

Article



# Influence of Several Phosphate-Containing Additives on the Stability and Electrochemical Behavior of Positive Electrolytes for Vanadium Redox Flow Battery

Xukun Zhang <sup>1,2,3</sup>, Fancheng Meng <sup>1,2,3,\*</sup>, Linquan Sun <sup>1,2,3</sup>, Zhaowu Zhu <sup>1,2</sup>, Desheng Chen <sup>1,2,4</sup> and Lina Wang <sup>1,2,3,\*</sup>

- Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
- <sup>2</sup> National Engineering Research Center of Green Recycling for Strategic Metal Resources, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
- <sup>3</sup> School of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 101408, China
- <sup>4</sup> Hebei Zhongke Tongchuang Vanadium & Titanium Technology Co., Ltd., Hengshui 053000, China
- Correspondence: fcmeng@ipe.ac.cn (F.M.); linawang@ipe.ac.cn (L.W.)

Abstract: The poor operational stability of electrolytes is a persistent impediment in building redox flow battery technology; choosing suitable stability additives is usually the research direction to solve this problem. The effects of five phosphate containing additives (including 1-hydroxyethylidene-1,1diphosphonic acid (HEDP), hexamethylene diamine tetramethylene phosphonic acid (HDTMPA), amino trimethylene phosphonic acid (ATMPA), sodium ethylenediamine tetramethylene phosphonate (EDTMPS), and diethyl triamine pentamethylene phosphonic acid (DTPMP)) on the thermal stability and electrochemical performance of the positive electrolyte of vanadium redox flow battery were investigated. With 0.5 wt% addition, most of the selected additives were able to improve the thermal stability of the electrolyte. HEDP and HDTMPA extended the stability time of the pentavalent vanadium electrolyte at 50  $^{\circ}$ C from 5 days (blank sample) to 30 days and 15 days, respectively. The electrochemical performance of the electrolyte was further investigated by cyclic voltammetry, steady state polarization, and electrochemical impedance spectroscopy tests. It was found that most of the additives enhanced the electrochemical activity of the positive electrolyte, and the diffusion coefficients, exchange current densities, and reaction rate constants of V(IV) species became larger with the addition of these additives. It is verified that the thermal stability and electrochemical stability of the electrolyte are significantly improved by the combination of ATMPA + HEDP or ATMPA + HDTMPA. This study provides a new approach to improve the stability of the positive electrolyte for vanadium redox flow battery.

**Keywords:** vanadium redox flow battery; positive electrolyte; phosphate containing additives; stability; electrochemical behavior

## 1. Introduction

The vanadium redox flow battery (VRFB), proposed by Maria Skyllas-Kazacos and dating back to 1970, is considered the most promising renewable energy storage system, with the advantages of high capacity, excellent stability, high operation security, and long cycle, and it has attracted widespread attention and been investigated worldwide [1]. The positive and negative electrolytes of VRFB are stored in two separate tanks, and they flow through a separate half-cell during operation and then return to the tank for recirculation. Each half-cell of VRFB consists of an electrode and bipolar plate, and two half-cells are separated by a membrane that allows selective ion exchange while preventing cross-contamination of the electrolyte [2]. The chemical reactions occurring at the electrodes of positive and negative half-cell, as well as the overall cell reaction, are as follows:



Citation: Zhang, X.; Meng, F.; Sun, L.; Zhu, Z.; Chen, D.; Wang, L. Influence of Several Phosphate-Containing Additives on the Stability and Electrochemical Behavior of Positive Electrolytes for Vanadium Redox Flow Battery. *Energies* 2022, *15*, 7829. https://doi.org/10.3390/en15217829

Academic Editors: Luis Hernández-Callejo, Jesús Armando Aguilar Jiménez and Carlos Meza Benavides

Received: 16 September 2022 Accepted: 18 October 2022 Published: 22 October 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Positive cell reaction:

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \tag{1}$$

Negative cell reaction:

$$\mathbf{V}^{2+} \rightleftharpoons \mathbf{V}^{3+} + \mathbf{e}^{-} \tag{2}$$

Overall cell reaction:

$$VO_2^+ + V^{2+} + 2H^+ \rightleftharpoons VO^{2+} + V^{3+} + H_2O$$
 (3)

Under the fully discharged circumstance, the positive and negative electrolytes contain only V(IV) (VO<sup>2+</sup>) and V(III), respectively. During charging, the V(III) ions in the negative electrolyte are reduced to V(II), and the VO<sup>2+</sup> ions in the positive electrolyte are oxidized to V(V) (VO<sub>2</sub><sup>+</sup>). The electrons move through the bipolar plate from the positive electrode to the negative electrode, causing hydrogen ions (H<sup>+</sup>) to diffuse across the membrane to the negative electrode. The same reaction occurs in reverse when discharging [3].

Despite the rapid development of VRFB in recent years, some issues limiting its commercialization need to be addressed, one of which is the fact that the vanadium compound, as the active substance in the electrolyte, accounts for a substantial part of the capital cost (40%) [4]. In addition, the battery capacity depends on the vanadium concentration, and the pentavalent vanadium species have a low solubility in sulfuric acid (<2 M) and a narrow operating temperature window (10–40 °C), thus limiting the energy density of the battery (typically < 25 Wh L<sup>-1</sup>) [5]. At higher temperatures (>40 °C), the precipitation of V<sup>5+</sup> in the positive electrolyte is as follows [6]:

$$2[VO_2(H_2O)_3]^+ \to 2VO(OH)_3 + 2H_2O + 2H^+$$
(4)

$$2\text{VO(OH)}_3 \rightarrow \text{V}_2\text{O}_5 + 3\text{H}_2\text{O} \tag{5}$$

