV}}$ charge transfer event located at 430 nm ($\epsilon = 489 \text{ M}^{-1} \text{cm}^{-1}$). The long-term stability of the resulting oxidized and reduced solutions at room temperature were assessed *via* CV over a span of 7 days. No substantial changes were observed in peak potential or current response for the CVs of the oxidized and reduced solutions, indicating that $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$ is also stable at room temperature in the one-electron oxidized and reduced states (Fig. S4†).

Our primary motivation behind the organic functionalization of TiPOV-alkoxide clusters is to improve the solubility of

Table 1 Electrochemical parameters of complexes Ti_2V_4 , $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{CH}_3}$, $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ and $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$

Complex	2 nd $\text{Ti}^{\text{III}}/\text{Ti}^{\text{IV}}$ couple		1 st $\text{Ti}^{\text{III}}/\text{Ti}^{\text{IV}}$ couple		1 st $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ couple		2 nd $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ couple	
	$E_{1/2}$ (V)	i_c/i_a	$E_{1/2}$ (V)	i_c/i_a	$E_{1/2}$ (V)	i_c/i_a	$E_{1/2}$ (V)	i_c/i_a
Ti_2V_4	-2.10	1.67	-1.58	1.12	+0.15	1.05	+0.64	0.99
$\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{CH}_3}$	-2.12	1.53	-1.60	1.15	+0.14	1.01	+0.65	1.14
$\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$	-2.11	1.33	-1.53	1.14	+0.22	1.1	+0.7	1.25
$\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$	-2.02	1.25	-1.5	1.01	+0.25	1.2	+0.73	1.3

Standard potentials (vs. $\text{Ag}^{+|0}$) are identified using cyclic voltammetry at 100 mV s^{-1} of 5 mM solutions of each complex with 0.1 M $[\text{tBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte in MeCN. Values in parentheses indicate ratios of the cathodic and anodic peak heights (i_c/i_a).

