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An oxo-verdazyl radical for a symmetrical non-aqueous redox flow battery

Aleksandr Korshunov,^a Matthew James Milner,^b Mariano Grünebaum,^c Armido Studer,^b Martin Winter^{*a,c} and Isidora Cekic-Laskovic^{*c}

Verdazyl free radical compounds are promising candidates for symmetrical all-organic redox flow batteries (RFBs) due to their redox stability, the ease with which their chemical structure can be varied, and their unique bipolar nature. The present work reports a preliminary screening of a selection of oxo-verdazyl compounds for key redox electrolyte parameters. Of the considered candidates, the 1,5-diphenyl-3-isopropyl-6-oxo-verdazyl radical performed best and is investigated in extensive RFB experiments to compare its electrochemical behavior in cyclic voltammetry (CV) to that within an actual battery. The symmetrical oxo-verdazyl non-aqueous electrolyte RFB provides a mean voltage of 1.42 V and demonstrates good stability as well as high Coulombic (>97%) and energy efficiencies over more than 100 charge/discharge cycles. The redox electrolyte is characterized at different stages within a single cycle ('state of charge' experiments) independently for each half-cell. To address the specifics of the electrolyte transition to RFB cell setup an 'in-cell' CV flow-enabled electrochemical study are conducted, introduced here as a new step towards standardization of the electrochemical description of RFB electrolytes. The electrochemical performance results highlight oxo-verdazyls as versatile materials for energy applications and indicate great promise for their further development and optimization in the field of RFBs.

Introduction

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The contemporary speed of technological advance gives rise to an increasing demand for energy supply worldwide. In contrast, the natural stock of available fossil fuels is declining steadily, making the path towards alternative sources of less convenient but practically limitless energy more attractive. However, harvested energy output from most of the promising renewable sources (e.g. solar or wind) still struggles to satisfy the key requirement of consistent supply.¹⁻³ Redox flow batteries (RBFs) offer an effective static grid-scale measure to manage and ease the energy delivery procedure. Their high adaptivity to frequent and unregulated energy inputs and outputs over unbound periods of time, as well as their safety and scalability, make RFBs a promising technology for buffering (or so-called 'peak shaving') and, thereafter, effectively conveying energy generated from inherently intermittent sources to consumers.4,5

Despite their potential advantages, widespread application of RFBs to actual grid-scale solutions encounters limitations due

to, for instance, the excessively high cost of essential cell elements (e.g. separators, pumps) or commercial electrolytes (in particular, those based on vanadium) relative to the competitive cost of the energy carrier units (\$100 per kWh).⁶ In order to bypass the practical issues of inorganic electrolytes and follow modern ecological trends, the scientific community is directing considerable attention towards organic redox electrolyte formulations. Organic molecules represent an almost unlimited framework in which theory meets target application for material science.⁷⁻⁹ The numerous properties crucial for consistent RFB energy storage, such as exceptional bulk electrolyte stability, high solubility for each oxidative state, and prevention of irreversible capacity loss, can be reverse engineered into organic redox materials with the desired tailored properties. It is hardly surprising, then, that redoxactive organic molecules (ROMs) are frequently purported to be a promising and sustainable scaffold for modern RFB electrolytes.10-12

While aqueous redox flow batteries are still dominant among those reported to date – with the vanadium redox flow battery standing out as the 'uncontested leader'^{13,14} – there has recently emerged a rising interest in non-aqueous systems.¹⁵⁻¹⁸ To an extent, the trend is that the development of suitable commercially available separators, and specific membrane research more generally, will be the determining factor of the rate at which non-aqueous redox flow batteries (NARFBs) will evolve.¹⁹⁻²² One of the greatest challenges for contemporary

 ^{a.} MEET Battery Research Center, University of Münster, 48149 Münster, Germany.
^{b.} Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Corrensstraße

^{40, 48149} Münster, Germany. ^c Helmholtz Institute Münster, IEK-12, Forschungszentrum Jülich GmbH, 48149 Münster, Germany

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non-aqueous RFBs lies in combining selective separation of two half-cell compartments to prevent irreversible co-mixing of electrolyte constituents with sufficient resilience against swelling and external mechanical action. Even the state-of-theart separators for NARFBs offer only a trade-off between ionic and molecular selectivity and the high conductivity necessary to complete the cell electric circuit and operate at higher current densities. To date, ion-selective membranes and porous separators from companies like Fumatech GmbH,^{9,23,24} Daramic^{®25,26} or Astom Corp.^{27,28} have been successfully employed for non-aqueous laboratory-scale static and flow battery systems.

Despite the posed technical challenges, a transition from aqueous to non-aqueous redox electrolytes offers expanded scope to select electrolytes offering higher capacity and higher voltages. Simultaneously, the wide electrochemical stability window of organic solvents, their compatibility with modern RFB cell elements, their wide working temperature range, and beneficial hydrodynamic properties explain the modern trend of utilizing organic solvents in flow battery applications.⁷ Among the common aprotic electrolyte solvents, acetonitrile plays an important role since it provides an exceptionally wide electrochemical stability window (6.1 V, from -2.6 V to 3.5 V vs. the standard hydrogen electrode (SHE)), low dynamic viscosity (η_d = 0.341 mPa·s) and density (ρ = 786 kg·m⁻³) as well as high conductance (σ) of the resulting supporting salt solutions (for instance, $\sigma_{Bu4NCIO4, 1M}$ = 27.0 mS·cm⁻¹ and $\sigma_{Et4NBF4, 1M}$ = 55.5 mS·cm⁻¹).²⁹ Overall, the use of acetonitrile has a positive impact on energy density, allowing an NARFB electrolyte to eventually deliver a higher energy density than aqueous analogues.