The precipitation process of  $V_2O_5$  is irreversible, which is mainly responsible for the loss of battery capacity. In order to improve the solubility of vanadium compounds in the sulfuric acid electrolyte, the introduction of additives is commonly performed. Owing to their being cost-effective and not interfering with electrolyte performance, they have been investigated widely nowadays [7]. Skyllas-Kazacos et al. used phosphoric acid and ammonium phosphate as additives. The results show that phosphate anions enhance the stability of V(V) compounds at high temperatures, whereas for ammonium cations, the opposite is true—ammonium cations stabilize the negative half-cell electrolyte at low temperatures. The effects of sodium triphosphate and sodium hexametaphosphate as additives were also studied; they both retarded the precipitation to a certain extent [8,9]. Roznyatovskaya et al. investigated the mechanism of precipitation retarding by phosphate in the vanadium electrolyte using nuclear magnetic resonance (NMR) spectroscopy and dynamic light scattering (DLS). It was concluded that the electrolyte stabilization mechanism by phosphoric acid at high temperatures could be attributed to the interaction between them and V(V) monomers or dimers forming two phosphate-containing substances, thus retarding the  $V_2O_5$  precipitation [10]. Park et al. used 0.05 M sodium pyrophosphate as an additive in the positive electrolyte with 2.0 M V(V) and 4.0 M  $H_2SO_4$ , and the long-term stability of electrolyte was improved compared with the blank solution. In addition, none of the new precipitation was proved to have been generated in the electrolyte. Nonetheless, its electrochemical cycling performance was optimized [11]. Zhang et al. investigated the effect of  $Na_3PO_4$  as an electrolyte additive and found that it indeed delayed the  $V_2O_5$ precipitation, but the VOPO<sub>4</sub>·2H<sub>2</sub>O precipitation was detected on the positive graphite mat after several cycle tests [12]. Li et al. reported some organic additives containing hydroxyl (-OH), such as sorbitol, mannitol, glucose, and fructose, and elaborated their stabilizing mechanism, indicating that these organic additives can clad the hydrated V(V) species and thus inhibit the formation of precipitation [13]. Zhang et al. selected 1 wt% HEDP as an

electrolyte additive and confirmed that it can improve the electrolyte thermal stability and battery cycle efficiency of VRFB. Besides, the research confirmed in two ways (the Job plot and the Benesi–Hildebrand plot methods) that HEDP interacts with  $VO_2^+$  in a 1:1 binding stoichiometry, which is the reason for the enhancement in the stability of the electrolyte [14]. Through the above studies, it is found that both phosphate and –OH have a good effect on stabilizing pentavalent vanadium. In summary, some research results on additives of the positive electrolyte are summarized in Table 1.

Additive	Amount	V(V)/M	H <sub>2</sub> SO <sub>4</sub> /M	Temperature/°C	Effect of Thermal Stability	References
Sodium tripolyphosphate	1 wt%	2	-	44	Improved	[8]
Sodium hexametaphosphate	1 wt%	2	-	44	Improved	[9]
Sodium pyrophosphate	0.05 M	2	4	25	Improved	[11]
glucose	1 wt%	1.8	4.8	20-60	Improved	[13]
K <sub>3</sub> PO <sub>4</sub>	1 wt%	3	5	30/50	Improved	[15]
Polyacrylic acid	0.5  wt/vol%	4.7	6	50	Slightly improved	[16]
$(NH_4)_2SO_4$	2 wt%	1.8	5	50	Improved	[17]
H <sub>3</sub> PO <sub>4</sub>	1 wt%	2	5	50	Significantly improved	[17]
CH <sub>3</sub> SO <sub>3</sub> H	2.1–3 wt%	2	5	40	Improved	[12]
Hexadecyl trimethyl ammonium bromide (CTAB)	0.00106–0.0053 M	1.5	4.5	45	Improved	[18]
Phytic acid	N/A	1.8	3	25-60	Improved	[19]

Table 1. Some research results on additives of the VRFB positive electrolyte.

In the present work, five additives containing both phosphate and more –OH, including 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), hexamethylene diamine tetramethylene phosphonic acid (HDTMPA), amino trimethylene phosphonic acid (ATMPA), sodium ethylenediamine tetramethylene phosphonate (EDTMPS), and diethyl triamine pentamethylene phosphonic acid (DTPMP), were selected and added into the V(V) electrolyte to investigate their effects on precipitation inhibition and electrochemical behavior, and the obtained results were compared with those of the original blank electrolyte. Among the five selected additives, except HEDP, other additives have not been used and discussed in such studies. The novelty of this paper is that this research has explored five kinds of phosphate containing positive electrolyte additives and their effects on stability and electrochemical performance and found two combinations that can improve the thermal stability and electrochemical performance of the electrolyte at the same time.

# 2. Materials and Methods

## 2.1. Materials

 $VOSO_4 \cdot 3.5H_2O$  (99%) was provided by Shenyang Haizhongtian Fine Chemical Co., Ltd.(Shenyang, China). The additives are listed in Table 2. HEDP (60% in water), ATMPA (50% in water), EDTMPS (98%), and DTPMP (50% in water) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China. HDTPMA (>98%) was obtained from Adamas-beta Co., Ltd.(Shanghai, China). Other chemicals used in the experiment are of analytical grade. The previous experiment shows that, under the experimental conditions selected in this study, the five additives are stable.