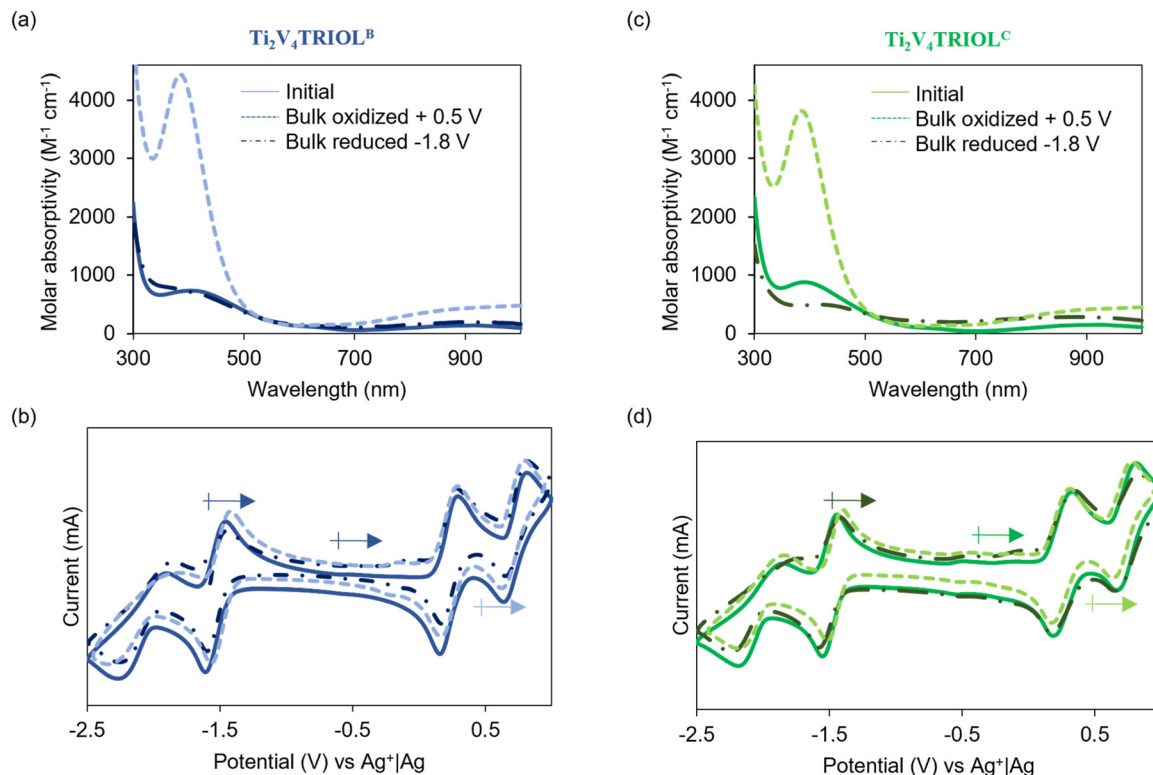


Fig. 4 (a) Electronic absorption spectra and (b) cyclic voltammograms of $\text{Ti}_2\text{V}_4\text{TRIOLB}$ demonstrating successful bulk oxidation and reduction. All experiments were performed at room temperature in MeCN with 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte. The analogous data for bulk electrolysis of $\text{Ti}_2\text{V}_4\text{TRIOLC}$ are shown in panels (c) and (d). Note that the CV data in panels (b) and (d) were shifted vertically to overlay the data; the vertical positions of the crossed arrows demarcate zero current flow.

the heterometallic assembly in MeCN for flow battery applications. As such, we measured the solubility of analytically pure samples of $\text{Ti}_2\text{V}_4\text{TRIOLB}$ (Fig. S5 and Table S2†) and $\text{Ti}_2\text{V}_4\text{TRIOLC}$ (Fig. S6 and Table S3†) in MeCN with 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$. These conditions were selected to mimic the working conditions of our NAqRFB cell. The solubility of $\text{Ti}_2\text{V}_4\text{TRIOLB}$ and $\text{Ti}_2\text{V}_4\text{TRIOLC}$ are measured as 0.32 ± 0.02 M and 0.66 ± 0.02 M, respectively. These values are significantly higher than those reported by our group for Ti_2V_4 (0.044 ± 0.003 M).³⁴ The improved solubility of the TiPOVs upon alkoxyether functionalization are consistent with our prior work on organic functionalization of the hexavandate clusters.³¹

Electrokinetic behaviour of alkoxyether-substituted Ti-POVs

Efficient RFB charge carriers must exhibit rapid diffusivity in the electrolyte media.⁴⁵ Thus, we evaluated the diffusion coefficients (D_0) of both TRIOL functionalized clusters in MeCN (Fig. 5 and Fig. S7–S9†). The redox events associated with one-electron oxidation ($1^+/0$) and one-electron reduction ($0/1^-$) for both TiPOV alkoxide clusters were isolated and CVs were recorded at scan rates ranging from 10–10 000 mV s^{-1} (Fig. 5a). The plot of the peak current (i_p) versus the square root of scan rate ($\nu^{1/2}$) exhibits a linear dependence (Fig. 5b and Fig. S10†). This behaviour is characteristic of a diffusion-limited electrochemical process, allowing for the assessment of the D_0 of

both TiPOVs using the Randles–Sevcik (R–S) equation.⁴⁶ The calculated D_0 values for $1^+/0$ and $0/1^-$ of $\text{Ti}_2\text{V}_4\text{TRIOLB}$ are $1.18 \pm 2.27 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $8.92 \pm 1.89 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. Compared to the short-chain ether functionalized cluster, $\text{Ti}_2\text{V}_4\text{TRIOLC}$ exhibits marginally slower diffusion coefficients ($1^+/0 = 5.11 \pm 0.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $0/1^- = 4.28 \pm 0.04 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The diffusion coefficients measured for both TiPOV alkoxide clusters are similar to values reported previously for molecular charge carriers.^{45,47}

Next, we evaluated the heterogeneous electron transfer rate constants (k_0) for each relevant redox event in the two assemblies using Nicholson's method.⁴⁸ From CVs spanning the scan rate from 10–10 000 mV s^{-1} , the difference in peak potential (ΔE_p) was correlated with a dimensionless kinetic parameter (Ψ) (Fig. S11 and S12†).⁴⁹ The calculated k_0 for $1^+/0$ and $0/1^-$ for the organofunctionalized TiPOV-alkoxide clusters are given in Table 2.