Besides the choice of a suitable membrane separator, a further strategy to preclude irreversible capacity fading is to utilize the same redox material for both negolyte and posolyte (where a negolyte is a redox electrolyte characterized by a lower half-cell reaction potential in comparison to the posolyte). Such a requirement introduces a considerable design limitation as any selected substance must possess three or more oxidative states at sufficiently separated redox potentials. Naturally, other requirements for ROMs - such as high solubility in a given solvent, or electrochemical (or at least chemical) reversibility for each of the half-cell reactions - still apply. To our knowledge, only a limited number of pure ROM cases (i.e. not including metal-coordinated complexes) have been reported as being adopted as an electrolyte for non-aqueous RFBs. Among them are diaminoanthraquinone (DAAQ),³⁰ croconate violet,³¹ nitronyl nitroxides 2-phenyl-4,4,5,5-(e.g. tetramethylimidazoline-1-oxyl-3-oxide (PTIO)),^{32,33} N-(αferrocenyl)ethylphthalimide,³⁴ and porphyrin.³⁵ For the sake of diversification and better understanding of how symmetrical ROM-based electrolytes fundamentally function, novel examples are indispensable.

Verdazyl radicals (Figure 1) have grown as a group in recent decades to become one of the largest families of stable free radicals. They are, with only a few exceptions, stable indefinitely both as solids and in solution, are air- and water-stable, and

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have no tendency to dimerize.³⁶ The tunability, *iew* Artelevant physicochemical properties and chemical stability over greater than that of the well-known nitroxide radicals^{37,38} has fed a high demand for these compounds in the fields of molecular magnetochemistry³⁹ and radical probing⁴⁰. Verdazyls have long been foreseen to be promising materials for battery applications owing to their bipolar redox activity.^{41,42} Even within those synthetic frameworks already developed, verdazyls can be engineered to bear substituents beneficially affecting electrochemical potentials and reversibility in redox processes, targeting a higher energy capability of the final electrolyte product.



Figure 1. General structure of verdazyl free radicals: A) Kuhn verdazyl; B) oxoverdazyl.

Despite their promise, it was only recently that Dyker and coworkers demonstrated the potency of verdazyl radicals as a redox electrolyte for RFBs using a static 2032 coin cell battery setup.⁴³ Their battery made use of 3-phenyl-1,5-p-tolylverdazyl, a Kuhn-type verdazyl, to generate a cell voltage of 0.97 V. A small study by Hicks and co-workers characterized the redox potentials of a selection of verdazyls and found that the oxoverdazyls possessed significantly higher cell voltages than the Kuhn-type verdazyls, and essentially complete electrochemical reversibility.³⁸ However, to the best of our knowledge there has been no report of an oxo-verdazyl radical being used as a redox electrolyte, nor has any verdazyl ever been studied under actual flow conditions. In the present work we report a systematic study on oxo-verdazyl-based electrolytes as a core electrolyte element of a symmetrical non-aqueous RFB. The main discussion will revolve around 1,5-diphenyl-3-isopropyl-6-oxoverdazyl (isoV), identified as the most promising redox material for further investigation by means of a preselection process.

Although the nature of a symmetrical electrolyte introduces undeniable simplification and unification to the setup, there is no guarantee of a similar electrochemical response from each of the two oxidative state transitions. As such, a more detailed description of electrode processes must be continuously assessed and updated for each of the half-cell compartments in order to determine where the redox electrolyte tends to fail most severely within the RFB lifespan. Incorporating a reference electrode into the common redox flow battery cell setup introduces a powerful tool for decoupling and monitoring of the corresponding states of electrolytes.4,44 Modern technologies incessantly offer state-of-the-art solutions to make common and well-described reference electrode chemistries more versatile and thus to introduce a new tool of comparison, necessary for advanced battery systems.^{45,46} For a complete electrochemical picture, one should therefore take advantage of the possibility to integrate electrochemical techniques common in RFB research (e.g. cyclic voltammetry (CV) and

electrochemical impedance spectroscopy (EIS)) directly into the applied battery setup. Gathering these data within the frame of battery cell conditions opens a way to include and evaluate a multivariate influence of the setup on redox electrochemical properties; for example, through the type and geometry of current collector,⁴⁷⁻⁴⁹ the given kind of ion exchange membrane or porous separator,^{50,51} and the velocity of the flow.⁵² Such an approach aids in deciphering the true nature of existing overvoltages for operational RFBs.44,53 Although the physicochemical impact of RFB cell components on electrochemical performance is not doubted, it is rarely taken into account and described. Here we address the issue by extending the standard redox electrolyte characterization routine, thereby demonstrating how the transition to a battery cell affects the electrochemical properties of a given studied material.

Experimental

Chemicals and Reagents

Tetrabutylammonium perchlorate (TBAP, >98%) and Al₂O₃ nanopowder (>98%, <50 nm TEM size) were purchased from Sigma Aldrich, anhydrous acetonitrile (MeCN, ROTIDRY®Sept, >99.9%, < 10 ppm H₂O) from Carl Roth, and ferrocene (>99.5%, high purity) from Alfa Aesar. Dimethylformamide (DMF, 99.8%, Extra Dry) was purchased from Acros Organics. Reagents and all other chemicals required for synthesis were purchased from ABCR, Acros Organics, Alfa Aesar, Sigma Aldrich, Fisher Scientific, Fluorochem, or TCI, and were used as received.

Synthesis of oxo-verdazyl radicals

The synthesis of all screened radicals was reported previously.⁵⁴ Each is easily prepared in three steps, beginning with a Goldberg reaction between carbohydrazide and an aryl iodide, followed by condensation with an aldehyde to form the tetrazinanone precursors (Figure S1). Oxidation to the radicals is straightforward with e.g. benzoquinone. Further details, a general procedure, and full synthetic details and characterization data for **isoV** can be found in the Supporting Information.

