*Bulgarian Chemical Communications, Volume 58, Issue 4 (pp. 550-558) 2026* *DOI: 10.34049/bcc.58.4.5765*

# Impact of polyvinylpyrrolidone as an additive to the positive electrolyte of a vanadium redox flow battery

P. Nikolov*, B. Mladenova, M. Matrakova, T. Stankulov, R. Boukoureshtlieva, L. Soserov

*Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. Georgi Bonchev Str., Block 10, 1113 Sofia, Bulgaria*

Received: May 11, 2025; Revised: May 22, 2026

Charge and discharge reactions at the positive electrode of a vanadium redox flow battery involve intermediate protonation and deprotonation steps. Polyvinylpyrrolidone (PVP), added to the positive electrolyte of the battery, may function as a proton donor or acceptor and thereby modify the electrochemical reactions occurring at the positive electrode. Linear cyclic voltammetry measurements demonstrated that PVP with a molecular weight (MW) of 40 000 is more effective in increasing the oxidation and reduction peak current densities of vanadium ions than PVP with an MW of 360 000. Increasing the dosage level (from 0.0125 to 0.05 wt. %) of the PVP additive in the electrolyte does not lead to a proportional increase in the current associated with vanadium-ion oxidation and reduction reactions. The optimal PVP concentration is 0.025 wt.%. Electrical tests performed with a vanadium flow cell with an active area of 25 cm² and anion-exchange membrane demonstrated that the addition of 0.025 wt.% of PVP with an MW of 40 000 to the positive electrolyte results in enhanced discharge capacity, coulombic efficiency, and energy efficiency at various discharge-charge current densities (10–100 mA $cm^{-2}$) compared with a control cell without the additive. It was established that the PVP additive reduces the open-circuit voltage values of the test cell by 20–30 mV during both charge and discharge. This effect of PVP could be associated with active interactions of PVP polymer chains with $VO^{2+}$, $VO_2^+$, and protons ($H^+$). Volume imbalance in the electrolyte reservoirs was mitigated by a continuous electrolyte bridge connecting the positive and negative compartments. Prolonged constant-current (80 mA $cm^{-2}$) discharge and charge cycling of the test cells further proved that the beneficial effect of PVP is stable over time. The cell containing 0.025 wt.% of PVP achieved up to 98% utilization of electrolyte discharge capacity, compared with 94% for the control cell. The coulombic efficiency was greater than 98% for the PVP-containing cell and greater than 95% for the control cell.

**Keywords:** vanadium redox flow battery, VRFB, positive electrolyte, additive, polyvinylpyrrolidone, PVP.

## INTRODUCTION

In recent years, vanadium redox flow batteries (VRFBs) have attracted increasing scientific and industrial interest. This is driven by the growing energy storage sector and the advantages of VRFBs over conventional electrochemical systems. VRFBs offer high energy efficiency, deep-discharge capability without significant degradation, and long service life. They also provide fast electrochemical kinetics, low self-discharge, and limited cross-contamination between electrolytes. These features make VRFBs attractive for large-scale storage and renewable energy integration [1-5]. Energy is stored through reversible changes in vanadium oxidation states in acidic electrolyte [6]. The main electrochemical reactions are [7]:

Positive electrode ($V^{4+}/V^{5+}$): $VO^{2+} + H_2O - e^- \leftrightarrow VO_2^+ + 2H^+$
Negative electrode ($V^{2+}/V^{3+}$): $V^{3+} + e^- \leftrightarrow V^{2+}$

Despite these advantages, VRFBs require further material and design optimization. Key limitations include low energy density, about 20–30 Wh $L^{-1}$, and a narrow electrolyte stability range [8]. System efficiency and durability depend on membranes with low vanadium permeability and high chemical resistance, as well as electrodes with high activity and limited side reactions [9]. Even with optimized components, electrolyte stability remains critical because vanadium ions may precipitate under specific temperature and concentration conditions. Therefore, additives are needed to improve solubility and suppress precipitation.

Various additive-based strategies have been reported to stabilize and improve vanadium electrolytes. Skyllas-Kazacos *et al.* [10] showed that suitable precipitation inhibitors can extend operational life and improve cycling stability. However, many organic additives are unstable in highly oxidizing $V^{5+}$ media, requiring substances of higher chemical stability.

Li *et al.* [11] studied the effects of fructose, mannitol, glucose, and D-sorbitol on VRFB performance. D-sorbitol significantly reduced precipitation, improved electrochemical activity, and increased energy efficiency from 79.8% to 81.8%. Ding *et al.* [12] found that phosphate

* To whom all correspondence should be sent:
E-mail: *p_nikolov@iees.bas.bg*

© 2026 Bulgarian Academy of Sciences, Union of Chemists in Bulgaria

additives effectively suppress V(V) precipitation in the positive electrolyte.

Wen *et al*. [13] showed that controlling thermal stability and precipitation is critical for widening the operating temperature range and improving efficiency. Yu *et al.* [14] noted that additives can suppress precipitation, optimize viscosity, improve ionic conductivity, and limit corrosion. Increasing the concentration of vanadium ions using mixed electrolytes, and applying appropriate additives enhance the energy density and electrochemical performance of VRFBs while further improvements in stability, ionic conductivity, and control of active-species crossover are necessary for practical applications [15]. Zheng *et al.* [16] further demonstrated the role of polymer materials in vanadium systems, demonstrating that doping of membranes with polyvinylpyrrolidone (PVP) improves their stability and selectivity.