## 2.2. Preparation of the V(V) Electrolyte Solution

 $VOSO_4 \cdot 3.5H_2O$  (99%) was dissolved in a 3 M H<sub>2</sub>SO<sub>4</sub> solution to prepare 2 M VOSO<sub>4</sub> solution, and the prepared V(IV) electrolyte solution was placed in a double-chamber electrolytic cell with 50 mL and 25 mL of positive and negative electrolyte tank capacity, respectively. The electrolyte was then charged (cut-off potential: 1.55 V, stepwise current

density:  $200-10 \text{ mA cm}^{-2}$ ) until the V(IV) ions in the positive electrolyte were converted to V(V) and the V(IV) ions in the negative electrolyte were converted to V(II). When the electrolysis was done, the total vanadium concentration in the positive electrolyte was determined by redox titration using a potentiometric titrator (PHS-3C, Shanghai Leici Co., Ltd., Shanghai, China).

**Table 2.** Molecular structure of the studied organic additives.

Chemical Name (Short Form)	Molecular Structure			
Hexamethylenediamine tetramethylene phosphonic acid (HDTMPA)	$H_2O_3P-CH_2$ $CH_2-PO_3H_2$ $N-(CH_2)_6-N$ $H_2O_3P-CH_2$ $CH_2-PO_3H_2$			
1-hydroxyethylidene-1,1-diphosphonic acid (HEDP)	$\begin{array}{c} OH OH OH \\ HO - P - C - P - OH \\ HO - P - C + OH \\ O - C + OH \\$			
Amino trimethylene phosphonic acid (ATMPA)	$\begin{array}{c} O \\ O \\ HO - P - CH_2 - N \\ OH \\ $			
Sodium ethylenediamine tetramethylene phosphonate (EDTMPS)	$\begin{array}{c c} O & O \\ HO-P-H_2C & CH_2-P-ONa \\ ONa & N-CH_2-CH_2-N & ONa \\ ONa & ONa & ONa \\ HO-P-H_2C & CH_2-P-ONa \\ O & ONa & ONa \\ HO-P-H_2C & ONa \\ O & ONa & ONa \\ O & O & O \\ O & O & O \\ O & O & O \\ O & O &$			
Diethyl triamine pentamethylene phosphonic acid (DTPMP)				

## 2.3. Thermal Stability Test of V(V)

To investigate the effect of various phosphonates additives on the long-term stability of the V(V) electrolyte, electrolyte samples containing 0.05 wt% additives and blank sample were stored in a sealed oven at 50 °C until measurable orange precipitation was observed. All thermal stability tests were performed without any agitation. Each sample was visually monitored more than twice a day during the test to record the V<sub>2</sub>O<sub>5</sub> precipitation and the change in solution color. The samples were filtered and their equilibrium concentrations of vanadium were determined by redox titration again, at the end of the 30-day test.

## 2.4. Electrochemical Tests

The CV cycle test and steady-state polarization curve test of the electrolyte were performed using a CHI 760B electrochemical workstation (Shanghai Chenhua Instrument, Shanghai, China). We recorded the current versus potential curves using a three-electrode

electrochemical cell in the CV cycling test with a scan rate range of 10–200 mV s<sup>-1</sup> in a potential range of -0.6-1.8 V at 25 °C, in which the graphite electrode (surface area of 3.14 mm<sup>2</sup>), saturated calomel electrode, and platinum electrode (surface area of 1 cm<sup>2</sup>) are the working electrode, reference electrode, and counter electrode, respectively. The steady-state polarization curve was tested with a potential range of 0.49–0.56 V and a scan rate of 1 mV s<sup>-1</sup>, because the current and voltage are closer to a straight line under the condition of lower potential. Electrochemical impedance spectroscopy (EIS) was also obtained at room temperature with the sinusoidal excitation voltage of the electrolyte of 5 mV and the frequency range between 0.01 Hz and 100 kHz. Prior to each electrochemical measurement, the working electrode was polished with SiC paper and then washed with distilled water. The reference electrode was washed with distilled water and the solution

## 3. Results and Discussion

water and ultrasonically treated.

#### 3.1. Effect of Additives on the Stability of the V(V) Electrolyte

The effect of different additives (Table 1) on the thermal stability of the V(V) electrolyte was investigated by adding 0.5 wt% of additives at 50 °C. Table 3 shows the very time when  $V_2O_5$  started to precipitate in the V(V) electrolyte samples with different additives and the V(V) concentration in the positive electrolyte after 30 days.

in salt bridge was replaced before use. Platinum plate electrode is cleaned with distilled

**Table 3.** Effect of several additives (dosage 0.5 wt%, 50 °C) on the thermal stability of the  $2 \text{ M V}(\text{V})/3 \text{ M H}_2\text{SO}_4$  electrolyte.

	Blank	HDTMPA	HEDP	ATMPA	EDTMPS	DTPMP
Time to precipitation	5 days	15 days	30 days	4 days	10 days	12 days
V(V) concentration after 30 days	1.27 M	1.46 M	1.86 M	1.20 M	1.40 M	1.44 M

It was observed that the selected additives, except for ATMPA, delayed the precipitation of V(V) in the electrolyte under the same experimental conditions. The blank sample started to precipitate after 5 days and the retarding effect for the additives follows the order: HEDP (30d) > HDTMPA (15d) > DTPMP (12d) > EDTMPS (10d) > ATMPA (4d). The remaining V(V) concentration in the electrolyte after 30 days showed the same variation pattern as the initial time of precipitation. The remaining V(V) concentration in the electrolyte with HEDP was 1.86 M, followed by 1.46 M for HDTMPA, and that of the blank electrolyte sample was 1.27 M after 30 days. As for ATMPA, it was 1.20 M, which had a negative effect in this test. The vanadium concentration in the electrolyte directly determines the energy density and capacity of the battery [20], and the experimental results show that the thermal stability of the V(V) electrolyte is improved by the additives (except ATMPA). This means that these additives facilitate the VRFB to improve its energy density and capacity.