Preliminary electrochemical studies

Cyclic voltammetry (CV) and potentiostatic electrochemical impedance spectroscopy (P-EIS) experiments were carried out within a custom three-electrode electrochemical cell, with a volume of 2 mL, using platinum disc electrodes (eDAQ, 3 mm diameter) as the working and counter electrodes, and a leakless miniature Ag|AgCl(sat.) reference electrode (ET072-1, eDAQ, Australia). Calibration of the leakless Ag|AgCl (sat.) reference electrode was carried out within the described three-electrode setup with the help of 10 mM ferrocene in a 0.1 M acetonitrile solution of TBAP as a supporting salt (Figure S2 in SI). Working and counter electrodes were polished prior to each measurement session with fine sandpaper (1200 grit) to remove coarse contaminants from the electrode surface, with fresh alumina paste on a glass substrate to reduce the roughness of the surface, and were then sequentially sonicated in distilled water and acetonitrile to remove residuals of

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alumina particles. Considered redox electrolyte solutions consisted of 2 mM of each given oxo-verda2yl1radicaland039M TBAP as the supporting salt in 2 mL of anhydrous acetonitrile. The chosen potential scan rate range for CV measurements was set from -1 V to 1 V with a starting point of 0 V vs. Ag | AgCl(sat.). The set of P-EIS measurements was collected by applying an alternating voltage of magnitude 3 mV at a frequency in the range 0.1 – 100000 Hz, with a number of starting potentials in the vicinity of the corresponding half-cell reaction potential (vs. Ag|AgCl (sat.)). Before each individual CV or P-EIS experiment, the filled electrochemical cell was purged with nitrogen gas for two minutes to remove oxygen. Electrochemical data were collected using a connected stack of an SI 1287 Electrochemical Interface (Solartron) and an SI 1260 Impedance/Gain-phase Analyzer (Solartron) together with dedicated software (Scribner, USA).

Flow cell experiments

Galvanostatic and potentiodynamic cycling experiments in static and flow conditions were carried out with a custom-made zero-gap flow cell. Conductive end plates consisted of two mirrored graphite blocks (Alfa Aesar) with CNC-processed flow frames of predefined exposed area 0.9 cm², and were liquidtight inserted to polypropylene flow-through supporting blocks with inlet and outlet for electrolyte access as well as additional inlets for the connection of the reference electrode. The sealing set for the flow cell included handmade silicon (MaTecK, Germany) gaskets with 0.9 cm² exposed area and commercial Nylon O-rings (Arcus, Germany) of appropriate size. Each experiment involving RFBs employed 6 mm thick carbon felt electrodes (Alfa Aesar, uncompressed), a leakless miniature Ag|AgCl(sat.) reference electrode (ET072-1, eDAQ, Australia) and a fresh piece of anion exchange membrane (AEM) Fumasep®FAP-375-PP (FUMATECH, Germany) as a cell separator. Carbon felt electrodes were preliminarily treated several times with acetonitrile in order to wash away any organic contaminants present, and the membrane was predried for 20 minutes under reduced pressure at room temperature. All measurements were carried out within a nitrogen-filled SEKUROKA® glove-bag (Carl Roth) under a constant stream of gas. Redox electrolyte preparation and final RFB cell assembly proceeded within the inflated glove-bag after prior continuous N₂ gas purging for 30 minutes. The pumping line system consisted of a peristaltic dual TVP15 pump (Medorex, Germany) providing a constant flow rate (2 mL·min-1) and stretchable PharMed®BPT tubing (Saint-Gobain Performance Plastics, France) jointed with PTFE tubing (Bohlender, Germany) to ensure secure and prolonged pumping through the flow-cell. A 2 mL solution of 0.3 M tetrabutylammonium perchlorate and 10 mM of the redox material 1,5-diphenyl-3-isopropyl-6-oxo-verdazyl in anhydrous acetonitrile was used as a standard electrolyte formulation for all RFB cell experiments. Galvanostatic charge/discharge cycling of the RFB cell proceeded between -0.20 V and 2.00 V threshold potentials at current density of 2.22 mA·cm⁻².

For 'in-cell' cyclic voltammetry investigations in static mode (no pump-induced flow), a potential scan rate range of 2 mV·s⁻¹ –

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30 mV·s⁻¹ was employed. On a working pumping line a potentiostatic pre-electrolysis step for 200 s preceded every measurement, at -0.20 V and 0 V vs. Ag | AgCl(sat.) for negolyte and posolyte half-cells, respectively, to minimize the initial current response from a potential step. For flow mode (pumpinduced flow) a potential scan rate range of 0.2 mV·s⁻¹ – 0.8 mV·s⁻¹ was employed without preliminary treatment.

State of charge studies

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Open Circuit Potential (OCP) measurements

After each galvanostatic step of ±1.1 mA·cm⁻², corresponding to a change of 10% of the theoretical state of charge, continuous OCP measurement was applied until the OCP no longer deviated for more than 5 mV over 30 s.

UV-Vis measurements

After galvanostatic steps of 1.1 mA·cm⁻², corresponding to 20%, 40%, 60%, 80% and 100% changes in the state of charge (SOC) and, in order to ascertain complete mixing inside the half-cell, continuous measurement of the OCP until it no longer deviated for more than 5 mV over 30 s, 0.1 mL aliquots of the negolyte and posolyte were taken and diluted up to 3 mL with anhydrous acetonitrile. Spectra of the resulting samples were recorded in the 350-800 nm wavelength region with 1 nm resolution, using a Shimadzu UV-2450 spectrometer and a quartz High Precision Cell with a pathlength of 10 mm (Hellma Analytics).

Linear Sweep Voltammetry (LCV) measurements

Initially each analyzed RFB cell was completely pre-charged. After galvanostatic steps of $\pm 1.1 \text{ mA} \cdot \text{cm}^{-2}$ and a rest step to allow adequate mixing of the resulting half-cell electrolyte, the pumps were switched off and static LSV data were recorded at a 50 mV·s⁻¹ potential sweep rate and, starting from the value of OCP, down to -1.75 V vs. Ag|AgCl (sat.) for negolytes and up to 1.40 V vs. Ag|AgCl (sat.) for posolytes. Since an LSV scan inherently changes the ratio of oxidized and reduced forms of a given redox couple due to the Faradaic process of interest, a capacity balance was updated after every scan.