The electrochemical reactions occurring at the positive electrode of the vanadium flow cell involve proton participation in several intermediate protonation and deprotonation steps of vanadium ion species. Altering the properties of the electrode/electrolyte interface with the aim of influencing proton-involved reactions could result in improved battery performance. One class of suitable additives to the vanadium electrolyte that could modify the characteristics of the electrode /electrolyte interface includes substances exhibiting proton-acceptor or proton-donor properties. One such material is the polymer polyvinylpyrrolidone (PVP). The polymer chains of PVP may interact with both vanadium ions and protons, as well as adsorb on the surface of the carbon electrode. A very recent study [17] demonstrated that the addition of PVP with a molecular weight of 3 600 000, in combination with ammonium phosphate (50:50 wt.%), considerably suppresses the agglomeration of oxovanadium species and the detrimental formation of precipitates in solution at elevated temperatures (>40 °C), thereby having a positive impact on the cell's electrical characteristics.

In this study, the effect of polyvinylpyrrolidone (PVP) with different molecular weights as an additive to the positive electrolyte was evaluated, aiming to improve the overall electrical performance of a vanadium redox flow battery.

## EXPERIMENTAL

### *Cells, electrodes, and peripheral accessories*

A three-electrode cell configuration using a vanadium electrolyte (in-house modified ParaCell model, Gamry Instruments, USA) was employed for electrochemical measurements. In-house-made PTFE holders with inserted graphite electrodes (graphite rods, Gamry Instruments, USA) were used as the working electrode (area exposed to the electrolyte: 0.5 $cm^2$) and counter-electrode (area exposed to the electrolyte: 2.0 $cm^2$). The electrolyte volume was 120 mL. An in-house-made mercury/mercurous sulfate electrode ($Hg/Hg_2SO_4$/4.8 M $H_2SO_4$; -0.610 V *vs* SHE) served as the reference electrode.

Furthermore, electrical performance tests were conducted using laboratory-scale redox flow cells with an integrated flow field (A-Cell model, Redox-Flow B.V., Netherlands) and an active area of 5 cm × 5 cm (25 $cm^2$). Thermally activated AVCarb G280 graphite felt (AvCarb Specialty Materials LLC, USA), with a thickness of 2.8 mm, was used as the electrode material. This material was selected owing to its high specific surface area which facilitates redox reactions. The electrodes were mechanically compressed by 25–30% for the positive electrode and 20–25% for the negative electrode using appropriate gaskets to ensure optimal electrical contact and proper system sealing.

A Fumasep® FAPQ-330 anion-exchange membrane (Fumatech BWT GmbH, Germany), with a nominal thickness of 30 μm, was used to separate the half-cells. The electrolyte was continuously pumped through the positive and negative compartments of the test cell using PTFE tubes with an inner diameter (ID) of 1.6 mm and an outer diameter (OD) of 3.2 mm, together with a two-channel peristaltic pump (BT600L-YZ15T model, Redox-Flow B.V., Netherlands), at a flow rate of 20 mL $min^{-1}$. A small open-circuit voltage cell (OCV cell, Redox-Flow B.V., Netherlands) was connected in series before the main flow cell for electrode or full-cell potential measurements. The electrolyte reservoirs were 150 mL-capped glass bottles (Duran, Germany) containing appropriate tube fittings and adapters. The electrolyte volume for each measurement was 50 mL for both the positive and negative compartments.

### *Electrolyte and additives*

In this study, an industrial vanadium electrolyte (Yinhui New Energy, China) was used. The main characteristics of the electrolyte were as follows: 0.80–0.85 mol $L^{-1}$ $V^{3+}$, 0.80–0.85 mol $L^{-1}$ $V^{4+}$, 2.15 mol $L^{-1}$ $H_2SO_4$, total $SO_4^{2-}$ = 4.3 mol $L^{-1}$, and density = 1.37 g $cm^{-3}$. The selection of a commercial product with established properties allowed precise monitoring of the effect of the applied additives.

Polyvinylpyrrolidone (PVP) with two different molecular weights — 40 000 and 360 000 — was obtained from Sigma-Aldrich, USA. The

experiments were conducted at various concentrations, with the additives pre-dissolved in the electrolyte before their introduction into the system.

### *Electrochemical measurements*

The electrochemical screening tests were performed on a vanadium electrolyte, without initial pre-charge, using an Interface 1010E potentiostat/galvanostat (Gamry Instruments, USA). Cyclic voltammetry studies were carried out at a scan rate of 20 mV $s^{-1}$, and 20 voltammetric cycles were performed. The following working potential windows, relative to the $Hg/Hg_2SO_4$ reference electrode, were applied to evaluate the electrochemical behavior: 0.0 to +1.2 V for the positive electrode and −1.5 to −0.4 V for the negative electrode. The overall working potential window of the cell ranged from −1.5 V to +1.2 V. Before each measurement, the working graphite electrodes were mechanically polished with P800-grit emery paper and rinsed with ethanol (96%).

### *Electrical performance tests*

The impact of the studied additives on the electrical performance characteristics of the vanadium redox flow cell was evaluated under constant-current discharge and charge conditions at currents of 0.25, 0.50, 1.00, 1.50, 2.00, and 2.50 A, corresponding to 10, 20, 40, 60, 80, and 100 mA $cm^{-2}$, respectively. For all measurements, the volumes of the positive and the negative electrolyte were 50 mL each. The calculated usable theoretical capacity of 50 mL of vanadium electrolyte was 1.10 Ah (1100 mAh). The initial pre-charge of the electrolyte was performed at a current of 1.0 A until the input charge capacity reached 2.20 Ah (2200 mAh). During the various testing profiles, the end-of-discharge cell voltage was limited to 0.80 V, and the upper charge voltage was limited to 1.60 V or until the input charge capacity reached 1100 mAh. Numerous electrical cell parameters were monitored, recorded, and calculated during discharge and charge testing, such as cell voltage, open-circuit voltage, positive and negative electrode polarization, Ah capacity, Wh energy, coulombic efficiency, and energy efficiency.