The stabilizing mechanism of HEDP for the electrolyte might be attributed to the synergism of –OH and phosphate. –OH could clad the hydrated penta-coordinate V(IV) vanadate, which prevents it from being oxidized at a low concentration and inhibits its precipitation [9,21]. Phosphate could interact with V(V) monomers or dimers, forming a stable phosphate-containing substance, and thus retarding the precipitation [10]. Similarly, the stabilizing capability of HDTMPA and DTPMP is probably due to the presence of more phosphate. The EDTMPS, with good chemical stability and temperature resistance, is soluble in water, non-toxic, and environmentally friendly. It can dissociate into eight anions/cations in aqueous solution, and thus chelate with multiple V(V) ions, forming multiple monomeric structured reticular macromolecular complexes that are loosely dispersed in water, so the normal precipitation process of V(V) was disrupted [22]. Although ATMPA was reported to have low limit inhibition, good chelation, and lattice distortion effects [23], it exhibited the worst effect on the thermal stability, which was likely due to the formation of chelate, which is not conductive to solution stability.

## 3.2. CV Test

Figure 1 shows the CV curves of V(IV) electrolyte samples with additives and blank one, and it can be observed that all CV curves show the similar peak position and one pair of redox peaks with a similar shape. The additives slightly changed the shape and position of the peak, which means that these additives will affect the reversibility of V(IV)/V(V)redox pairs to some extent [19]. The relevant data derived from Figure 1 are summarized in Table 4. The effect of additives on the V(IV)/V(V) redox coupling is characterized by  $I_{pO}/I_{pR}$  (ratio of the oxidation peak current to reduction peak current) and  $\Delta V_{p}$  (separation between the oxidation and reduction peak potential). The HDTMPA just incurred a minor decrease in the  $\Delta V_p$  of the electrolyte and a small increment in the  $I_{pO}/I_{pR}$  as if it had little effect on the reversibility of the V(IV)/V(V) redox pair. In addition, it had a small effect on the oxidation peak current and reduction peak current as well as the overall peak shape of the curve, indicating that its effect on the electrode reaction kinetics of the electrolyte was not that significant either [24]. The addition of HEDP increased the  $\Delta V_p$  of the electrolyte while decreasing  $I_{pO}/I_{pR}$  significantly. The addition of HEDP, DTPMP, ATMPA, and EDTMPS had a greater effect on the reversibility of V(V)/V(IV) redox pairs, and the HEDP significantly increased the peak oxidation current and peak reduction current, indicating that it might enhance the electrode reaction kinetics of the electrolyte. The main reason for the improvement in electrode reaction kinetics by HEDP might be attributed to the fact that the -OH could complex with V(IV)/V(V) ions, which provide more available -OH to the stable electrode reaction of V(IV)/V(V) for ion exchange on the electrode surface, thus resulting in a higher oxidation peak current and reduction in peak current [25]. Among all additives, ATMPA best enhanced the electrode reaction kinetics of electrolyte, but it caused a decrease in electrolyte thermal stability. HDTMPA, EDTMPS, and DTPMP probably affect the cyclic reversibility performance and electrode reaction kinetics of the electrolyte by, firstly, phosphate and, secondly, according to calculations, the C atoms adjacent to N atoms have a high positive charge density, counteracting the strong electron affinity of N atoms [26], and the positively charged C atoms activated by the N atoms can work as an active site, affecting electron distribution, thereby improving the electrochemical performance. In addition, EDTMPS benefits from its Na<sup>+</sup> ions, increasing the number of ionizable cations in the solution, which enhances the electrode reaction kinetics [12]. As for HDTMPA, its large groups slightly hinder the ion exchange and charge transfer on the electrode surface owing to the steric hindrance, which is obviously unfavorable [18]. When ATMPA and HDTMPA are used in combination,  $\Delta Vp$  of the electrolyte declined compared with the blank sample and  $I_{pO}/I_{pR}$  displayed a small change. The combination of ATMPA and HEDP also showed the same performance. At the same time, compared with the CV curve of the blank sample, the peak current and the peak area of these two complex schemes are larger, which indicates that the electrolytes affected by these two schemes have better electrochemical performance.

A series of CV curves on graphite electrode for the blank electrolyte and the electrolyte with different additives at different scan rates are depicted in Figure 2, which further reveals the effect of additives on the electrode reaction kinetics. The peak potential of the anode and cathode varies gradually with the scan rate, presenting the typical characteristics of a quasi-reversible single-electron process [27]. The diffusion coefficient of the quasi-reversible reaction (*D*) is between that of the reversible reaction (*D*<sub>1</sub>) and irreversible reaction (*D*<sub>2</sub>) [28]. As for the reversible and irreversible one-step single-electron reactions, their peak current ( $i_p$ ) can be represented as follows [29]:

$$i_p = 0.4463 (F^3/RT)^{1/2} CAn^{3/2} v^{1/2} D_1^{1/2}$$
 (Reversible reaction) (6)

$$i_p = 0.4958 (F^3/RT)^{1/2} CA\alpha^{1/2} n^{3/2} v^{1/2} D_2^{1/2}$$
(Irreversible reaction) (7)

where R is the universal gas constant; F is the Faraday constant; T is the Kelvin temperature; n is the amount of substance of transferred electrons during electrode reaction; A is the

surface area of working electrode; *C* is the bulk concentration of primary reactant; *v* is the scanning rate;  $\alpha$  is the transfer coefficient for an irreversible reaction; and  $D_1$  and  $D_2$  are the diffusion coefficients of reversible and irreversible reactions, respectively.