Galvanostatic Electrochemical Impedance Spectroscopy (G-EIS) measurements

Initially each analyzed RFB cell was completely pre-charged. For this measurement no reference electrode was applied. After galvanostatic steps of 1.1 mA·cm⁻², and a rest step required for the stabilization of open circuit voltage (OCV) upon continuous convective mixing of redox electrolyte, galvanostatic impedance electrochemical spectra were recorded. Measurement was then conducted by applying an alternating current of magnitude 0.2 mA in the absence of direct current, with frequency range 5 – 100000 Hz and starting voltage of 0 V vs. OCV. During each GEI scan, peristaltic pumps provided a continuous flow of electrolyte through the cell.

Results and discussion

Flectrochemical Studies

An exploratory preselection process was first carried out on a set of previously synthesized oxo-verdazyl radidals, Pto Obtain initial insight into their electrochemical properties. The structure of the radicals varied by the identity of a single substituent at the 3-position, including both aliphatic and aromatic groups of varying polarity (Figure 2a). Each considered redox species, within supporting media closely resembling a desirable RBF electrolyte formulation, was subjected to a general screening protocol: solubility determination, threeelectrode cyclic voltammetry (CV) measurements and, in the of reasonably satisfying results, potentiostatic electrochemical impedance spectroscopy (P-EIS) experiments. Further synthetic details and full electrochemical data are given in the Supporting Information (Figure S4, S5).

Among the screened verdazyl radicals, the most optimal performance was observed for 1,5-diphenyl-3-isopropyl-6-oxoverdazyl (isoV). 1,5-diphenyl-3-methyl-6-oxo-verdazyl (4) behaved similarly and even marginally outperformed the former, due primarily to its inherently lower molecular mass. However, application of isoV was expected to be more reasonable as the isopropyl group introduces additional steric bulk in comparison to the methyl analogue and thus higher resistance to envisaged undesirable crossover action through an ion-exchange membrane^{9,20} and due to the high solubility in acetonitrile (up to 2.4 M) as shown in Figure S6. Furthermore,



Figure 2. a) Oxo-verdazyl radicals for preselection: 1.5-diphenyl-3-4-nitrophenyl-6-oxo-verdazyl (1), 1,5-diphenyl-3-4-N,N'-dimethylphenyl-6-oxo-verdazyl (2), 1,5diphenyl-3-4-fluorophenyl-6-oxo-verdazyl (3), 1,5-diphenyl-3-methyl-6-oxoverdazyl (4), 1,5-diphenyl-3-ethyl-6-oxo-verdazyl (5), 1,5-diphenyl-3-isopropyl-6oxo-verdazyl (isoV); b) Oxidative states of 1,5-diphenyl-3-isopropyl-6-oxoverdazyl.

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some verdazyls with methyl groups at the 3-position are known to exhibit reduced long-term stability.³⁶

The 1,5-diphenyl-3-isopropyl-6-oxo-verdazyl radical participates in two different electrochemical redox processes (Figure 2b) at the surface of the platinum electrode, accompanied by either electron abstraction (oxidation to isoV⁺) at 0.70 V vs. Ag|AgCl (sat.), or electron capture at -0.72 V vs. Ag|AgCl (sat.) (reduction to isoV⁻) (Figure 3a). The half-cell reaction potentials of the observed processes are separated by a difference of 1.42 V, providing a theoretical cell voltage for a symmetrical NARFB based on this radical. Observed anodic and cathodic peaks near the mentioned potentials have similar shapes of equal heights (the ratios of the corrected current peaks are close to unity) and a separation of ~70 mV for both oxidative and reductive processes, with only slight variation upon increasing the potential sweep rate, thus indicating diffusion-limited electrochemically reversible redox reactions. The aforesaid, together with a reasonable assumption of established semi-infinite type diffusion to a planar electrode surface, permits Randles-Sevcik analysis for each of the considered redox couples isoV⁺/isoV and isoV/isoV⁻ (Figure 3b), through the related analytical expression, shown in Equation 1:55

$$i_{\rm p} = 0.4463nFAC \left(\frac{nFvD}{RT}\right)^{0.5} \tag{1}$$

where *n* is the number of transferred electrons, *A* is the electroactive surface area (in cm²), *D* is the diffusion coefficient (in cm²·s⁻¹), *C* is the concentration of the redox compound (in mol·cm⁻³), *v* is the potential scan rate (in V·s⁻¹), *T* is the temperature (in K), and *F* is the Faraday constant (96485 C·mol⁻¹).

Derived diffusion coefficients for isoV*/isoV and isoV/isoVamount to $2.8 \cdot 10^{-7}$ cm²·s⁻¹ and $1.8 \cdot 10^{-7}$ cm²·s⁻¹, respectively, at 298 K. These values lie within the typical range for redox materials used in symmetrical NARFBs.³²⁻³⁵

The P-EIS method provides a rapid tool to treat the kinetics of heterogeneous electrochemical processes quantitively and, more importantly, conveniently, without changing the threeelectrode CV setup. The approach described (see Experimental) allows for decoupling of charge-transfer resistance from mass transfer resistance and for the evaluation of a standard electrochemical rate constant given a known diffusion coefficient, similar to 'De Levie-Husovsky' analysis.⁵⁶ To apply this approach, it is necessary to convert the resulting P-EIS spectra to a tantamount representation of a Bode phase diagram, where the cotangent of the registered phase angle and correspondent square root of frequency are used in place of phase angle and frequency, respectively. The final goal consists of the appropriate fitting of the result for the intermediate frequency region, where mass-transfer impedance³⁷ and potential-dependent charge-transfer impedance have a comparable impact on total impedance, to a mathematical model derived specifically for Faradaic processes governed by semi-infinite planar diffusion, shown in Equation 2:

$$\cot \varphi_{E_{1/2}} = 1 + \left(\frac{D_0^{1-\alpha} D_R^{\alpha}}{2}\right)^{1/2} \frac{\omega^{1/2}}{k^0}$$
(2)

where D_o is the diffusion coefficient of oxidized form (in cm²·s⁻¹), D_r is the diffusion coefficient of reduced form (in cm²·s⁻¹), α is the current exchange coefficient, ω is the frequency (in Hz), and k^0 is the standard rate constant (in cm·s⁻¹).