### *UV–Vis spectroscopy*

The qualitative changes in the positive electrolyte after cycling were analyzed using UV–Vis spectroscopy (Shimadzu UV-1900i, Japan). The absorption spectra were recorded in the range of 300–900 nm. A 500 µL sample of the electrolyte was diluted in an acid solution with the same $H_2SO_4$ concentration as the electrolyte, after which the sample was analyzed in a quartz cuvette.

## RESULTS AND DISCUSSION

### *Cyclic voltammetry measurements*

As a preliminary screening study, the effects of PVP molecular weight and dosage level in the vanadium electrolyte on the discharge and charge reactions at the positive and the negative electrode were evaluated by cyclic voltammetry. Fig. 1a shows the recorded voltammograms after 20 cycles in the full potential window for the blank electrolyte solution and solutions containing 0.0125, 0.025, and 0.050 wt.% of PVP with a molecular weight of 360 000.

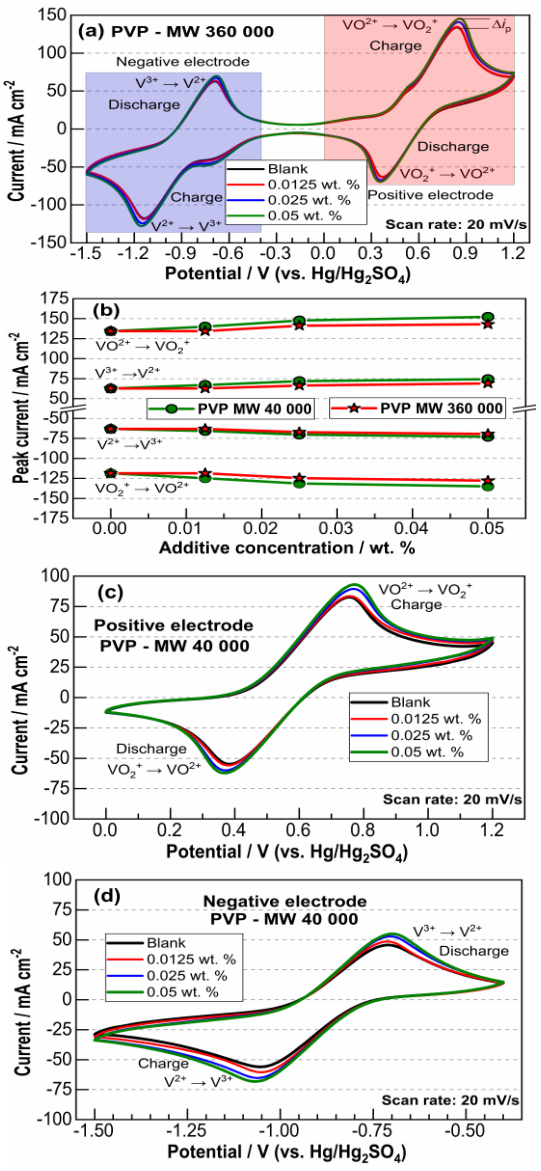


**Figure 1.** Cyclic voltammetry measurements at a scan rate of 20 mV $s^{-1}$: (a) Full-cell potential window; (b) Values of peak currents *vs.* PVP concentration in the electrolyte; (c) Negative-electrode potential window; (d) Positive-electrode potential window.

The profiles of the current–voltage curves indicate that the addition of PVP to the vanadium electrolyte results in increased current peak values compared with the blank electrolyte, which is associated with enhanced electrochemical reactions at both the positive and the negative electrode. The impact of the PVP additive with an MW of 360 000 is more pronounced on the charge reactions of the positive and the negative electrode. The increase in peak current is not proportional to the PVP dosage level. The addition of 0.0125% of PVP has no effect, whereas 0.025% of PVP results in a noticeable increase in current peaks. A further increase in the PVP dosage to 0.05% produces only a slight additional increase in peak current compared with the effect of 0.025%. Fig. 1b summarizes the effect of PVP dosage levels in the electrolyte and its molecular weight on reaction peak currents. It can be seen that the positive effect of PVP on the reactions occurring at the positive electrode is more pronounced, and the optimal concentration is 0.025 wt.%.

The influence of PVP on the peak currents of the positive and negative electrode reactions was quantified by calculating the change in peak current in the presence of the PVP additive relative to the control values (blank electrolyte) denoted as $\Delta i_p$. The calculated values for the additives under investigation are summarized in Table 1. The voltammetry measurements conducted in the potential windows of −1.5 to −0.4 V for the negative electrode and 0.0 to +1.2 V for the positive electrode are plotted in Figs. 1c and 1d, respectively. The current–voltage curves recorded at different concentration levels of PVP with a molecular weight of 40,000 confirm that in the presence of the studied additive the peak current values increase. Based on the obtained voltammetry data it can be concluded that the addition of PVP with a molecular weight of 40 000 or 360 000 to the vanadium electrolyte has a beneficial impact on the discharge and charge reactions at both the positive and the negative electrode. Based on the data listed in Table 1, it can be concluded that PVP with a molecular weight of 40 000 exhibits a stronger effect on the peak current values compared with its counterpart with a molecular weight of 360 000. The PVP 40 000 additive is more effective in enhancing the charge reactions of both the positive and the negative electrode.

*Electrical performance testing*

- *Approach to suppressing electrolyte imbalance.* In the present study, we employed an anion-exchange membrane. One of the major drawbacks of anion-exchange membranes used in vanadium redox flow batteries is the substantial volume imbalance between the positive and the negative electrolyte, which results in a decline in electrical performance characteristics [17]. This phenomenon is attributed to substantial water transfer through the anion-exchange membrane by osmosis and electroosmosis mechanisms, which causes an increase in volume of the negative electrolyte reservoir and a decrease in volume of the positive one.