For a single-electron reaction at room temperature, Equations (6) and (7) can be simplified as follows:

$$i_p = 2.69 \times 10^5 A C D_1^{1/2} v^{1/2} \tag{8}$$

$$i_p = 2.99 \times 10^5 \alpha^{1/2} A C D_2^{1/2} v^{1/2} \tag{9}$$

According to the present experimental conditions, Equations (10) and (11) can be further derived from Equation (8) and Equation (9), respectively:

$$i_v/A = 538D_1 v^{1/2} = v^{1/2}k \tag{10}$$

$$i_p/A = 598D_2^{1/2}v^{1/2} = v^{1/2}k \tag{11}$$

Equations (10) and (11) indicate that the current density  $(i_p/A)$  is linearly related to the square root of scan rate  $(v^{1/2})$  and k denotes the slope of this line, illustrated in Figure 3, thus  $D_1$  and  $D_2$  were calculated. The values of k for the blank electrolyte and those with 0.5 wt% of different additives are concluded in Table 5.

$$D_1 = 3.45 \times 10^{-6} k^2 \tag{12}$$

$$D_2 = 2.80 \times 10^{-6} k^2 \tag{13}$$



**Figure 1.** CV curves of the electrolyte (2.0 M V(IV)/3.0 M  $H_2SO_4$ ) with additives (0.5 wt%) and the blank one at a scan rate of 20 mV s<sup>-1</sup> at room temperature.

**Table 4.**  $\Delta V_p$  and  $I_{pO}/I_{pR}$  of the electrolyte (2.0 M V(IV)/3.0 M H<sub>2</sub>SO<sub>4</sub>) with additives (0.5 wt%) and the blank one on the graphite electrode.

Additives	Blank	HDTMP	A HEDP	DTPMP	ATMPA	EDTMPS	ATMPA + HEDP	ATMPA + HDTMPA
$\Delta V_p/V$	0.241	0.231	0.340	0.320	0.275	0.285	0.208	0.200
I <sub>pO</sub> /I <sub>pR</sub>	1.462	1.496	1.242	1.299	1.432	1.246	1.470	1.474



**Figure 2.** CV curves of the electrolyte (2.0 M V(IV)/3.0 M H<sub>2</sub>SO<sub>4</sub>) with/without additives ((**a**) blank sample; (**b**) HDTMPA; (**c**) HEDP; (**d**) DTPMP; (**e**) ATMPA; (**f**) EDTMPS; (**g**) ATMPA + HDTMPA; (**h**) ATMPA + HEDP) on the graphite electrode at different scan rates at room temperature.



**Figure 3.** Linear plot of  $i_p$  versus  $v^{1/2}$ .

Table 5. Diffusion coefficients	$(D_1$	and $D_2$ ) of V(	IV	) species at 25 $^\circ$	°C
---------------------------------	--------	-------------------	----	--------------------------	----

Additives	Diffusion Coefficient $D_1$ and $D_2$ of V(IV) Species (cm <sup>2</sup> s <sup>-1</sup> )					
Additives	$D_1$	<i>D</i> <sub>2</sub>	Error (%)			
Blank	$2.20  imes 10^{-7}$	$1.88 imes10^{-7}$	1.9			
HDTMPA	$2.26 imes10^{-7}$	$1.84 imes10^{-7}$	1.3			
HEDP	$3.89 imes10^{-7}$	$3.15 imes10^{-7}$	1.5			
DTPMP	$4.86 imes10^{-7}$	$3.94 imes10^{-7}$	1.3			
ATMPA	$6.80 imes10^{-7}$	$5.52  imes 10^{-7}$	1.3			
EDTMPS	$3.48 imes10^{-7}$	$2.83  imes 10^{-7}$	1.6			
ATMPA + HDTMPA	$4.34 imes10^{-7}$	$3.53 imes10^{-7}$	1.8			
ATMPA + HEDP	$5.43 imes10^{-7}$	$4.40  imes 10^{-7}$	1.7			

In fact, the diffusion coefficient of the electrolyte is between  $D_1$  and  $D_2$  for the quasireversible process. Under the present experimental conditions, the diffusion coefficient is  $1.88-2.20 \times 10^{-7}$  for the blank electrolyte and  $1.84-2.26 \times 10^{-7}$  for the sample with HDTMPA, and the result of the latter is close to that of the blank electrolyte. When it comes to the rest, their diffusion coefficients are  $3.15-3.89 \times 10^{-7}$  (HEDP),  $3.94-4.86 \times 10^{-7}$  (DTPMP),  $5.52-6.80 \times 10^{-7}$  (ATMPA), and  $2.83-3.48 \times 10^{-7}$  (EDTMPS), respectively. These increased diffusion coefficients of the electrolyte with additives indicate that the additives (except HDTMPA) can effectively improve the diffusion of vanadium species at the electrodes and enhance the mass transfer and charge transfer of the V(V)/V(IV) redox pair, thus increasing the corresponding reactivity. Compared with the blank sample, the combination of ATMPA + HDTMPA and ATMPA + HEDP also have a larger diffusion coefficient, showing that the compounding scheme has played a positive role in mass transfer and charge transfer in the electrolyte.

## 3.3. Steady-State Polarization Test

The steady-state polarization curve of the V(IV) electrolyte allows the determination of the polarization resistance, the exchange current density, and the electrochemical reaction rate constant.

In the relatively-low-overvoltage region, the overvoltage and current density are approximately linearly correlated [6]. These parameters can be calculated by Equation (14).

$$R_{ct} = \frac{\eta}{i}, \ i_0 = \frac{RT}{nFR_{ct}}, \ k_0 = \frac{i_0}{nFC_0}$$
 (14)

where  $R_{ct}$ ,  $i_0$ , and  $k_0$  refer to the charge-transfer resistance, exchange current density, and rate constant, respectively; R, T, n, F, and  $C_0$  are the universal gas constant, Kelvin temperature, amount of transferred electrons in the electrode reaction, Faraday constant, and solution concentration, respectively [30].