Additional precautions must be first considered to diminish any influence from the inherent impedance of the reference electrode, even though it barely affects the frequency region of interest. To this end, a sequence of spectra was recorded for each redox reaction near the corresponding half-wave potentials, converted to an appropriate format and, finally, a dataset with the highest cotangent values related to the frequency band of interested was selected (Figure 3c,d). Further fitting to the mathematical model (Equation 2) provides an estimate for the standard electrochemical rate constant of k^0 = 0.0081 cm·s⁻¹ for the redox couple isoV⁺/isoV, which is on a reasonable level typical for an NARFB. Unfortunately, the total electrochemical impedance is extremely sensitive to background processes such as potential drifts or electrode contamination,^{56,57} sometimes making an appropriate fitting impossible. This was observed for the redox couple isoV/isoV-, for instance.

As an actual RFB setup has many structural differences compared to a three-electrode setup, additional efforts must be made to characterize the transition between them in order to have a better overview of processes occurring inside the RFB during operation. The geometry of the mechanically 'zero-gap' attached flow-through 'carbon felt-on-graphite plate' electrode combination differs significantly from that of a disc electrode. Thereby, for potentiodynamic studies on porous electrodes in static mode (flow rate 0 mL·min⁻¹), two diffusion regimes prevail for the most part: external linear semi-infinite and, predominantly, external finite cylindrical. To date there is only a limited number of works where such problems are treated quantitively as there is no simple analytical description as for redox processes governed by semi-infinite linear diffusion.58-60 In light of this, effects of the transition from a three-electrode setup to an RFB cell on a 10 mM oxo-verdazyl-based redox electrolyte were studied.

For the posolyte half-cell with the **isoV+/isoV** redox couple (Figure 3f), apparent separation between cathodic and anodic peaks increased up to ~200 mV, accompanied by noticeable

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broadening and an additional resolved anodic peak at 1.10 V vs. Ag|AgCl (sat.). Observed signal broadening corresponds to the expected 'in pore' external finite cylindrical diffusion response for the carbon felt electrode since it can be treated as a microelectrode network with randomly distributed distances between fibers. The seemingly irreversible oxidation process at 1.10 V vs. Ag|AgCl (sat.) relates to an unresolved cathodic peak at ~0.45 V vs. Ag|AgCl (sat.), implying a very slow electrochemical response with regard to linear diffusion to the surface of the conductive graphite end plate or the external surface of the carbon felt block.

For the negolyte half-cell with the **isoV/isoV**⁻ redox couple (Figure 3e), only a slight amount of lateral splitting at -0.60 V vs. Ag |AgCl (sat.) is present for the anodic process, although the cathodic peak potential strongly depends on the potential scan rate whereas the connected potential of the anodic peak rests mostly unaffected at -0.72 V vs. Ag|AgCl (sat.). Marked interaction with an associated induced broad peak separation makes the negolyte part of the symmetrical electrolyte a plausible overvoltage source, which may preclude efficient RFB charging at high current densities.

As a further step, the symmetrical oxo-verdazyl-based redox electrolyte was subjected to potentiodynamic bulk electrolysis. By adding convection to an analyzed system, the observed electrolyte redox behavior closely approaches that of the actual battery of interest. Characteristics like 'in-flow' overvoltage as a function of potential sweep rate or efficiency of mass convection under mass transfer limits pertain to the final performance of any RFB system. It is no secret that the flow of redox electrolyte through a porous hydrodynamic electrode significantly reshapes the dimensional distribution of the concentration of redox-active species, supplying more efficient flux of redox material near the electrode surface beyond Fickian limits and, as a consequence, enabling higher current densities.^{4, 61} In comparison to the static case, porous electrodes subjected to a flow of redox material paint a decisively different picture within the scope of otherwise technically identical potentiodynamic studies.

For the negolyte, a similar profile was observed for both cathodic ('charge') and anodic ('discharge') processes with peak splitting near -1.2 and -0.35 V vs. Ag|AgCl (sat.), respectively, due to delayed 'convectional' mixing within the electrolyte tank and the same electrochemical reaction occurring on the surface of graphite end plate (Figure 3h). The observed symmetry of the current maximum peaks for the acquired set of cyclic voltammograms suggests that the observed anodic electrochemical process possesses a lower current exchange coefficient in terms of Butler-Volmer theory.⁵⁸ This phenomenon strongly affects the discharge time required for reaching the maximum current value and, furthermore, makes the concentration gradient less pronounced under the constant electrolyte flow. As a result, a so-called diffusional tail of secondary 'convectional' current peak is observed at higher

scan rates. Obviously, a redox retardation negatively influences the final Coulombic efficiency of potential mic⁰⁷ bulk electrolysis. Nevertheless, related coulometric analysis of the cathodic process at -0.60 to -1.40 V vs. Ag|AgCl(sat.) suggests a relatively low dependency on the potential sweep rate as similar values of total charge for both lowest or highest scan rate are registered, whilst the potential shift for corresponding current peak does not exceed 200 mV.