To overcome this disadvantage of anion-exchange membranes, we designed an electrolyte bridge connecting the positive and the negative electrolyte reservoir, which operates on the principle of interconnected vessels (Fig. 2a). When electrolyte volume imbalance appears between the positive and the negative reservoir, it triggers liquid transfer until balanced electrolyte volumes are restored. The electrolyte bridge was constructed using a thin PTFE tube, with both ends submerged at different levels in the positive and the negative electrolyte reservoir, allowing a liquid flow predominantly from the negative to the positive compartment. Figure 2b shows the appearance of noticeable electrolyte imbalance after only 20 discharge-charge cycles.

**Table 1.** Changes in the voltammetric oxidation and reduction peak current densities for $VO^{2+}$, $VO_2^+$, $V^{3+}$, and $V^{2+}$ in the presence of PVP additives with different molecular weights.

| Additive | Amount, wt. % | $\Delta i_p$, mA cm$^{-2}$ (current with additive *versus* control) | | | |
|---|---|---|---|---|---|
| | | Positive electrode | | Negative electrode | |
| | | Charge | Discharge | Charge | Discharge |
| | | $VO^{2+} \rightarrow VO_2^+$ | $VO_2^+ \rightarrow VO^{2+}$ | $V^{3+} \rightarrow V^{2+}$ | $V^{2+} \rightarrow V^{3+}$ |
| PVP MW 40 000 | 0.0125 | +5.6 | +2.6 | +6.2 | +4.4 |
| | 0.0250 | +13.2 | +7.2 | +12.8 | +9.2 |
| | 0.0500 | +17.7 | +10.0 | +16.4 | +11.6 |
| PVP MW 360 000 | 0.0125 | 0.0 | 0.0 | 0.0 | 0.0 |
| | 0.0250 | +6.8 | +4.0 | +6.0 | +3.6 |
| | 0.0500 | +8.4 | +6.4 | +9.2 | +6.4 |

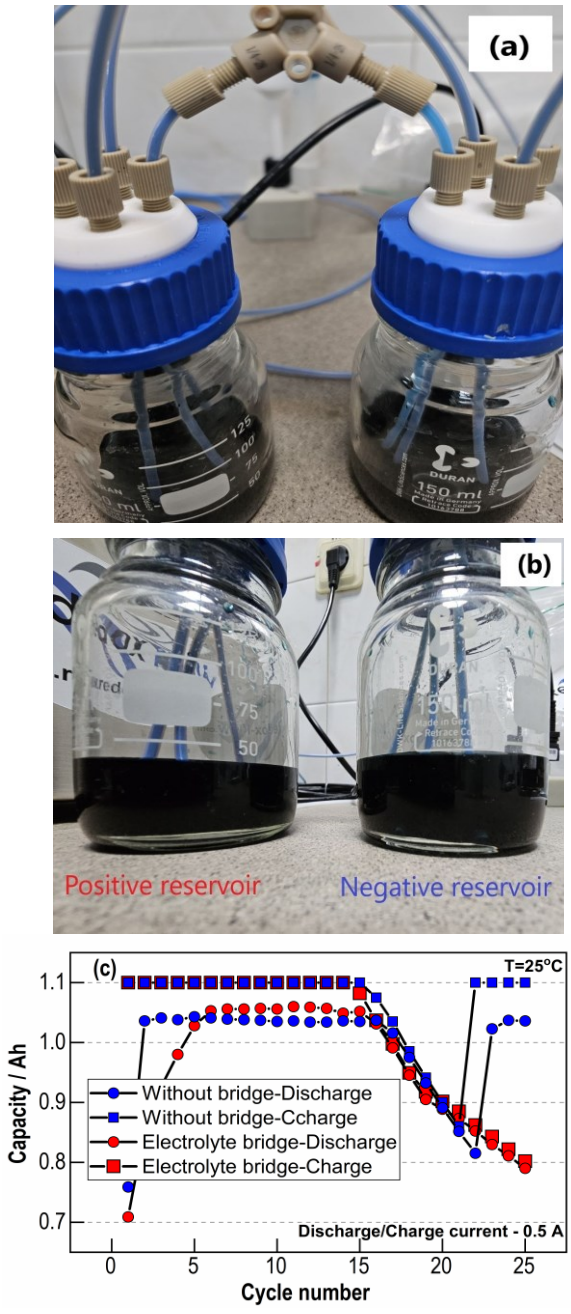


**Figure 2.** (a) Photograph depicting the electrolyte bridge connecting the reservoirs; (b) Photograph of vanadium flow-cell electrolyte reservoirs showing the appearance of volume imbalance; (c) Changes in discharge and charge capacity of the cell with and without an electrolyte bridge.

Fig. 2c compares the electrical performance of cells with and without an electrolyte bridge. It is evident that after 15 cycles the cell without an electrolyte bridge exhibits a decline in both discharge and charge Ah capacity. The cell with an electrolyte bridge initially follows the same trend; however, once a certain electrolyte volume imbalance is reached, liquid begins to transfer from the negative reservoir to the positive reservoir until the volumes are balanced. This results in a complete restoration of the cell discharge and charge Ah capacity to maximum values. The slightly lower discharge capacity of the cell with the electrolyte bridge compared with the cell without the bridge could be explained by a self-discharge process due to the continuous connection between the positive and the negative reservoir. All further studies were carried out using the electrolyte bridge.

- *Influence of PVP on the electrical characteristics of a vanadium flow cel.* The preliminary screening study by voltammetry technique revealed that PVP with a molecular weight of 40 000 exhibits a more pronounced positive effect on the electrochemical reaction at the positive electrode. Therefore, its effect on the electrical characteristics of vanadium flow cells was further investigated. Figure 3 summarizes the impact of 0.025 wt.% of PVP added to the electrolyte, compared with the blank sample, on the positive and the negative electrical characteristics of the cell during charge and discharge at a constant current of 1.0 A.