The steady-state polarization curves of the 2.0 M VOSO<sub>4</sub>/3.0 M H<sub>2</sub>SO<sub>4</sub> electrolyte with different additives on graphite electrode are demonstrated in Figure 4, and the corresponding parameters derived from Equation (14) are listed in Table 6. One can see that the charge transfer resistance of electrolyte samples with additives decreased and the electrochemical reaction rate constant and the exchange current density increased compared with the blank sample. The charge transfer resistance of the electrolyte with EDTMPS and DTPMP, for example, decreased from 12.40  $\Omega$  cm<sup>2</sup> (blank sample) to 8.15  $\Omega$  cm<sup>2</sup> and  $8.84 \,\Omega \,\mathrm{cm^2}$ , respectively, at 25 °C, while the exchange current density of these two samples increased from 2.07 mA cm<sup>2</sup> (blank sample) to 3.15 mA cm<sup>2</sup> and 2.91 mA cm<sup>2</sup>, respectively. The corresponding electrochemical reaction rate constant increased from  $1.07 \times 10^5$  cm s<sup>-1</sup> (blank sample) to  $1.63 \times 10^5$  cm s<sup>-1</sup> and  $1.51 \times 10^5$  cm s<sup>-1</sup>, respectively, at 25 °C. The other additives also accelerated the chemical reaction process of V(IV) on the electrode surface to varying degrees. The rest of the selected additives also accelerated the kinetics process of V(IV) species on the electrode surface to a certain level. Compared with the blank sample, the combination of ATMPA + HDTMPA and ATMPA + HEDP also had lower charge transfer resistance and higher exchange current density and electrochemical reaction rate constant, which was consistent with the CV tests.



**Figure 4.** Steady-state polarization curves for the 2.0 M V(IV)/3.0 M  $H_2SO_4$  blank electrolyte and those with 0.5 wt% additives on graphite electrode at a scan rate of 1 mV s<sup>-1</sup>.

Table 6. Kinetic parameters for the  $2.0 \text{ M VOSO}_4/3.0 \text{ M H}_2\text{SO}_4$  experimental electrolyte with different additives on the graphite electrode.

Additives	$R_{ct}$ ( $\Omega$ cm <sup>2</sup> )	$i_0$ (mA cm $^{-2}$ )	$k_0$ (10 <sup>-5</sup> cm s <sup>-1</sup> )
Blank	12.40	2.07	1.07
HDTMPA	11.48	2.24	1.16
HEDP	9.40	2.73	1.42
DTPMP	8.84	2.91	1.51
ATMPA	9.01	2.85	1.48
EDTMPS	8.15	3.15	1.63
ATMPA + HDTMPA	10.35	2.48	1.29
ATMPA + HEDP	9.11	2.82	1.46

#### 3.4. Electrochemical Impedance Spectroscopy Test

For the further analysis of the electrode reaction diffusion kinetics of vanadium and the charge transfer and mass transfer of the V(IV)/V(V) redox pair, Nyquist plots of the eight (including two compound schemes) V(IV) electrolyte samples at room temperature were recorded by electrochemical impedance spectroscopy. Figure 5 shows that each plot consists of a semicircle in the high-frequency region and a diagonal line in the lowfrequency region, indicating that the redox reaction of the V(IV)/V(V) pair is controlled by both high-frequency charge transfer and low-frequency diffusion. The radius of the semicircle corresponds to the charge transfer resistance and the linear part relates to the diffusion of vanadium species on the electrode [31]. The equivalent circuits of these Nyquist plots were fitted, and the corresponding parameters were obtained using ZView software, which are listed in Table 7. In the equivalent circuit, R<sub>1</sub> is the resistance consisting of the solution resistance, electrode resistance, and contact resistance, and R<sub>2</sub> and W<sub>0</sub> represent the charge transfer resistance and diffusion impedance, respectively. The constant phase element (CPE) represents the bilayer capacitance at the electrode–electrolyte interface.



**Figure 5.** Nyquist plots of the 2.0 M V(IV) electrolyte on the graphite plate and the corresponding equivalent circuit.

Additives	$\mathbf{P}/\mathbf{O}$ cm <sup>2</sup>	CPE/S s <sup><math>n</math></sup> cm <sup>-2</sup>		$R_{\rm e}/O~{\rm cm}^2$	$W_{2} V_{2} / S s^{-5} cm^{-2}$
Additives	K1/32 Cm	Y <sub>0,1</sub>	п	$ R_2/12$ cm	vv <sub>0</sub> , 1 <sub>0,2</sub> ,5 s em
Blank	0.218	$5.33  imes 10^{-3}$	0.775	0.168	0.409
HDTMPA	0.223	$9.11  imes 10^{-3}$	0.727	0.215	0.411
HEDP	0.268	$\begin{array}{c} 10.85 \times \\ 10^{-3} \end{array}$	0.707	0.205	0.397
DTPMP	0.268	$8.18 imes10^{-3}$	0.737	0.152	0.397
ATMPA	0.286	$8.70 imes10^{-3}$	0.727	0.154	0.408
EDTMPS	0.279	$5.61 imes10^{-3}$	0.769	0.116	0.390
ATMPA + HDTMPA	0.276	$\begin{array}{c} 16.87 \times \\ 10^{-3} \end{array}$	0.621	0.206	0.283
ATMPA + HEDP	0.282	$18.63 \times 10^{-3}$	0.552	0.186	0.288

 Table 7. Model parameters of equivalent circuits corresponding to Nyquist plots.

