Redox-Flow Batteries

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# Aqueous Redox-Flow Battery with High Capacity and Power: The TEMPTMA/MV System

*Tobias Janoschka, Norbert Martin, Martin D. Hager, and Ulrich S. Schubert**

***Abstract:*** *Redox-flow batteries (RFB) can easily store large amounts of electric energy and thereby mitigate the fluctuating output of renewable power plants. They are widely discussed as energy-storage solutions for wind and solar farms to improve the stability of the electrical grid. Most common RFB concepts are based on strongly acidic metal-salt solutions or poorly performing organics. Herein we present a battery which employs the highly soluble N,N,N-2,2,6,6-heptamethylpiperidinyl oxy-4-ammonium chloride (TEMPTMA) and the viologen derivative N,N′-dimethyl-4,4-bipyridinium dichloride (MV) in a simple and safe aqueous solution as redox-active materials. The resulting battery using these electrolyte solutions has capacities of 54 Ah L*$^{-1}$*, giving a total energy density of 38 Wh L*$^{-1}$* at a cell voltage of 1.4 V. With peak current densities of up to 200 mA cm*$^{-2}$* the TEMPTMA/MV system is a suitable candidate for compact high-capacity and high-power applications.*

In the advent of a shift from fossil fuels to renewable power plants, large-scale batteries are being investigated globally to counteract the volatile output of wind farms and photovoltaics, which puts the reliability of grid operation at risk.[1] For applications, such as peak-shifting and grid stabilization, the redox-flow battery (RFB) stands out among the other battery technologies, such as lithium ion or lead acid. This is because RFBs can easily be tailored to the needs of a broad range of applications with relatively low cost, long life-time, and low self-discharge.[2] In contrast to capsuled, solid-state batteries, the RFB uses redox-active materials dissolved in electrolyte solutions, which are circulated between storage tanks and a cell, which performs the energy conversion. The tank volume defines the capacity and the size of the cell the power capability of the RFB. Conventional RFBs rely on toxic active materials, such as vanadium salts, bromine or chromium in corrosive electrolyte solutions, such as concentrated sulfuric acid.[2–3] Recent developments have targeted organic active materials, such as quinones,[4] stable radicals,[3c,5] and polymers[6] to establish a new raw material source. Unfortunately, organic RFBs that employ organic solvents suffer from low power capability, while acid-based systems demonstrate low energy densities. Both approaches generally go along with inherent safety risks resulting from flammable solvents or corrosive materials. To date, only for TEMPO/viologen systems—either as polymer[6a] or organic small molecules[5b]—could a mild electrolyte consisting of water and sodium chloride be used. The polymer-based system introduced a novel principle of separating the cathode and anode by size-exclusion. Current efforts are, for example, directed at reducing the intrinsic viscosity of the electrolyte; the overall energy densities of both systems is currently limited by the solubility of the materials to under 12 Wh L$^{-1}$. Additional restrictions in peak current density (ca. 100 mA cm$^{-2}$) and the cell voltage (ca. 1.2 V) limit the systems' applicability; intensive efforts have been undertaken to overcome the limitations. As an alternative approach we describe herein the evaluation of TEMPO and viologen derivatives that feature superior water solubility as well as fast redox reactions. An organic-RFB that excels in energy density and power capability while employing a safe, water-based electrolyte can therefore be presented for the first time.

2,2,6,6-Tetramethylpiperidin-1-yl oxyl (TEMPO) is employed as a spin probe, a polymerization mediator, and in organic radical batteries (ORBs) as the cathode active material because it shows a fast and reversible one-electron redox reaction.[7] The TEMPO$^{\bullet}$ free radical is oxidized to its corresponding oxoammonium salt TEMPO$^{+}$ at potentials between 0.6 and 0.9 V (vs. AgCl/Ag), depending on the substituent in 4-position (Figure 1 a). In particular, strong electron-withdrawing groups increase the redox potential, which benefits the cell voltage of the battery and, thus, its energy density. Besides tuning the redox potential, the substituent strongly influences TEMPO's solubility. Established electrolytes use TEMPOL (-OH substituent) with a solubility of 0.5 mol L$^{-1}$ in 1.5 M $NaCl_{aq}$ solution, limiting the capacity to 13 Ah L$^{-1}$ and causing detrimental side reactions through the self-catalyzed oxidation of the alcohol.[5b] An improved molecular design is required to overcome this problem. We therefore chose the ionic trimethylammonium chloride group as a substituent (-$N(CH_3)_3^{+}Cl^{-}$) because of its high hydrophilicity, a strong electron-withdrawing effect as well as the inertness of the chloride ion in the applied electrochemical voltage window. The introduced chloride ion is also a charge carrier inside the electrolyte solution, which leads to an increase in electrical conductivity compared to TEMPOL, for example.