Fig. 3a shows that adding PVP shifts the cell-voltage profile downward by about 20 mV during both charge and discharge while slightly prolonging discharge duration. Comparison of Figs. 3a and 3b shows that the lower cell voltage does not negatively affect the discharge energy output or the charge energy input. The data collected from the open-circuit voltage cell during the charge and discharge processes indicate that the addition of 0.025 wt.% of PVP results in voltage values approximately 0.02 V (20 mV) lower than those of the control cell (blank). The downward shift in OCV by 20 mV could occur if the PVP additive:

(i) *complexes V(V) more strongly than V(IV)*. If it stabilizes $VO_2^+$, the effective activity of free $VO_2^+$ decreases, shifting the positive electrode potential to a lower value;

(ii) *changes proton activity*. As in the Nernst equation for the positive electrode potential, proton activity appears as a second-order term, small changes in acidity/activity can shift the potential value;

(iii) *changes activity coefficients*. Even if the concentrations of vanadium ions are unchanged, ionic strength or specific interactions can change vanadium-ion activities;

(iv) *adsorbs on the electrode surface*. This may shift the measured open-circuit potential through double-layer/interfacial effects, even without large bulk chemical changes.

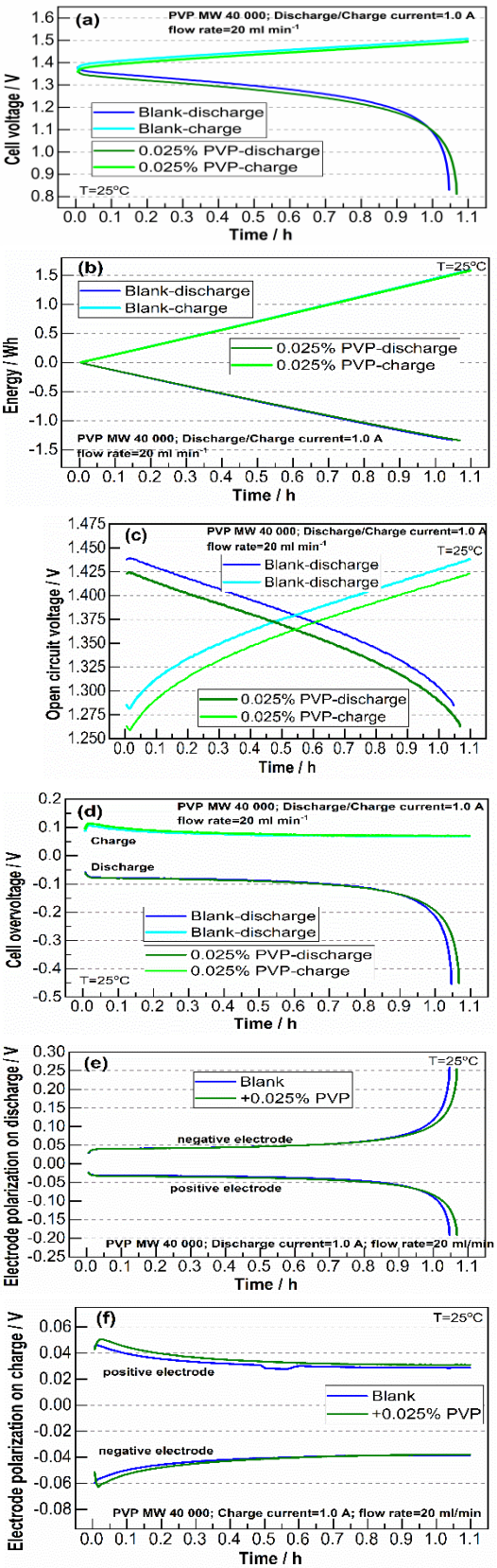


**Figure 3.** Changes in the electrical characteristics of a vanadium flow cell with PVP during discharge and charge: (a) Cell voltage; (b) Discharge and charge energy; (c) Open-circuit voltage; (d) Calculated cell overvoltage; (e) Electrode polarization during discharge; (f) Electrode polarization during charge.

The obtained experimental information is not sufficient to determine the dominance of one of the above-mentioned mechanisms. The cell overvoltage, calculated by subtracting the OCV values from the cell voltage under current and plotted in Fig. 3d, together with the respective positive and negative electrode polarizations (Figs. 3e and 3f), reveals that the addition of 0.025 wt.% of PVP has no effect on these electrical characteristics associated with the kinetics of the electrode reactions. The observed small increase in positive electrode polarization during charge for the cell with the 0.25 wt.% PVP additive compared with the blank cell could be attributed to the low open-circuit potential of the positive electrode.

The kink observed in the positive-electrode polarization profile of the blank cell after 0.45 h results from a small electrolyte transfer from the negative to the positive storage compartment through the electrolyte bridge. This transfer balances the electrolyte volume and composition. In conclusion, the PVP additive modifies the electrochemical properties of the positive electrolyte by shifting the open-circuit potential and slightly extending the discharge time.

The graphical plots in Fig. 4 summarize the influence of the 0.025 wt.% PVP additive on the integral electrical characteristics of cells tested at different discharge/charge current densities: 10, 20, 40, 60, 80, and 100 mA cm$^{-2}$.

The effect of the PVP additive on discharge capacity is shown in Fig. 4a. It is evident that for cycling at a current density of 10 mA cm$^{-2}$, the discharge-capacity values of the blank cell and the cell containing PVP in the positive electrolyte are highly scattered. The cycling data for discharge capacity at a current density of 20 mA cm$^{-2}$ are almost identical for the cell with the 0.025 wt.% PVP additive and the control cell. The cycling results for discharge capacity obtained under current regimes of 40, 60, and 80 mA cm$^{-2}$ clearly demonstrate that the addition of PVP has a noticeable positive impact on discharge capacity, but the beneficial effect decreases as the current density increases.