According to Marcus's model of electron transfer, the molecular structure of redox active species is expected to affect electron transfer kinetics in both outer- and inner-sphere redox processes.⁵⁰ Furthermore, the probability of electron transfer events decreases with increasing distance between the donor and acceptor in the transition state. We thus hypothesized that differences in steric bulk and solvent interactions would yield differences in the kinetics of TiPOV-alkoxide clusters substi-

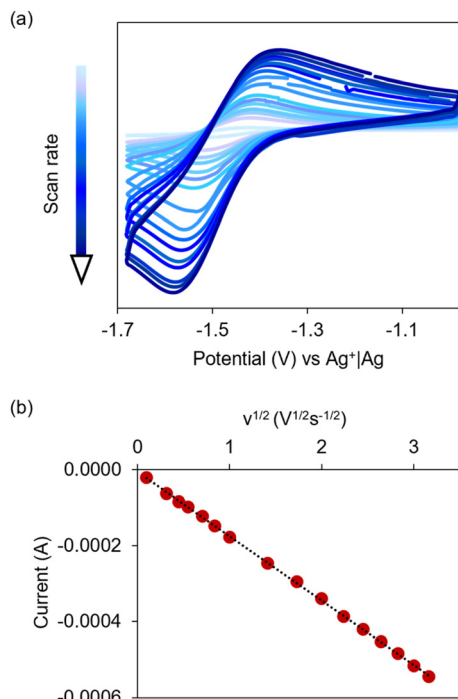


Fig. 5 (a) Representative CV measurements of 0/1⁻ redox couple of 5 mM Ti₂V₄TRIOL^C with 0.1 M [nBu₄N][PF₆] in acetonitrile at scan rates ranging from 10–10 000 mV s⁻¹; (b) Randles–Sevcik analysis of the corresponding data.

tuted with distinct TRIOL ligands. The electron transfer rate constants for each of the redox events of the homoleptic cluster, Ti₂V₄, are reported as 1^{+/0} = 7.20 ± 0.8 × 10⁻² cm s⁻¹ and 0/1⁻ = 1.40 ± 0.04 × 10⁻² cm s⁻¹ in MeCN.³⁴ In comparison, the observed *k*₀ values for Ti₂V₄TRIOL^B are 1^{+/0} = 7.55 ± 0.24 × 10⁻³ cm s⁻¹ and 0/1⁻ = 2.97 ± 0.07 × 10⁻³ cm s⁻¹. Heterogeneous electron transfer rate constants for Ti₂V₄TRIOL^C were determined to be similar to Ti₂V₄TRIOL^B, 1^{+/0} = 3.24 ± 1.11 × 10⁻³ cm s⁻¹ and 0/1⁻ = 5.72 ± 0.15 × 10⁻³ cm s⁻¹.

The observed *k*₀ values for both TRIOL-substituted TiPOV-alkoxide clusters are reduced by up to 10-fold in comparison to those of Ti₂V₄. We attribute this observation to the fact that TRIOL-functionalization decreases the extent of delocalization within the hexametalate core. This suppression of electronic communication across the cluster core manifests as slower rates of electron transfer to and from the cluster assembly. We note that the suppression in rate of electron transfer is more

significant for the oxidative process (1^{+/0}); this observation is consistent with the fact that the TRIOL ligand is attached to the vanadium atoms. Accordingly, redox processes occurring at vanadium centres, like the oxidation reactions in both Ti₂V₄TRIOL^B and Ti₂V₄TRIOL^C, are more substantially affected than rates of Ti-based reduction processes. While the rates of electron transfer are significantly slower for complexes Ti₂V₄TRIOL^B and Ti₂V₄TRIOL^C as compared to Ti₂V₄, it should be noted that these values of heterogeneous rate constants remain high enough to facilitate flow battery operation that is not fundamentally limited by kinetic overpotentials.⁴⁷

Extended charge–discharge cycling

The solubility of the TRIOL functionalized TiPOV-alkoxide clusters, coupled with fast electron transfer kinetics, suggest that these heterometallic complexes can serve as charge carriers in symmetric RFBs, capable of transferring one electron at each electrode. As such, we transitioned from fundamental electrochemical studies to proof-of-concept analyses through static H-cell charge–discharge cycling experiments. Using the expression derived by Sanford and Thompson for calculating the theoretical energy density of a charge carrier (eqn (1)) we can evaluate the theoretical volumetric energy density for each cluster:⁵¹

$$E = 0.5 \times n \times V_{\text{cell}} \times C_{\text{active}} \times F \quad (1)$$

where *E* is the volumetric energy density, *n* is the number of electrons transferred, *V*_{cell} is the average cell voltage, *C*_{active} is the concentration of active species, and *F* is Faraday's constant. A *V*_{cell} of 1.73 V and a solubility of 0.32 M yields an energy density of 27 kJ L⁻¹ for Ti₂V₄TRIOL^B, which represents a 600% improvement over that of Ti₂V₄. In contrast, a solubility of 0.66 M for Ti₂V₄TRIOL^C results in a theoretical energy density of 55 kJ L⁻¹. This value is about 14-fold greater than that obtained for the homoleptic precursor (*C*_{active} = 0.044 M, *V*_{cell} = 1.73 V).