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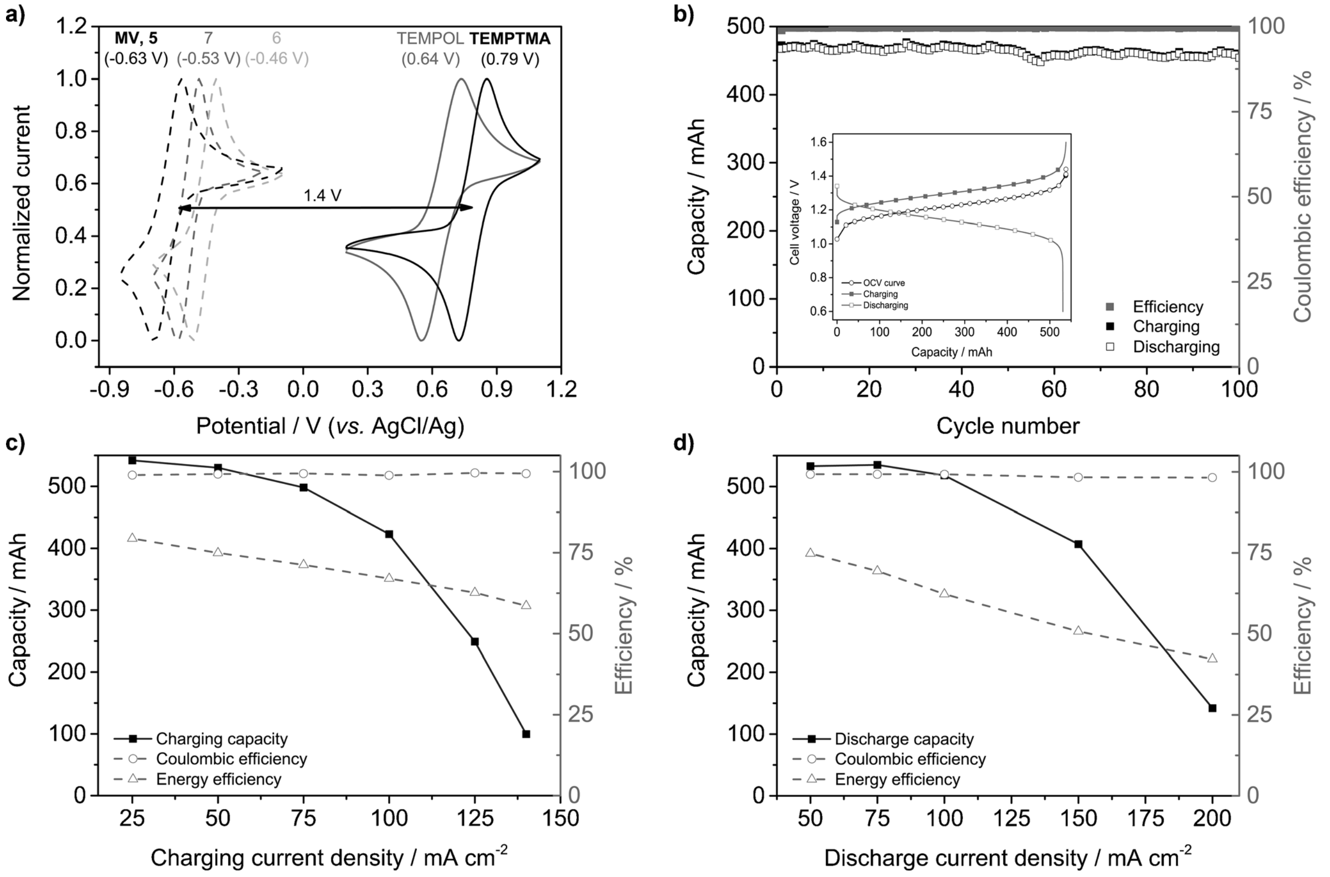
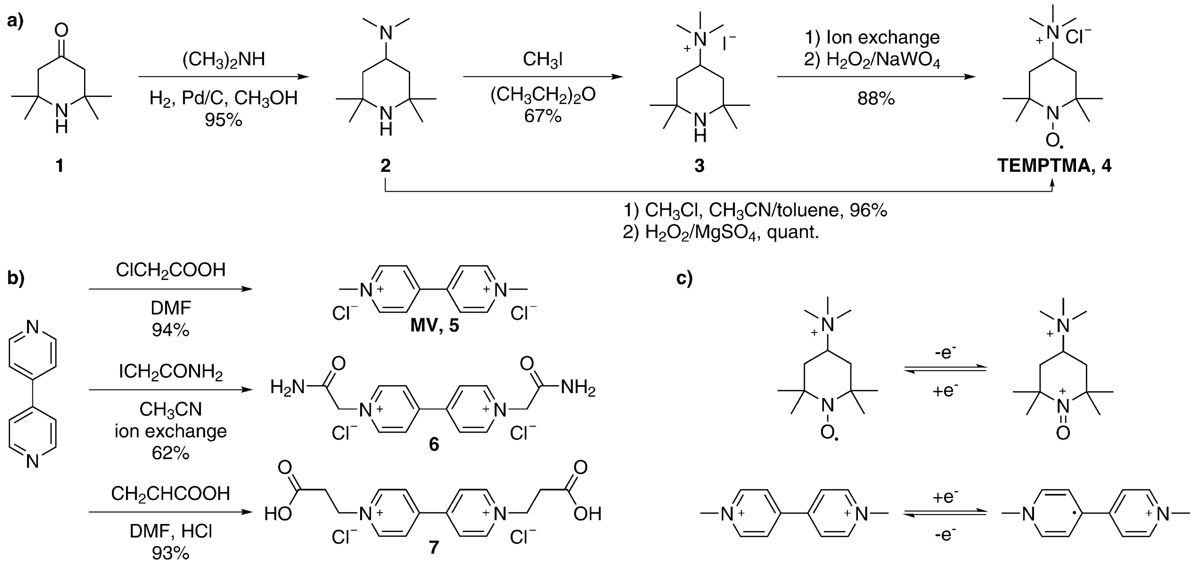