The additives slightly increased the contact resistance of the electrolyte, and all additives except HDTMPA and HEDP decreased the charge transfer resistance of the solution. The decrease in charge transfer resistance implies a faster charge transfer process, which is consistent with the above study. All of the additives except HDTMPA decrease the diffusion resistance of the electrolyte, which facilitates the diffusion process on the electrode surface and enhances the electrochemical reaction kinetics. In addition, all additives lead to an increase in the CPE parameter  $Y_{0,1}$ , indicating an enhanced bilayer capacitance at the electrode–electrolyte interface. *n* represents the index of CPE, ranging from 0 to 1. The larger the *n*, the higher the capacitive property and the lower the resistive property of CPE.

Compared with the samples using HDTMPA and HEDP additives alone, the charge transfer resistance of the two compounding schemes (ATMPA + HDTMPA and ATMPA + HEDP) is reduced, which accelerates the charge transfer in the solution, indicating that the compounding schemes (HDTMPA + ATMPA and HEDP + ATMPA) improve the electrochemical performance of the electrolyte.

After the above experimental investigation, it was found that the different additives selected could have a positive effect on the positive electrolyte of VRFB in terms of thermal stability and electrochemical performance. In future studies, it is expected that these additives may work better if used in combination, rendering these additives potential and promising for development.

## 4. Conclusions

In this study, five phosphate-containing scale inhibitions, including HDTMPA, HEDP, DTPMP, ATMPA, and EDTMPS, were employed as additives for the VRFB positive electrolyte and their effects on the electrolyte thermal stability and electrochemical performance were investigated. HDTMPA has a great positive effect on the thermal stability of the electrolyte, extending the time at which the electrolyte begins to precipitate to 15 days, while it has a lesser effect on the electrochemical performance; HEDP, DTPMP, and EDTMPS effectively improve the thermal stability of electrolyte and simultaneously accelerate its electrochemical reaction kinetics, but they have a greater effect on the cyclic reversibility of electrolyte, among which HEDP extended the time at which the electrolyte began to precipitate to 30 days, and the charge transfer resistance of the electrolyte decreased to 9.40  $\Omega$  cm<sup>2</sup>; and the addition of ATMPA greatly improves the mass transfer kinetics of the electrolyte, increasing the electrolyte diffusion coefficient on the electrode surface to  $6.80 \times 10^{-7}$ , simultaneously causing poor thermal stability of the electrolyte. In addition, the compounding effect of additives was studied. It was verified that the compounding combination of ATMPA + HDTMPA and ATMPA + HEDP had a good effect on the electrochemical performance of the electrolyte. In conclusion, most of the additives selected in this study have positive effects on the positive electrolyte of VRFB in terms of thermal stability and electrochemical performance; the diffusion coefficients of the electrolyte were  $4.34 \times 10^{-7}$  and  $5.43 \times 10^{-7}$ , respectively. The necessity of combined utilization of these additives should be recognized, which may work better and has great potential for future development.

**Author Contributions:** Conceptualization, X.Z. and L.W.; Data curation, X.Z.; Formal analysis, F.M.; Project administration, Z.Z. and D.C.; Resources, L.W.; Writing—original draft, X.Z.; Writing—review and editing, X.Z., F.M., L.S. and Z.Z. All authors have read and agreed to the published version of the manuscript.

**Funding:** National Key R&D Program of China (2018YFC1900500), the National Natural Science Foundation of China (51804289), General project of Beijing Municipal Natural Science Foundation (2202053), Strategic Priority Research Program of the Chinese Academy of Sciences (XDC04010100), Special Project for Transformation of Major Technological Achievements in Hebei Province (19044012Z), and Province Key R&D Program of Hebei (20374105D).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

