



An aqueous all-organic redox-flow battery employing a (2,2,6,6-tetramethylpiperidin-1-yl)oxyl-containing polymer as catholyte and dimethyl viologen dichloride as anolyte

Tino Hagemann^{a, b}, Jan Winsberg^{a, b}, Mandy Grube^{a, c}, Ivo Nischang^{a, c}, Tobias Janoschka^d, Norbert Martin^d, Martin D. Hager^{a, b}, Ulrich S. Schubert^{a, b, c, *}

^a Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstrasse 10, 07743 Jena, Germany

^b Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany

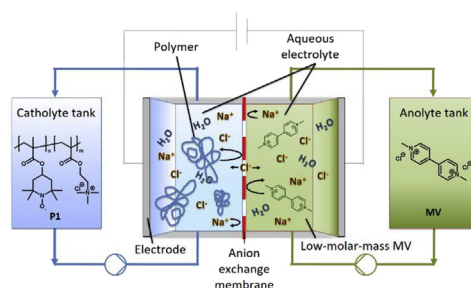
^c Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany

^d JenaBatteries GmbH, Botzstrasse 5, 07743 Jena, Germany

HIGHLIGHTS

- A redox-flow battery utilizing polymer and low-molar-mass compound was manufactured.
- Safe aqueous sodium chloride solution and cheap anion-exchange membranes were used.
- A TEMPO copolymer and paraquat were employed as active materials.
- Various flow conditions, conductive salt concentrations, membranes were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein we present a new redox-flow battery (RFB) that employs a (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) containing copolymer (**P1**) as catholyte and the viologen derivative *N,N'*-dimethyl-4,4'-bipyridinium dichloride (**MV**) as anolyte in an aqueous sodium chloride solution. This is the first time that a combination of an organic polymer and a low-molar-mass organic redox-active material is presented. The electrochemical behavior of the utilized charge-storage materials were investigated by cyclic voltammetry (CV) and feature reversible redox-reactions at $E_{1/2} = 0.7$ V (TEMPO/TEMPO⁺) and $E_{1/2} = -0.6$ V vs. AgCl/Ag (MV²⁺/MV^{•+}), which lead to a promising cell voltage of 1.3 V in the subsequent battery application.

Studies were performed to determine the most suitable anion-exchange membrane (AEM), the ideal conducting salt concentration and the optimal flow rate. The resulting battery reveals a stable charge/discharge performance over 100 consecutive cycles with coulombic efficiencies of up to 95%, a high energy efficiency of 85% and an overall energy density of the electrolyte system of 3.8 W h L⁻¹.

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* Corresponding author. Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstrasse 10, 07743 Jena, Germany.

E-mail address: ulrich.schubert@uni-jena.de (U.S. Schubert).

1. Introduction

The climate change, caused primarily by greenhouse gas emissions, provoked a rethinking of the world energy production [1–4].

In order to reduce CO₂ emissions, research is directed towards 'greener' and more sustainable sources such as solar and geothermal energy as well as hydroelectricity and wind power [5–7]. Thereby, solar energy and wind power, which are in comparison to hydroelectricity and geothermal energy not limited by several crucial preconditions such as certain geographical circumstances, will become the most relevant renewable energy source for the future [8–10]. Unfortunately, the present electricity grids are not suitable for this kind of intermittent electricity production, and have to be advanced by the incorporation of flexible and scalable energy-storage systems to render the energy transition successful [5,11].

In particular, redox-flow batteries (RFBs) are convenient for the storage of wind and solar electricity, since they can be adapted to the generator unit. Unlike most electrochemical energy-storage technologies, flow batteries exhibit the benefit of independent scalability in capacity and in power [5,12]. State-of-the-art, commercially available systems such as the all-vanadium [13–16] and Fe/Cr [17–19] RFB have the disadvantage of utilizing critical and high-priced metal salts and/or corrosive electrolyte solutions (e.g., sulfuric acid) together with expensive cation-exchange membranes such as Nafion[®] [12,20–22]. Therefore, current research focuses on aqueous electrolyte systems, inexpensive membranes and organic charge-storage materials featuring safety, environmental, and cost benefits. Low-molar-mass compounds such as quinones [23–27], stable nitroxide radicals [28–33], and *N,N'*-disubstituted 4,4'-bipyridine (viologen) derivatives [12,30,33,34] as well as polymers bearing these functionalities [22,35–41] were investigated for this purpose [5].

For aqueous electrolyte systems, viologen species are better suited as anolytes than anthraquinones because of their high water solubility and low reduction potential [5,12]. Care however, should be taken to use these viologen derivatives, in particular the *N,N'*-dimethyl-4,4'-bipyridinium dichloride (**MV**), since they are widely used herbicides and known for their phytotoxicity. Notwithstanding, due to their chemical reversibility, fast reaction kinetics and economical aspects (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO) derivatives are attractive catholyte materials. Consequently, aqueous all-organic RFBs with high capacity and power utilizing TEMPO/viologen derivatives as active materials were published in the last few years. For example, Janoschka et al. [22] developed a novel RFB concept based on TEMPO- and viologen-containing polymers and utilized pH-neutral sodium chloride solution as well as affordable dialysis membranes [22]. In addition, Liu et al. [30] and Janoschka et al. [12] utilized *N,N'*-dimethyl-4,4'-bipyridinium dichloride as well as the TEMPO derivatives 4-HO-TEMPO [30] and TEMP-TMA [12] as a low-molar-mass-compound based version of this aqueous all-organic RFB.