***Figure 1.*** a) Cyclic voltammograms of TEMPO and viologen derivatives. The half-wave potentials ($E_{1/2}$) are provided in parentheses (supporting electrolyte: 0.1 M $NaCl_{aq}$). b) Long-time stability test of the TEMPTMA/MV cell with repeated charging/discharging over 100 cycles at 80 $mA\,cm^{-2}$ at room temperature. After 57 cycles the tubes were replaced because of abrasion caused by the peristaltic pump. Fluctuations in capacity of ±3% are the result from temperature changes and the intrinsic experimental error. Inset: Representative charging/discharging voltage profiles (25 $mA\,cm^{-2}$) and open-circuit voltage (OCV) as a function of the attained capacity. c) Influence of the charging current density (discharging at 50 $mA\,cm^{-2}$) on the achievable capacity, coulombic efficiency and energy efficiency. d) Influence of the discharging current density (charging at 50 $mA\,cm^{-2}$) on the achievable capacity, coulombic efficiency and energy efficiency. (All experiments: Pumped 5 $cm^2$ test cell; 12 mL of 2.0 M solutions of TEMPTMA and MV.).

Starting from 4-oxo-2,2,6,6-tetramethylpiperidine (**1**, triacetonamine), a low-cost commodity produced at kiloton scale, the cathode material *N,N,N*,2,2,6,6-heptamethylpiperidinyloxy-4-ammonium chloride (TEMPTMA) was prepared by a three step synthesis (Scheme 1 a): Reductive amination of **1** with the two gases dimethyl amine and hydrogen was employed to introduce a dimethylamine functionality (**2**), which was further methylated with methyl iodide forming ammonium salt **3**. Subsequent ion exchange and oxidation with hydrogen peroxide provided the redox-active species. In an improved procedure, the ion exchange was omitted by the direct introduction of the methyl group as well as the chloride ion via the reaction of **2** with chloromethane gas at a pressure of around 3 bar. These economic routes were developed instead of using the commonly described methods starting from the 4-oxo-2,2,6,6-tetramethyl piperidinyloxy radical, because these paths would involve the use of expensive selective reducing agents, such as sodium cyanoborohydride, and protecting groups as well as produce additional side products and waste.[8]

TEMPTMA revealed a high solubility that strongly depends on the concentration of the supporting electrolyte (Figure S1 in the Supporting Information). In 0.3 M $NaCl_{aq}$ solution a TEMPTMA maximum concentration of 3.2 $mol\,L^{-1}$ can be attained while a 1.5 M $NaCl_{aq}$ solution allows a concentration of 2.3 $mol\,L^{-1}$ (20 °C), corresponding to theoretical capacities between 85 and 61 $Ah\,L^{-1}$. It thereby surpasses TEMPOL by a factor of four.[5b] No precipitation at elevated temperatures, as common for vanadium-based RFB electrolytes,[3a] was observed up to 95 °C.