In the case of the posolyte, the resulting picture (Figure 3g) is generally more complex. Sequential potentiodynamic cycling at various sweep rates induced additional peak splitting for the single-electron oxidation process. Interestingly, the same electrochemical process seems to proceed at different electrode domains and has a predominant dependence on diffusional mode, producing anodic current peak splitting at 0.60 - 0.80 V and 0.80 - 1.00 V vs. Ag|AgCl (sat.), where each peak group exhibits a different dependence on the potential sweep rate. Regarding the cathodic process ('discharge'), corresponding groups of current peaks appear almost completely overlapped, giving a sharp response at 0.30 - 0.40 V vs. Ag | AgCl, which from coulometric analysis does not scale up with increasing potential sweep rate. This, together with a subsequent fairly constant but sluggish mass transfer current response, suggests that oxidized isoV⁺ has a high propensity for reduction back to the initial oxidative state, although the total overvoltage in comparison to the negolyte is higher. Another important aspect to highlight is the average maintained current throughout the potentiodynamic cycle: it is systematically lower for the posolyte compared to the negolyte for each applied scan rate. This can be considered responsible for premature overvoltage development during the late stage of charge and discharge processes.

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Figure 3. a) Cyclic voltammograms for **isoV** at different potential scan rates (5 mV/s – 100 mV/s) in the potential range –1 V vs. Ag|AgCl (sat.) to 1 V vs. Ag|AgCl (sat.). b) Randles-Sevcik analysis for each electrochemical process of **isoV**. c) Potentiostatic electrochemical impedance spectra for **isoV**-/**isoV** recorded close to the corresponding half-reaction potential (–0.723 to –0.732 V vs. Ag|AgCl (sat.)) and converted for cotangent analysis. d) Potentiostatic electrochemical impedance spectra for **isoV**-/**isoV** recorded close to the corresponding half-reaction potential (0.701 to 0.710 V vs. Ag|AgCl (sat.)) and converted for cotangent analysis. e) Cyclic voltammograms for isoV-based negolyte recorded within the static RFB setup at different potential scan rates (2.5 mV/s – 30 mV/s) in the potential range from –0.2 V to 1.4 V vs. Ag|AgCl (sat.). f) Cyclic voltammograms for isoV-based posolyte recorded within the static RFB setup at different potential scan rates (2.5 mV/s – 30 mV/s) in the potential range from –0.2 V to –1.6 V vs. Ag|AgCl (sat.). g) Potentiodynamic bulk electrolysis series for **isoV**-based posolyte recorded within the 'in-flow' RFB setup for different potential scan rates (0.2 mV/s – 0.8 mV/s) in the potential range -0.6 V to 1.1 V vs. Ag|AgCl (sat.). h) Potentiodynamic bulk electrolysis series for **isoV**-based negolyte recorded within the 'in flow' RFB setup at different potential scan rates (0.2 mV/s – 0.8 mV/s) in the potential range -0.2 V to –1.6 V vs. Ag|AgCl (sat.). e) Notentiodynamic bulk electrolysis series for **isoV**-based negolyte recorded within the 'in flow' RFB setup at different potential scan rates (0.2 mV/s – 0.8 mV/s) in the potential range -0.2 V to –1.6 V vs. Ag|AgCl (sat.). e) Notentiodynamic bulk electrolysis series for **isoV**-based negolyte recorded within the 'in flow' RFB setup at different potential scan rates (0.2 mV/s – 0.8 mV/s) in the potential range -0.2 V to –1.6 V vs. Ag|AgCl (sat.).

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State of Charge Studies

In order to assess battery cycling behavior, electrochemical properties of the symmetrical redox electrolyte were studied ex situ within a single arbitrary galvanostatic cycle via a sequential cycle interruption. Multidimensional state of charge (SOC) analysis can help to explain the observed asymmetry of electrochemical responses from both half-cells.

As a starting point, OCP measurements were conducted at various SOCs for each half-cell (Figure 4a). Surprisingly, even at this stage the resulting asymmetric OCP profile revealed inconsistency in the simultaneous processes of oxidation and reduction. For the electrochemical oxidation of 1,5-diphenyl-3isopropyl-6-oxo-verdazyl, the determined OCP for starting and finishing iterations does not follow classical Nernstian behavior, reaching the formal plateau by 20% SOC for the charging process and leaving it by 30% SOC for the discharge process, thus hindering achievement of the theoretical capacity. Since this is an indication that the oxidized form of the verdazyl (isoV⁺) does not reach thermodynamic (Nernstian) equilibrium near the working porous electrode in the expected way for a given SOC, a plausible explanation for the posolyte issues is a specific but reversible interaction with the membrane (membrane fouling) (Figure S9). In further galvanostatic RFB cycling sessions higher applied current densities were therefore favored, causing the active area of membrane to be exposed to intermediate concentrations of isoV⁺ for less time. On the other hand, the negolyte shows no sign of a negative effect on final performance of the symmetric battery cell, corroborating the preceding potentiodynamic 'in flow' experiments.

To further address the issue with the discharge process, the precharged (1.60 V) RFB was subjected to stepwise discharge with a set of electrochemical impedance spectra recorded after each step. Since it was intended that the RFB should be studied at intermediate states of charge, even a minor change of voltage amplitude would result in an inconsistent non-linear current response, thus necessitating the choice of a galvanostatic mode of EIS instead of potentiostatic. The real part of the electrochemical impedance, Ω_{re} , of both frequencyindependent charge transfer resistance and frequency- and symmetry-dependent mass transfer impedance, comprising a total Faradaic impedance, has an essential dependency on the composition of the electrolyte at a given instant.⁵⁶ When a stable OCV is present, an established thermodynamic equilibrium near the surface of a given porous electrode provides an opportunity to interrelate the OCV to a snapshot of the redox electrolyte, as according to the Nernst equation. Therefore, mapping a set of the real part of impedance spectra at different OCVs helps to trace deviations from ideal thermodynamic behavior. As expected, the absolute minima of the observed real impedances present over the whole frequency band appear close to the OCV (Figure 4b). Relatively low Ω_{re} values are observed in the region 1.25–1.50 V, where the expected galvanostatic discharge plateau should emerge; otherwise, a steady increase of Ω_{re} , especially for the low

frequency band, is observed and attributed to <u>limited</u> mass transfer. As in the previous OCP measurements, where dimited performance at a late stage in the discharge process was governed by the posolyte, a corresponding early cell voltage drop correlates with a significant increase in the real part of the mass transfer impedance, supporting the hypothesis of specific interactions with the ion-exchange membrane. In order to achieve a theoretical 0% charge state, a potentiostatic step at 0 V vs. OCV was employed and a respective electrochemical impedance measurement provided, as expected, the highest values of $\Omega_{\rm re}$ for the low frequency region.