At a discharge current density of 80 mA cm$^{-2}$, the discharge capacity of the cell with the 0.025 wt.% PVP additive reaches stable peak values of 1080 mAh corresponding to 98% utilization, whereas the blank cell exhibits 1070 mAh corresponding to 97% utilization of vanadium ions. Although this difference appears small, it may become significant in practical systems using hundreds of cubic meters of electrolyte and operating over long periods.

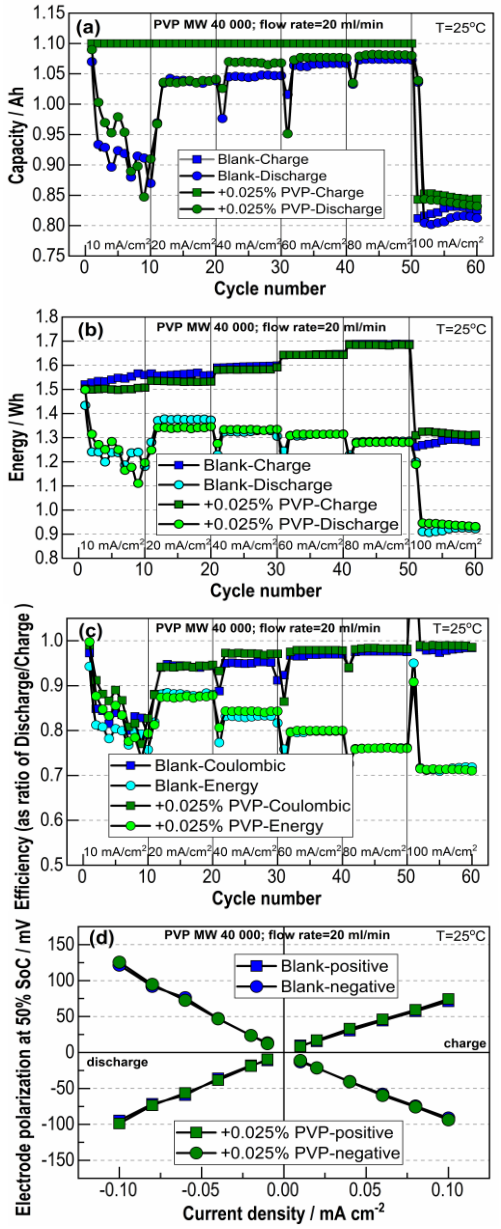


**Figure 4.** Influence of PVP in the positive electrolyte on the electrical characteristics of a vanadium flow cell measured at various current densities: (a) Discharge and charge capacity; (b) Discharge and charge energy; (c) Coulombic and energy efficiency; (d) Positive and negative electrode polarizations at 50% SoC during charge and discharge.

A further increase in discharge current density to 100 mA cm$^{-2}$ causes a sharp drop in cell discharge and charge capacity to values of 800–850 mAh, but the cell with the PVP additive still demonstrates greater discharge capacity. This abrupt decline is associated with a considerable increase in internal resistance due to cell-design features such as electrode contact and electrolyte supply through the integrated flow field. Fig. 4b shows the recorded changes in discharge and charge energy as a function of current density for cells with and without PVP. PVP does not negatively affect the charge or discharge energy values. A slight decrease is observed only at 20 mA cm$^{-2}$, whereas a minor increase is registered at 100 mA cm$^{-2}$. Similarly, the coulombic efficiency and the energy efficiency, calculated as the ratio of the discharge to charge parameters, are plotted in Fig. 4c. The addition of PVP to the positive electrolyte improves coulombic efficiency, although the improvement ranges from noticeable to minor depending on the current density. This effect indicates that the PVP additive improves the reversibility of the processes related to the conversion of $VO^{2+}$ to $VO_2^+$ and *vice versa*. The tendency of coulombic efficiency to increase at high current densities could be attributed to a decrease in charge and discharge time, thus minimizing the influence of undesired phenomena such as ion and liquid crossover through the membrane and reducing irreversible side reactions. The coulombic efficiency at a current density of 40 mA cm$^{-2}$ is 95% for the blank cell and 97% for the cell with the PVP additive, while at 80 mA cm$^{-2}$, the blank cell yields 97.6% and the cell with the PVP additive yields 98.3%. Even small differences in this parameter could improve battery life and moderate capacity fading. The calculated values of energy efficiency at various current densities show that the 0.025 wt.% PVP additive in the positive electrolyte has no impact on this parameter. The positive and the negative electrode polarizations at 50% SoC during discharge and charge at various current densities, plotted in Fig. 4d, indicate that the PVP additive has no influence on this electrochemical parameter.

The impact of the PVP additive in the positive electrolyte on the cycling performance of a vanadium flow cell was evaluated during repetitive discharge-charge cycles at a constant current density of 80 mA cm$^{-2}$. The data obtained for various electrical characteristics of the test cell with the additive and the control cell are plotted in Figure 5.

The data in Fig. 5a clearly show that the addition of 0.025 wt.% of PVP to the positive electrolyte results in stable discharge capacity values of 1050 to 1080 mAh during all 250 cycles, whereas the control cell exhibits values of 1030 mAh in the first 100 cycles, which then drop to 950–1000 mAh. The cell with the PVP additive maintains the ability to accept full charge throughout all 250 cycles, while the control cell loses that ability after 100 cycles. Therefore, the addition of PVP with a molecular weight of 40 000 to the positive electrolyte ensures enhanced and stable cell discharge capacity. In terms of discharge energy (Fig. 5b), the cell with the PVP additive exhibits higher discharge-energy values than the control cell. The calculated values for

coulombic efficiency and energy efficiency, plotted in Fig. 5c, indicate that the PVP additive considerably improves and stabilizes coulombic and energy efficiency during the course of cell cycling. The observed abrupt variations in the cell's electrical characteristics were partially a consequence of liquid flow through the electrolyte bridge from the negative to the positive reservoir or *vice versa*.