To determine whether an organic polymer and a low-molar-mass organic compound can be used as charge-storage materials, a combined all-organic aqueous RFB utilizing sodium chloride as conducting salt and low cost AEMs was developed. The system was investigated in detail. Particular focus was on electrochemical performance and long-term stability in comparison to low-molar-mass- and polymer-based RFBs. As active materials and for comparability, the well-known low-molar-mass **MV** [12,30,34] in combination with the TEMPO-containing copolymer poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate-co-[2-(methacryloyl-oxy)ethyl]trimethylammonium chloride) [22] (**P1**) were utilized. Particular advantage of this combined system for cost benefits results from the low cost of the AEMs and the utilized **MV**, which is a well-known herbicide produced on 100,000 ton-scale. The flow rate of the electrolytes, the concentration of the supporting electrolyte, the behavior without the use of additional conducting salt and the type of anion-exchange membrane (AEM)

are key factors addressed in the present study. Except the latter, these important factors in terms of the battery performance have only partially been addressed in previously published studies so far.

2. Experimental

2.1. Materials, chemicals and methods

All starting materials were purchased from commercial sources and were used as obtained. Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate-co-[2-(methacryloyloxy)ethyl]trimethylammonium chloride) (**P1**) was a test sample provided as aqueous solution (capacity of 8.3 Ah L⁻¹) by Polymaterials AG (Germany). For the dialysis of **P1**, a regenerated cellulose-based dialysis membrane (Spectra/Por[®] 6, Spectrum Laboratories, Inc., USA) with a molecular-weight cut-off (MWCO) of 1000 g mol⁻¹ and a flat width of 45 mm was utilized. The used graphite felt (2.25 × 2.25 × 0.4 cm³, sigrancell[®] GFA6 EA, SGL Carbon, Germany), as well as the utilized anion-exchange membranes fumasep[®] FAA-3-PE30, FAP-PK-3130, FAS-30 and FAA-3-50 (all Fumatech BWT, Germany), were cut into appropriate pieces.

Reactions were monitored by using a Shimadzu (Japan) GCMS-1-system with a GC-QP2010S-detector and an Agilent (USA) DB-5ms-column. ¹H NMR spectra were recorded on a Bruker (USA) AC 300 (300 MHz) spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual signal of the deuterated solvent. Electrospray ionization (ESI) mass spectrometry measurements were performed on a micrOTOF Q-II (Bruker Daltonics Inc., USA) ESI time-of-flight (ESI-TOF) system. Asymmetric flow field-flow fractionation (AF4) coupled to a refractive index and multi angle laser light scattering (MALLS) detector (PN3621, Postnova Analytics GmbH, Germany) was used to determine the absolute molar mass and dispersity of **P1** with independently determined values of the refractive index increment dn/dc by an Optilab rEX system (Wyatt, Germany) (see Supporting Information for complete experimental details). The radical content of **P1** was determined via X-Band electron paramagnetic resonance (EPR) spectroscopy. The measurements were conducted on an EMXmicro CW-EPR spectrometer from Bruker (USA) using powdered samples. The total spin count was estimated by an average of nine measurements. The calculated errors of the determined theoretical charge storage capacities, including the volume errors, mass errors and errors of the measured EPR activities, are around 10%.

2.2. Synthesis and characterization of **MV** and **P1**

4,4'-Bipyridine (100 g, 0.64 mol) was dissolved in dimethylformamide (600 mL). Afterwards, chloroacetic acid (163.4 g, 1.72 mol) was added [42] and the suspension was heated to 140 °C, whereas the chloroacetic acid dissolved, followed by stirring at 130 °C overnight. After cooling to room temperature, the formed precipitate was filtered off and washed with hot dimethylformamide, chloroform, dichloromethane (each two times) to obtain the yellowish pure product **MV** (160.64 g, 0.63 mol) in a yield of 98%. ¹H NMR (Fig. S1, 300 MHz, D₂O, δ in ppm): 9.03 (d, *J* = 6.8 Hz, 4H, Ar H), 8.49 (d, *J* = 6.7 Hz, 4H, Ar H), 4.48 (s, 6H, CH₃); ESI-TOF MS (Fig. S2) *m/z* (%): 93 (100) [M²⁺], 171 (23) [M⁺ - CH₃].

Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate-co-[2-(methacryloyloxy)ethyl] trimethylammonium chloride) (**P1**) was a test sample provided as aqueous solution (capacity of 8.3 Ah L⁻¹) in a molar ratio (2,2,6,6-tetramethylpiperidin-4-yl-methacrylate:[2-(methacryloyloxy)ethyl]trimethylammonium chloride) of 1:1 by Polymaterials AG (Germany). The aqueous solution was dialysed against water (MWCO = 1000 g mol⁻¹) and lyophilized to

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