In order to characterize the electrochemical properties of the symmetrical verdazyl-based electrolyte more comprehensively, linear sweep voltammograms (LSV) were then recorded for both negolyte and posolyte. A series of LSVs extend and supplement the prior explicit OCP measurements, as the starting point for every individual voltammetry experiment lies exactly where the cell current equals zero - or, in other words, at the OCP. The following approach allows for surveying how instantaneous electrolyte constitution affects the resulting electrochemical response on porous electrodes. However, an SOC assignment gives the best result only for potential plateaus near corresponding half-wave potentials and is barely applicable for regions with an SOC of 80% or more, where the apparent current response from residual electroactive redox form is naturally low. For the sake of visibility, a contour map representation of an arbitrary galvanostatic cycle of interest was recorded starting from the discharge of the RFB. Although the resulting graphs for the negolyte (Figure 4d) and posolyte (Figure 4c) are essentially similar, featuring a high apparent degree of electrochemical reversibility and a gradual current peak value shift towards more negative or positive potentials, respectively, some details remain contrasted. For instance, each electrolyte behaves differently when the completely charged form of the electrolyte is considered. In particular, the electrochemical response of the posolyte exhibits a systematic current peak value upshift (50 mV) immediately after the charging process is switched to discharging. The negolyte does not do this to such an extent. Presumably, this discrepancy once again stems from the assumed susceptibility of the posolyte towards the membrane. Another important differing aspect is a pronounced lateral diffusional current observed for the posolyte, where the current response on porous electrodes is systematically 'smeared' towards higher potentials; the negolyte does not exhibit this trend, instead demonstrating more rapid current decay after reaching the corresponding reduction current peak.

Since solutions of each of the verdazyl oxidative states **isoV**⁺, **isoV** and **isoV**⁻ possess rather distinguishable colors, an additional approach applied was to carry out UV-Vis studies to determine the corresponding negolyte (Figure 4f) and posolyte (Figure 4e) compositions. Analyzed aliquots were sequentially extracted after each galvanostatic step-charge and rest-step sequence and diluted with dry acetonitrile under an inert Published on 19 October 2020. Downloaded by University of Rochester on 10/20/2020 1:13:11 PM

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Figure 4.a) Open circuit half-cell potential vs. state of charge dependency for the posolyte and negolyte of the symmetrical isoV RFB. b) Contour map representation of the real part of the galvanostatic electrochemical impedance evolution upon discharge of isoV RFB relative to the cell open circuit voltage and applied AC frequency. c) Linear sweep voltammograms for different states of charge for the posolyte. d) Linear sweep voltammograms for different states of charge for the negolyte. e) Difference UV-Vis spectra for different states of charge for the posolyte. f) Difference UV-Vis spectra for different states of charge for the negolyte.

atmosphere. It is worth noting that the rest step is essential for SOC measurements, as it enables redox electrolytes to effectively mix throughout the half-cell space and thus prevents undesirable mass gradients for both oxidative states of the redox material present within. Obviously, for any symmetrical electrolyte, the initial 'discharged' state remains the same no matter which half-cell is considered. A characteristic absorbance peak maximum for the **isoV** radical electrolyte solution appears at 490 nm, and a broad but minor absorption is observed at 380 nm (Figure S7). The broad absorption band at 490 nm hinders spectroscopic analysis of the posolyte. For this reason, each set of UV-Vis absorption spectra was transformed to a set of difference spectra by subtracting a dataset recorded previously of the initial 'discharged' state. The subsequent general observation regarding the posolyte is an initial absence of **isoV**⁺ related signal development until 40% of the theoretical state of charge (SOC), which does not contradict the previous OCP series of measurements. However, after this

point characteristic signals from both **isoV**⁺ and **isoV**⁻ appear at 547 nm and 388 nm respectively. Linear behavior of the absorbance indicates compliance with the Beer–Lambert law, making UV-Vis spectroscopy a method acceptable for SOC monitoring of the symmetrical verdazyl electrolyte.

Galvanostatic Cycling in Battery

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The RFB, filled with the non-aqueous verdazyl-based (isoV) electrolyte, was exposed to galvanostatic cycling at various current densities (Figure 5a). The choice of the lower limit ('cutoff') voltage is based on the fact that the initial state of any symmetrical redox flow electrolyte must have an OCV close to 0 V, although mass transfer limitations dictate a shift down to an optimal value of -0.20 V. The total voltage range for each galvanostatic cycling experiment conducted was set between -0.20 V and 2.00 V. Increasing the current density from 0.55 mA·cm⁻² to 2.2 mA·cm⁻² had a strong influence on the part of the cycle governed by mass transport. Notably, close to the cell voltage (1.42 V, as inferred from CV measurements) the welldefined charge and discharge plateaus appear, being mostly affected only by Ohmic voltage drop. The bottleneck for performance of the RFB cell setup lies primarily in the discharge process as at the lowest current density the applied Coulombic efficiency reaches 88%, while the resulting charge capacity fulfils theoretical expectations. As previously mentioned, inflow potentiodynamic behavior for the negolyte suggests a considerable shift in the secondary 'convectional' anodic current peak at high potential sweep rates, resulting in an incomplete bulk discharge process. Besides this, a persistent but minor current response for the posolyte remains down to very low discharge potentials, until right after a particularly sharp, yet narrow, Faradaic reduction process. Evidently, in terms of galvanostatic cycling, the prior current peaks must be interpreted as a discharge plateau, flat yet short, and the aforementioned minor current response as a mass transfer governed voltage drop. The same reasoning applied for the charge profile interpretation provides a link to the barely defined plateau at ~1.20 V, taking into account a set of broad current peaks in the range of 0.25 - 0.40 V vs. Ag | AgCl(sat.) for the posolyte.