The improved theoretical energies densities of Ti₂V₄TRIOL^B and Ti₂V₄TRIOL^C motivated preliminary investigations into battery cycling experiments through static charge–discharge experiments. Cycling experiments were performed with 5 mM solution of the cluster in MeCN with 0.1 M [nBu₄N][PF₆] supporting electrolyte in an H-cell. To minimize cell resistance, posolyte and negolyte chambers were separated by a glass frit. We adopted a galvanostatic–potentiostatic sequential cycling method initially reported by Goulet and Aziz,⁴¹ and adapted

Table 2 Diffusion coefficients and heterogeneous electron transfer rate constants for each redox event in complexes Ti₂V₄, Ti₂V₄TRIOL^B and Ti₂V₄TRIOL^C

Complex	Ti ^{III} /Ti ^{IV} couple (0/1 ⁻)		V ^{IV} /V ^V couple (1 ^{+/0})	
	<i>D</i> ₀ (cm ² s ⁻¹)	<i>k</i> ₀ (cm s ⁻¹)	<i>D</i> ₀ (cm ² s ⁻¹)	<i>k</i> ₀ (cm s ⁻¹)
Ti ₂ V ₄	9.40 ± 0.80 × 10 ⁻⁶	1.40 ± 0.04 × 10 ⁻²	1.03 ± 0.01 × 10 ⁻⁵	7.20 ± 0.80 × 10 ⁻²
Ti ₂ V ₄ TRIOL ^B	8.92 ± 1.89 × 10 ⁻⁶	2.97 ± 0.07 × 10 ⁻³	1.18 ± 2.27 × 10 ⁻⁵	7.55 ± 0.24 × 10 ⁻³
Ti ₂ V ₄ TRIOL ^C	4.28 ± 0.04 × 10 ⁻⁶	5.72 ± 0.15 × 10 ⁻³	5.11 ± 0.06 × 10 ⁻⁶	3.24 ± 1.11 × 10 ⁻³

for TiPOV -alkoxide clusters by our research team.³⁴ A charging current of 0.2 mA until the potential reached 1.9 V, followed by holding the potential at 1.9 V until the current dropped to 0.02 mA. Similarly, a discharging current of 0.2 mA was applied until a cut off potential of 1.4 V was reached, with a potentiostatic discharge at 1.4 V until the current reached a value of 0.02 mA. Fig. 6a depicts the first 5 cycles observed during the battery cycling experiment of $\text{Ti}_2\text{V}_4\text{TRIOI}^{\text{B}}$ (full

cycling data is provided in Fig. S13†). Coulombic efficiencies were maintained at 98% over 10 cycles (Fig. S14†). The rates of capacity loss for both the charge and discharge cycles are depicted in Fig. 6d. We observe a 62% capacity loss after 10 cycles. While this degradation is significant, the system reflects greater durability than other electrolyte systems reported in non-aqueous conditions. For example, while Clegg *et al.* report a 74% capacity fade rate for the $\text{V}(\text{acac})_3$ system, Savinell and