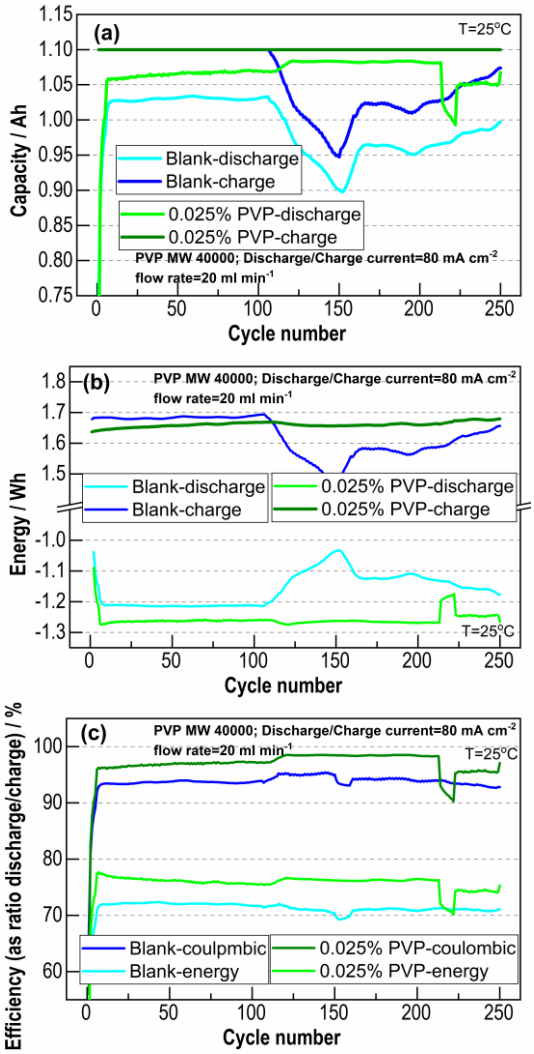


**Figure 5.** Impact of the PVP additive in the positive electrolyte on the evolution of cell electrical characteristics during discharge-charge cycling: (a) Discharge and charge capacity; (b) Energy; (c) Coulombic and energy efficiency.

To further understand the mode of action of the PVP additive during discharge and charge cycling, the cell-voltage and open-circuit-voltage profiles were compared for cycles 50 and 200 in Fig. 6. It can be seen that for the blank cell as cycling progresses, the cell voltage during charge (Fig. 6a) shifts to higher values, and the 1.60 V limit is reached earlier during the charge step. The cell voltage during charge for the cell with 0.025 wt.% of PVP remains stable during cycling and is lower than that of the blank cell. The cell voltage during discharge is less affected by the PVP additive. The trends of the open-circuit-voltage curves (Fig. 6b) reveal that the PVP additive acts to decrease the values by 20–30 mV. The impact of the PVP additive on open-circuit-voltage values is more distinct during charge than during discharge. Moreover, in the presence of PVP, the open-circuit-voltage values during charge are less affected by cycling than those of the blank cell.

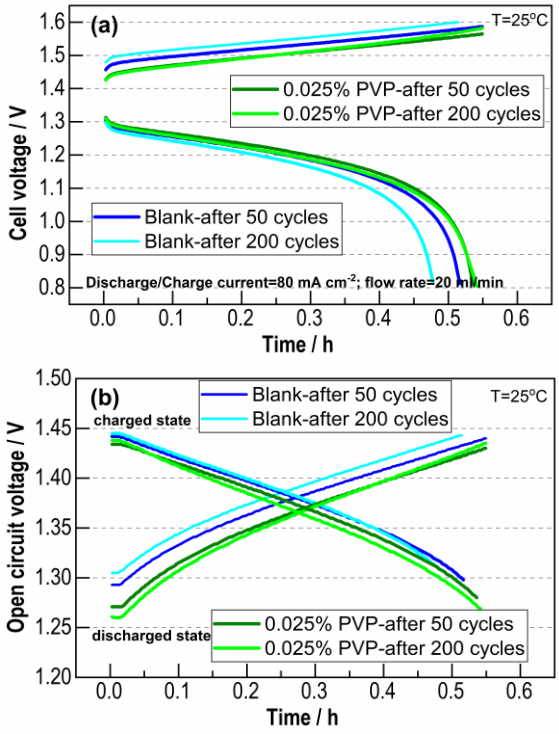


**Figure 6.** Comparison of voltage changes after 50 and 200 discharge-charge cycles for vanadium flow cells without and with the PVP additive in the positive electrolyte: (a) Cell voltage; (b) Open-circuit voltage.

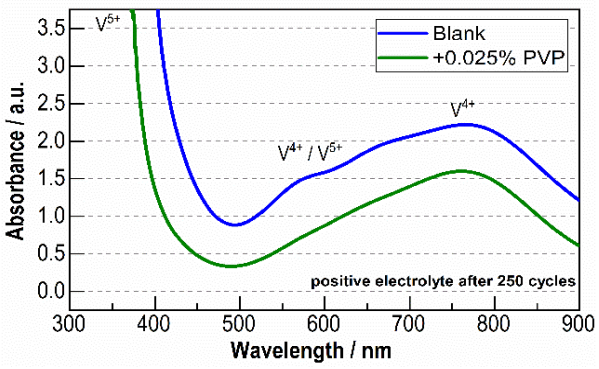


**Figure 7.** UV–Vis spectra of the positive electrolyte from vanadium flow cells with and without the PVP additive after 250 discharge-charge cycles.