Finally, the major requirement for any redox-active material intended for use as part of an RFB electrolyte is that of high long-term cycling stability. To evaluate this, a 10 mM solution of the isoV electrolyte was subjected to continuous galvanostatic charge/discharge sequences for 150 cycles at 2.2 mA·cm⁻². For this RFB setup as a battery separator a FAP-375-PP anionexchange membrane was selected as recently it demonstrated a decent for NARFB compromise between mechanical stability, selectivity and conductivity.9,24 Selected cycles from the experiment (Figure 5b) suggest fairly reproducible charge/discharge profiles in the vicinity of the theoretical open circuit voltage of 1.42 V, although they do show a steady moderate performance decay, meaning the duration of cycles constantly declines in time. Despite a low observed Coulombic efficiency of 85% for the first cycle, it rapidly increases during following cycles and averages of ~97% thereafter. With regard

to the evolution of the voltage efficiency and, therefore, energy efficiency upon cycling,⁶² they naturally to hver get as 78the Coulombic efficiency stabilizes. Moreover, the voltage efficiency (Figure 5d) had decreased by the 80th cycle from an initial 77% down to 52%, demonstrating reasonable cyclability, while after this point the rate of decay considerably increases and the energy efficiency approached 10% by the final cycle of the test. Most likely, a steady change of the voltage drop arises from the irreversible loss of redox active isoV through a specific sorption and from a developing of the membrane's areal resistance. Unsurprisingly, a similar trend is observed in the capacity fading (Figure 5c). In the 40th galvanostatic cycle only ~50% of the theoretical discharge capacity is extracted from the battery cell, and by the 80th cycle, which yields only 36% of the theoretical discharge capacity, an abrupt linear decay begins. The redox electrolyte instability mostly originates from an intrinsic flaw of ion-exchange membranes used for symmetrical systems like isoV. The initial oxidative state of isoV is charge neutral and hence both oxidized and reduced forms of the redox-active energy carrier possess opposite molecular charges. Since the sign of the charge carried by one of the forms inevitably matches the conductivity type of the chosen ionexchange membrane (e.g. anionic or cationic), the result is that undesirable mutual interactions such as irreversible membrane fouling can occur (Figure S9). This leads to a constant rise in areal resistance and interferes with the cycling protocol used, counteracting the pre-set voltage limits and eventually resulting in poor apparent battery performance.

Conclusions

After initial screening of oxo-verdazyl radical compounds for electrochemical properties relevant for battery applications, we introduced the best-performing candidate, the 1,5-diphenyl-3isopropyl-6-oxo-verdazyl radical (isoV), as a redox-active material with two reversible oxidative states for a 1.42 V symmetrical non-aqueous redox flow battery. A non-aqueous redox electrolyte formulation with this species is the first example of an oxo-verdazyl RFB and exhibits reasonable capacity retention of 36% of theoretical capacity after over 80 charge/discharge cycles, with a related average Coulombic efficiency of 97% at 2.2 mA·cm⁻² and an average discharge energy density of 0.147 Wh/L (a theoretical value of energy density - 0.380 Wh/L). These encouraging results constitute a successful proof of concept that will serve as the basis for further research comprising: an optimization of the oxyverdazyl structure to achieve better compatibility with a chosen type of separator by, for example, introduction of the constant molecular charge, additional steric hindrance. Regarding the supporting electrolytes, a proper selection of promising supporting salts might enable enhanced stability of every oxidative state and, therefore, extend the electrolyte life. Moreover, appropriate ion-exchange membranes for bipolar compounds require specific modifications as well.

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Figure 5. a) Cycling profiles for the 10 mM symmetrical isoV battery at various current densities. b) Voltage profiles: evolution of charge/discharge curves for the symmetrical isoV battery. c) Normalized (to the value of the theoretical capacity) capacity retention vs. number of cycles for the 10 mM isoV battery. d) Coulombic efficiency, voltage efficiency, and energy efficiency vs. number of cycles for the 10 mM isoV battery.

Introducing integrable reference electrodes to the RFB setup more sophisticated and electrode-local allowed electrochemical analysis compared to the usual three-electrode setup. This enabled deeper understanding of the performance imperfections related to specific electrolyte interactions with accessible interfaces and other pathways of capacity losses. An applied in-flow CV approach allowed the description of the electrochemical processes occurring at the surface of the porous hydrodynamic electrode of the working RFB and to accomplish it separately for each half-cell. For instance, it enabled the tracing of a mass transfer influence and explanation of the galvanostatic discharge behavior of the RFB. We propose this approach as a promising tool for the future evaluation of battery design, and particularly to assess, explain, and even quantify the impact of individual RFB optimizations and enhancements.

In the case of our **isoV** symmetrical electrolyte, the posolyte and negolyte both affect battery performance, but in different ways, rendered distinguishable and resolvable by our setup. It could

be demonstrated that the posolyte is the source of the major limiting impact on the battery's performance, especially for marginal states of charge. We expect the insights gained from this level of analysis to inform our future optimization of verdazyl-based batteries.

To our knowledge, the highlighted approaches to electrochemical analysis have not been previously employed for the description of RFBs and we consider the described protocol a good step towards method standardization in the field of modern redox flow battery research.

Conflicts of interest

There are no conflicts to declare.

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