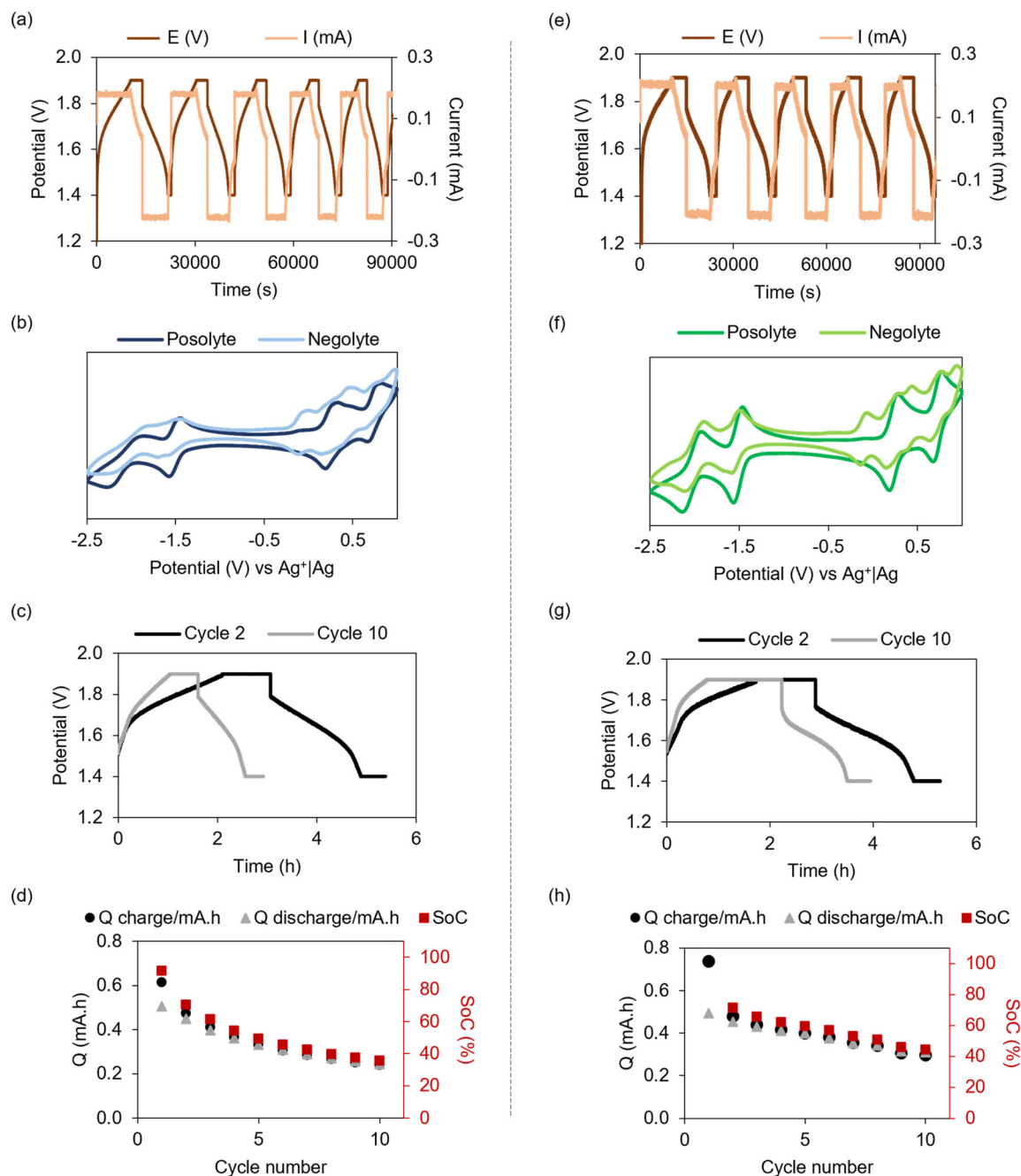


Fig. 6 (a) Voltage trace of cycles 1–5 in charge–discharge cycling of $\text{Ti}_2\text{V}_4\text{TRIOI}^{\text{B}}$ (b) cyclic voltammograms of solutions after charge–discharge cycling (c) comparison of cycles 2 and 10 from the battery cycling experiment (d) capacity fade over 10 cycles (black circles represent charging capacity; grey triangles represent discharging capacity; red squares represent percent state of charge (SoC) of the battery) (e)–(h) show similar characterizations for charge–discharge cycling of $\text{Ti}_2\text{V}_4\text{TRIOI}^{\text{C}}$.

co-workers have documented 80% capacity fade of the same system after 10 cycles.^{52,53} We hypothesize that the observed reduction in cell capacity results from chemical reactions to deactivate the redox couple in either or both reaction chambers during battery cycling.