Detailed analysis of the electrochemical properties by cyclic voltammetry (CV) confirmed the chemical reversibility of TEMPTMA oxidation at a redox potential of 0.79 V (vs. AgCl/Ag; Figure 1 a), surpassing TEMPOL by 150 mV. By rotating disk electrode (RDE) experiments the diffusion coefficient $D$ and the electron-transfer rate constant $k^0$ for the oxidation of TEMPTMA at a glassy carbon electrode in aqueous medium were found to be $4.8\times10^{-6}\,cm^2\,s^{-1}$ and $4.2\times10^{-3}\,cm\,s^{-1}$, respectively (Table 1, Figure S5). The reaction rate is faster than that of common inorganic materials used in RFBs and on par with organic compounds, such as hydroquinone, TEMPOL or 9,10-anthraquinone-2,7-disulfonic acid.[4b,c,5b]



***Scheme 1.*** Schematic representation of a) the synthesis of the cathode material TEMPTMA, b) the viologen-based anode materials and c) the basic electrode reactions employed in the TEMPTMA/MV redox-flow battery.

***Table 1:*** Electrochemical properties and solubility data of TEMPO and viologen derivatives at 20 °C.

| Compound | $E_{1/2}$ [V][a] | Solubility | | $D$ | $k^0$ |
|---|---|---|---|---|---|
| | | $NaCl_{aq}$ [mol $L^{-1}$][b] | water [mol $L^{-1}$] | [$10^{-6}$ $cm^2 s^{-1}$] | [$10^{-3}$ cm $s^{-1}$] |
| TEMPTMA, **4** | 0.79 | 2.3 | 3.2[c] | 4.8 | 4.2 |
| MV, **5** | −0.63 | 2.4 | 2.5 | 5.7 | 3.3 |
| **6** | −0.46 | 0.3 | 1.1 | 4.6 | 3.2 |
| **7** | −0.53 | 0.5 | 0.8 | 4.1 | 2.8 |

[a] Reference electrode: AgCl/Ag. [b] Solution in 1.5 M $NaCl_{aq}$. [c] Solution in 0.3 M $NaCl_{aq}$.

*N,N′*-Disubstituted 4,4′-bipyridines (viologens) are employed in biology, electrochromic windows, and as anode materials in batteries.[9] Divalent viologen cations ($Viol^{++}$) can undergo a two-step reduction to the neutral viologen ($Viol^0$) via the monovalent radical cation ($Viol^{+\bullet}$). Generally, the first reduction is fully reversible, while the second step leads to side reactions.[10] The redox-potential and solubility of viologens can be tuned by the choice of the *N*-substituents over a broad range.[11] While methyl viologen (MV) is highly soluble in water, unpolar substituents reduce the solubility significantly (e.g., 0.04 mol $L^{-1}$ for *N*-benzyl).[5b] Herein we compare three viologens with polar substituents for the use as a RFB anode material (Scheme 1 b): *N,N′*-Dimethyl-4,4′-bipyridinium dichloride (**5**, MV), *N,N′*-dicarbamido-4,4′-bipyridinium dichloride (**6**), and *N,N′*-bis(carboxyethyl)-4,4′-bipyridinium dichloride (**7**).

For the preparation of MV, the chloroacetic acid-approach by Yang et al.[12] was adopted to yield the product in one step without the need of ion exchange[13] or handling of gases[14] in high yields (94 %). Compound **6** was synthesized by the reaction of 2-iodoacetamide with 4,4′-bipyridine and a subsequent ion exchange,[15] while **7** was directly accessible via acrylic acid in combination with a hydrochloric acid-based purification scheme.[16] All three compounds are soluble in water and supporting electrolytes, such as 1.5 M $NaCl_{aq}$. While the solubility of MV is excellent with 2.4 mol $L^{-1}$, **6** and **7** only reveal solubility values below 1.1 mol $L^{-1}$ (Table 1).

The electrochemical properties of all three compounds were studied by CV and RDE revealing diffusion coefficients $D$ and electron-transfer rate constants $k^0$ typical for viologens and in the same range as found for TEMPTMA (Table 1, Figures S6–S8).[11] With a redox potential of −0.63 V (vs. AgCl/Ag) for the chemically reversible first reduction step and due to its good solubility MV is the most suitable anode material. In combination with TEMPTMA a theoretical cell voltage of 1.4 V can be achieved (Figure 1), allowing an overall energy density for the TEMPTMA/MV system of 38 Wh $L^{-1}$ at a concentration of 2 mol $L^{-1}$ and a capacity of 54 Ah $L^{-1}$ for the single electrolytes.