The registered difference in open-circuit-voltage values indicates that an increase in the number of discharge and charge cycles provokes a variation in the ratio of V(V) and V(IV) ions, leading to a decline

in electrical performance. This phenomenon is suppressed by the PVP additive in the positive electrolyte. The PVP additive mainly affects the positive-electrode charge reaction, which involves $H^+$ ions (protons). Hence, the PVP polymer, as a pronounced proton-donor or proton-acceptor substance, is readily involved in the intermediate elementary processes of protonation and deprotonation occurring at the positive electrode.

Fig. 7 compares the UV–Vis absorption spectra of vanadium electrolyte samples taken from the positive reservoir at the end of cycling, with and without PVP.

A broad absorption band with a maximum at approximately 765 nm is observed, characteristic of $VO^{2+}$ (V(IV), vanadyl), along with a weak shoulder around 580 nm, which is attributed to additional charge-transfer transitions in the $VO^{2+}/VO_2^+$ (V(IV)/V(V)) system. In the samples with added PVP, the positions of the characteristic absorption maxima are preserved, which indicates that the added polymer does not significantly affect the electronic structure of the vanadium species. At the same time, a significant decrease in the intensity of the absorption bands is observed along with the disappearance of the shoulder at 580 nm. These effects can be attributed to interactions between PVP and vanadium ions, which increase ion stabilization in solution and suppress ionic aggregation [18, 19]. The UV–Vis measurements support the conclusion that the improved electrical characteristics of the test cell result from close interactions between PVP polymer chains and vanadium ions in the positive electrolyte.

## CONCLUSIONS

In summary, cyclic voltammetry tests showed that the addition of polyvinylpyrrolidone (PVP) alone to the vanadium electrolyte has a positive impact on the electrochemical reactions occurring at the positive and the negative electrode of a vanadium redox flow cell. PVP with a molecular weight of 40 000 exhibits a more pronounced beneficial effect than PVP with a molecular weight of 360 000, with an optimal dosage level of 0.025 wt.%. Electrical tests conducted with flow cells demonstrated that adding 0.025 wt.% of PVP with a molecular weight of 40 000 to the positive electrolyte provides a stable, long-term enhancement of cell discharge capacity and energy while also improving coulombic efficiency compared with a control cell without the additive. Open-circuit voltage measurements during discharge and charge tests revealed that in the presence of PVP the voltage values shifted downward by 20–30 mV which results in better cell charging. This shift could be attributed to active interactions between the polymer chains, vanadium ions, and protons.

***Acknowledgement:*** *This research was carried out with the financial support of the National Recovery and Resilience Plan of the Republic of Bulgaria, co-funded by the European Union NextGenerationEU, under Project No. BG-RRP-2.011-0048 Improved Electrolyte for Vanadium Flow Batteries.*

## REFERENCES

1. J. Zhang, L. Li, Z. Nie, B. Chen, M. Vijayakumar, S. Kim, W. Wang, B. Schwenzer, J. Liu, Z. Yang, *J. Appl. Electrochem*., **41**, 1215 (2011).
2. T. M. Tseng, R. H. Huang, C. Y. Huang, C. C. Liu, K. L. Hsueh, F. S. Shieu, *J. Electrochem. Soc*., **161**, A1132 (2014).
3. H. Kaneko, K. Nozaki, Y. Wada, T. Aoki, A. Negishi, M. Kamimoto, *Electrochim. Acta*, **36**, 1191 (1991).
4. A. Shibata, K. Sato, *Power Eng. J.,* **13**, 130 (1999).
5. L. Cao, M. Skyllas-Kazacos, C. Menictas, J. Noack, *J. Energy Chem*., **27**, 1269 (2018).
6. L. Li, S. Kim, W. Wang, M. Vijayakumar, Z. Nie, B. Chen, J. Zhang, G. Xia, J. Hu, G. Graff, J. Liu, Z. Yang, *Adv. Energy Mater*., **1**, 394 (2011).
7. J. Martin, K. Schafner, T. Turek, *Energy Technol*., **8**, 2000522 (2020).
8. D. S. Aaron, Q. Liu, Z. Tang, G. M. Grim, A. B. Papandrew, A. Turhan, T. A. Zawodzinski, M. M. Mench, *J. Power Sources*, **206**, 450 (2012).
9. T. Jirabovornwisut, A. Arpornwichanop, *Int. J. Hydrog. Energy*, **44**, 24485 (2019).
10. M. Skyllas-Kazacos, L. Cao, M. Kazacos, N. Kausar, A. Mousa, *ChemSusChem*, **9**, 1521 (2016).
11. S. Li, K. Huang, S. Liu, D. Fang, X. Wu, D. Lu, T. Wu, *Electrochim. Acta*, **56**, 5483 (2011).
12. C. Ding, X. Ni, X. Li, X. Xi, X. Han, X. Bao, H. Zhang, *Electrochim. Acta*, **164**, 307 (2015).
13. Y. Wen, Y. Xu, J. Cheng, G. Cao, Y. Yang, *Electrochim. Acta*, **96**, 268 (2013).
14. Z. Yu, X. Jia, Y. Cai, R. Su, Q. Zhu, T. S. Zhao, H. Jiang, *Energy Storage Mater*., **69**, 103404 (2024).
15. X. Wu, J. Liu, X. Xiang, J. Zhang, J. Hu, Y. Wu, *Pure Appl. Chem.*, **86**, 1035 (2014).
16. L. Zeng, T. S. Zhao, L. Wei, Y. K. Zeng, Z. H. Zhang, *J. Power Sources*, **327**, 374 (2016).
17. T. D. Nguyen, A. Whitehead, N. Wai, G. G. Scherer, A. N. Simonov, Z. J. Xu, D. R. MacFarlane, *Small*, **20**, 2311771 (2024).
18. N. H. Choi, S. Kwon, H. Kim, *J. Electrochem. Soc*., **160**, A973 (2013).
19. D. N. Buckley, X. Gao, R. P. Lynch, N. Quill, M. J. Leahy, *J. Electrochem. Soc*., **161**, A524 (2014).