Post cycling analysis by CV (Fig. 6b) demonstrates that the positive electrolyte undergoes minimal changes under these cycling conditions. However, partial decomposition of the negative electrolyte (*i.e.*, the electrolyte based on the 0/1[−] charge states) was observed, suggesting that the reduced form of the cluster is less stable. New features emerge in the CV of the negative electrolyte after cycling, which correspond to the electrochemical signature of the mono-titanium derivative of the POV-alkoxide cluster, [TiV₅O₆(OCH₃)₁₃]^{1−} (TiV₅^{1−}) as has been previously reported by our research team (Fig. S20†).⁵⁴ We note that the synthetic conditions prescribed for the formation of TiV₅^{1−} require additional reductant, suggesting that formation of the mono-titanium derivative of the cluster is favoured over the neutral Ti₂V₄ complex under reducing conditions. As such, we pose that cluster rearrangement in the negolyte chamber is facilitated by the highly reducing conditions of our cycling experiment.^{32,36}

A thorough understanding of the prevalent decay mechanisms in RFBs, such as electrode passivation, crossover, electrolyte side reactions, and self-decomposition of the charge carrier, can aid in designing suitable analytical methods to probe sources of capacity fade.^{41,55} To further validate the observed capacity fade due to the instability of the cluster in its reduced charge state, we cycled volumetrically unbalanced compositionally symmetric cells, following methods developed by Aziz and co-workers.⁴¹ The volume of the posolyte was kept at 5 mL, whereas the negolyte was used in excess quantities (10 mL). As depicted in Fig. S15,† under the same experimental (dis)charging protocol, the overall rate of capacity fade was similar, and the average coulombic efficiency was notably reduced, compared to the case of a balanced configuration. However, less fractional degradation (20% formation of TiV₅^{1−} as compared to 58% in previous cases) of the negative electrolyte is observed. We believe that this is due to the fact that more cluster is present in the negolyte chamber, reducing the state of charge for the reductive cycling required. Similarly, we observe improved capacity retention on increasing the concentration of the negolyte (Fig. S17†). In the case of these battery cycling configurations, the capacity drops by only 40% for Ti₂V₄TRIOl^B after 10 cycles. This value of battery capacity degradation rate is less than that obtained using other charge-discharge techniques (*vide supra* 62% for equimolar and volumetrically balanced cell; 58% for equimolar, volumetrically imbalanced cell).

We also carried out galvanostatic polarity-reversal experiments of Ti₂V₄TRIOl^B to test whether it is possible to reduce degradation even further (Fig. S16†). Our hypothesis behind reversing the polarity of the electrochemical cell was to distribute the degradation over both electrolyte sides so that we can harness more charge-discharge cycles without significant decomposition of the negative electrolyte.⁶ Indeed, our results

demonstrate that the practical capacity remains higher (20% average capacity fade over 10 cycles as compared to 62% with prior techniques) when degradation is distributed over both of the symmetric battery electrolytes. We observe the least amount of TiV₅^{1−} formation (13%) using this methodology. It should be noted that the observed absolute capacity is lower in this case due to the purely galvanostatic mode of cycling. These results further support a purely chemical mechanism for the observed capacity fade.

Similar charge-discharge experiments were conducted for Ti₂V₄TRIOl^C. Analogous to Ti₂V₄TRIOl^B, we observe no decomposition of the positive electrolyte, while the negative electrolyte partially degrades to yield the mono-titanium cluster (Fig. 6(f)). No additional plateaus are detected during the experiment and coulombic efficiencies are maintained at 90% over 10 cycles (Fig. S13 and S14†). In contrast to the short-chain derivative, Ti₂V₄TRIOl^C reaches the voltage limit driving the programmatic transition to potentiostatic charging earlier during the charge cycle (Fig. 6(e)). We attribute this behaviour to the slower diffusion coefficients of Ti₂V₄TRIOl^C which increases polarization under galvanostatic conditions. This observation is consistent with our previously reported study on Ti₂V₄, where slower diffusivity of the charge carrier in mixed or more viscous solvents resulted in predominantly potentiostatic mode of charge-discharge.³⁴ Since the capacity observed during galvanostatic cycling with potential limits is directly related to the polarization resistance of the cell,⁴¹ we conclude that Ti₂V₄TRIOl^C is more susceptible to voltage efficiency losses as compared to Ti₂V₄TRIOl^B in pure galvanostatic mode of cycling. However, as pointed out by Goulet and Aziz in their seminal report, potentiostatic cycling with steady state current cut-offs enables to access nearly 100% of the theoretical capacity, thereby minimizing the impact of polarization resistance at the expense of longer charge-discharge cycles. Hence, the results presented here represent a rigorous preliminary assessment of the cyclability of these TiPOV-alkoxide clusters, and we speculate that cycle-life durability would be greater under galvanostatic operation in a flow cell.