A fully organic, aqueous redox-flow battery was fabricated employing the TEMPTMA/MV system at a concentration of 2 mol $L^{-1}$ in a setup consisting of a peristaltic pump (pump rate 20 mL $min^{-1}$), two electrolyte reservoirs (12 mL) and a 5 $cm^2$ electrochemical cell employing an anion-exchange membrane (fumasep FAA-3-PE-30) and graphite felt electrodes (SGL GFA6, 6 mm dry thickness). Owing to the excellent conductivity of the MV solution in water (131 mS $cm^{-1}$, 25 °C) and the resulting high mobility of chloride counterions of the MV, no additional supporting electrolyte is necessary for the proper functioning of the anolyte solution. In contrast, additional salt decreases the solubility of the more hydrophobic, reduced monovalent radical cation ($Viol^{+\bullet}$) and causes precipitation upon charging of the cell.

The RFB cell was safely charged and discharged within a voltage window of 0.6 to 1.6 V with no observable degradation of the electrolyte, that is, the formation of hydrogen, oxygen, or chlorine. Typical voltage profiles of the charging/discharging process at a current density of 25 mA $cm^{-2}$ and the state-of-charge dependent (SOC) open-circuit voltage (OCV) are displayed in Figure 1 b. They reveal a stable cell voltage over a wide range indicating a practical application of the RFB between 5 to 95 % SOC.

The rate performance of the discharging process was studied by varying the current at a fixed charging current density of 50 mA cm$^{-2}$ (Figure 1 c,d). A material utilization of 83 % with no significant impact on the cell performance could be attained up to 75 mA cm$^{-2}$ with an energy efficiency of over 70 %. Similar results were reached for the charging process. The cell can be operated at peak current densities of 200 mA cm$^{-2}$ for the discharging and 140 mA cm$^{-2}$ for the charging process, respectively.

A continuous cycling experiment was conducted at 80 mA cm$^{-2}$ revealing full capacity retention over 100 cycles and, therefore, indicating the long-time stability of the material system (Figure 1 b).

To evaluate the electrolyte solutions for practical redox-flow-battery applications their rheological properties were studied in addition to their electrochemical performance. At 25 °C the TEMPTMA catholyte and the MV anolyte show a viscosity of 7 mPas and 3 mPas, respectively (Figures S3, S4). Both solutions reveal a Newtonian behavior within the shear rate range that is applicable in RFB applications. Even at low temperatures (5 °C) the viscosity remains below 20 mPas. Hence, the solutions can be used in redox-flow batteries over a wide temperature range.

In summary, the TEMPTMA/MV electrolyte system is based on easily accessible and inexpensive organic raw materials. It demonstrates a cell voltage, energy, and current density that surpasses common organic-RFBs and can compete with the established vanadium system, while still maintaining the benefits of a pH-neutral, much less corrosive environment as well as a good solubility even at elevated temperatures (up to 95 °C). Additional tailoring of the electrolyte salts and cell engineering are expected to further increase the performance. Thus, the TEMPTMA/MV system sets a new standard in technical parameters and safety for all-organic, aqueous redox-flow batteries using small organic molecules. It appears to be a suitable candidate for real-life, large-scale redox-flow batteries, and the storage of renewable energy.

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**Keywords:** electrochemistry · energy storage · radicals · redox chemistry · redox-flow battery

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# Communications

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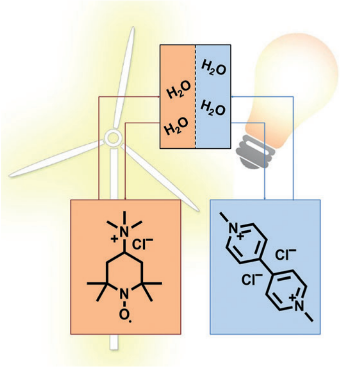
Aqueous Redox-Flow Battery with High Capacity and Power:The TEMPTMA/MV System



**Tempting solutions**: Redox-flow batteries (RFB) are widely considered as energy-storage solutions for wind generators and solar farms. A highly soluble, organic material system for aqueous RFBs is found to be *N*,*N*,*N*-2,2,6,6-heptamethyl piperidinyl oxy-4-ammonium chloride (TEMPTMA) and *N*,*N*′-dimethyl-4,4-bipyridinium dichloride (MV). It has capacities of over 54 Ah L$^{-1}$ (ca. 38 Wh L$^{-1}$), a cell voltage of 1.4 V, and peak current densities of up to 200 mA cm$^{-2}$.