The degradation of Ti₂V₄TRIOl^B and Ti₂V₄TRIOl^C during cycling experiments is surprising, given the stability of the oxidized and reduced forms of the TiPOV-alkoxide charge carriers over 7 days following bulk electrolysis (*vide supra*, Fig. S4†). In considering a justification for this observation, we note that our stability analysis was conducted with samples stored at room temperature. RFBs generate heat when consuming electric power in their working state.⁵⁶ As such, activation, ohmic and concentration losses can manifest during battery cycling as the reaction kinetics and transport properties of the electrolyte are functions of temperature.^{57,58} These losses can affect the battery performance metrics (such as state-of-charge, SOC) and can also result in the degradation of the active material. To evaluate whether the degradation in the TRIOl systems during charge-discharge is a result of heat generation, we heated the bulk oxidized and reduced samples of Ti₂V₄TRIOl^B at 30 °C and stirred them for 7 days to simulate the speculated heat generation during battery cycling. Our results demon-

strate degradation of both posolyte and negolyte after 7 days (Fig. S18†). These conditions are expected to be more extreme than the actual experiment and explain the deterioration of the posolyte solution contrary to that observed in the charge–discharge experiment. Hence, we hypothesize that the observed degradation of the negolyte for the TRIOL-capped TiPOVs during battery cycling is a result of the thermal effects that arise during the working of the battery. We note that we cannot rule out over-oxidation or over-reduction of the cluster to the doubly charged species under the employed cycling conditions. This fact may further contribute to the instability of the system. Hence, the chemical stability of the cluster would need to be improved across all charge states to further assess the implications of alkoxyether functionalization of TiPOVs in flow cell applications.

Conclusions

Understanding the physical and electrochemical implications of bridging alkoxide ligands appended with ether functional groups is essential for the future of POV-based charge carriers, as these moieties are established to yield improved solubility in MeCN.^{31,51,59} In this work, we demonstrate that synthetic modifications can impart substantial improvement to the solubility TiPOV-alkoxide assemblies. The enhancement in solubility and cell voltage for $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ and $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$ results in significant improvements of the *theoretical* energy storage capabilities of these heterometallic clusters over their hexavanadate congeners; however, the experimental cycling data demonstrates decomposition of the negolyte. The resulting TRIOL-substituted clusters exhibit heterogeneous rate constants of electron transfer that are an order of magnitude slower than those observed for Ti_2V_4 . We attribute this behaviour to decreased delocalization in the hexametalate core upon alkoxyether functionalization, but the effect is not large enough to preclude viability of this charge carrier in functional NAqRFBs.

Additional studies probing the charge–discharge behaviour of the TRIOL functionalized titanium-substituted POV-alkoxide clusters reveal distinct cycling response. While $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$ exhibits primarily galvanostatic mode of (dis)charge, $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{C}}$ demonstrates predominantly potentiostatic cycling and hence longer charging cycles. We ascribe this behaviour to the difference in the diffusion coefficients of the two assemblies that leads to polarization resistance in the electrochemical cell. Charge–discharge experiments of both TRIOL-substituted TiPOV-alkoxide clusters yield decomposition of the negolyte. Probing the decomposition of these complexes using temperature dependent bulk-electrolysis experiments indicate that the observed degradation of the negative electrolyte is likely a result of the thermal effects that arise during the working of the battery. Ongoing investigations in our laboratory are focused on the impact of temperature on the kinetics of electron transfer and degradation for further exploration in the development of efficient RFBs.

Author contributions

M. D., D. M. M. M. D., and E. M. M. conceived and planned the experiments. M. D., D. M. M. M. D., J. D. M., D. N. K., and M. C. performed all synthetic and electrochemical experiments and interpreted results. W. W. B. collected and refined data to determine the crystal structure of $\text{Ti}_2\text{V}_4\text{TRIOL}^{\text{B}}$. The manuscript was composed by M. D. and E. M. M.; all authors have given approval to the final version of the manuscript.

Conflicts of interest

J. R. M. is currently an advisory board member and may in the future gain equity interest in a company that develops technologies for redox flow batteries.

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