## References

- 1. Hsieh, C.; Tsai, P.; Hsu, N.; Chen, Y. Effect of compression ratio of graphite felts on the performance of an all-vanadium redox flow battery. *Energies* **2019**, *12*, 313. [CrossRef]
- 2. Chen, L.; Liu, T.; Zhang, Y.; Liu, H.; Ding, M.; Pan, D. Mitigating Capacity Decay by Adding Carbohydrate in the Negative Electrolyte of Vanadium Redox Flow Battery. *Energies* **2022**, *15*, 2454. [CrossRef]
- 3. Aramendia, I.; Fernandez-Gamiz, U.; Martinez-San-Vicente, A.; Zulueta, E.; Lopez-Guede, J.M. Vanadium redox flow batteries: A review oriented to fluid-dynamic optimization. *Energies* 2020, *14*, 176. [CrossRef]
- 4. Leung, P.; Mohamed, M.; Shah, A.; Xu, Q.; Conde-Duran, M. A mixed acid based vanadium–cerium redox flow battery with a zero-gap serpentine architecture. *J. Power Sources* **2015**, 274, 651–658. [CrossRef]
- 5. Behi, B.; Baniasadi, A.; Arefi, A.; Gorjy, A.; Jennings, P.; Pivrikas, A. Cost–benefit analysis of a virtual power plant including solar PV, flow battery, heat pump, and demand management: A western australian case study. *Energies* **2020**, *13*, 2614. [CrossRef]
- 6. Rahman, F.; Skyllas-Kazacos, M. Vanadium redox battery: Positive half-cell electrolyte studies. *J. Power Sources* 2009, 189, 1212–1219. [CrossRef]
- Cao, L.; Skyllas-Kazacos, M.; Menictas, C.; Noack, J. A review of electrolyte additives and impurities in vanadium redox flow batteries. J. Energy Chem. 2018, 27, 1269–1291. [CrossRef]
- Kazacos, M.; Skyllas-Kazacos, M. High Energy Density Vanadium Electrolyte Solutions, Methods of Preparation Thereof and All-Vanadium Redox Cells and Batteries Containing High Energy Vanadium Electrolyte Solutions. W.O. Patent 9,635,239 A1, 7 November 1996.
- Skyllas-Kazacos, M.; Kazacos, M. High Energy Density Vanadium Electrolyte Solutions, Methods of Preparation Thereof and All-Vanadium Redox Cells and Batteries Containing High Energy Vanadium Electrolyte Solutions. U.S. Patent 7,078,123 B2, 18 July 2006. Available online: https://patentimages.storage.googleapis.com/eb/d1/4a/83586dc481f159/US7078123.pdf (accessed on 15 September 2022).
- Roznyatovskaya, N.V.; Roznyatovsky, V.A.; Höhne, C.-C.; Fühl, M.; Gerber, T.; Küttinger, M.; Noack, J.; Fischer, P.; Pinkwart, K.; Tübke, J. The role of phosphate additive in stabilization of sulphuric-acid-based vanadium (V) electrolyte for all-vanadium redox-flow batteries. J. Power Sources 2017, 363, 234–243. [CrossRef]
- 11. Park, S.K.; Shim, J.; Yang, J.H.; Jin, C.S.; Lee, B.S.; Lee, Y.S.; Shin, K.H.; Jeon, J.D. Effect of inorganic additive sodium pyrophosphate tetrabasic on positive electrolytes for a vanadium redox flow battery. *Electrochim. Acta* 2014, 121, 321–327. [CrossRef]
- 12. Zhang, J.; Li, L.; Nie, Z.; Chen, B.; Vijayakumar, M.; Kim, S.; Wang, W.; Schwenzer, B.; Liu, J.; Yang, Z. Effects of additives on the stability of electrolytes for all-vanadium redox flow batteries. *J. Appl. Electrochem.* **2011**, *41*, 1215–1221. [CrossRef]
- Li, S.; Huang, K.; Liu, S.; Fang, D.; Wu, X.; Lu, D.; Wu, T. Effect of organic additives on positive electrolyte for vanadium redox battery. *Electrochim. Acta* 2011, *56*, 5483–5487. [CrossRef]
- 14. Zhang, Y.; Xi, J.; Liu, L.; Wu, Z. Boosting the thermal stability of electrolytes in vanadium redox flow batteries via 1-hydroxyethane-1, 1-diphosphonic acid. *J. Appl. Electrochem.* **2020**, *50*, 255–264. [CrossRef]
- 15. Roe, S.; Menictas, C.; Skyllas-Kazacos, M. A high energy density vanadium redox flow battery with 3 M vanadium electrolyte. *J. Electrochem. Soc.* **2015**, *163*, A5023. [CrossRef]
- 16. Rahman, F.; Skyllas-Kazacos, M. Evaluation of additive formulations to inhibit precipitation of positive electrolyte in vanadium battery. *J. Power Sources* **2017**, *340*, 139–149. [CrossRef]
- 17. Kausar, N.; Mousa, A.; Skyllas-Kazacos, M. The effect of additives on the high-temperature stability of the vanadium redox flow battery positive electrolytes. *ChemElectroChem* **2016**, *3*, 276–282. [CrossRef]
- Xuewen, W.; Suqin, L.; Kelong, H. Characteristics of CTAB as electrolyte additive for vanadium redox flow battery. *J. Inorg. Mater.* 2010, 25, 641–646.
- 19. Wu, X.; Liu, S.; Wang, N.; Peng, S.; He, Z. Influence of organic additives on electrochemical properties of the positive electrolyte for all-vanadium redox flow battery. *Electrochim. Acta* 2012, *78*, 475–482. [CrossRef]
- Yang, Z.; Zhang, J.; Kintner-Meyer, M.C.; Lu, X.; Choi, D.; Lemmon, J.P.; Liu, J. Electrochemical energy storage for green grid. *Chem. Rev.* 2011, 111, 3577–3613. [CrossRef] [PubMed]
- Skyllas-Kazacos, M. Stabilized Vanadium Electrolyte Solutions for All-Vanadium Redox Cells and Batteries. U.S. Patent 6,562,514, 13 May 2003.
- Sun, H.; Yang, B.; Zhu, Z.; Yin, W.; Sheng, Q.; Hou, Y.; Yao, J. New insights into selective-depression mechanism of novel depressant EDTMPS on magnesite and quartz surfaces: Adsorption mechanism, DFT calculations, and adsorption model. *Miner. Eng.* 2021, 160, 106660. [CrossRef]
- 23. Hu, Y.; Xu, Y.; Xie, M.; Huang, M.; Chen, G. Characterization of scalants and strategies for scaling mitigation in membrane distillation of alkaline concentrated circulating cooling water. *Desalination* **2022**, *527*, 115534. [CrossRef]
- 24. Peng, S.; Wang, N.-F.; Wu, X.-J.; Liu, S.-Q.; Fang, D.; Liu, Y.-N.; Huang, K.-L. Vanadium species in CH<sub>3</sub>SO<sub>3</sub>H and H<sub>2</sub>SO<sub>4</sub> mixed acid as the supporting electrolyte for vanadium redox flow battery. *Int. J. Electrochem. Sci.* **2012**, *7*, 643–649.
- 25. Wang, G.; Chen, J.; Xu, Y.; Yan, B.; Wang, X.; Zhu, X.; Zhang, Y.; Liu, X.; Wang, R. Several ionic organic compounds as positive electrolyte additives for a vanadium redox flow battery. *RSC Adv.* **2014**, *4*, 63025. [CrossRef]
- 26. Wu, T.; Huang, K.; Liu, S.; Zhuang, S.; Fang, D.; Li, S.; Lu, D.; Su, A. Hydrothermal ammoniated treatment of PAN-graphite felt for vanadium redox flow battery. *J. Solid State Electrochem.* **2012**, *16*, 579–585. [CrossRef]

- 27. Skyllas-Kazacos, M.; Menictas, C.; Kazacos, M. Thermal stability of concentrated V (V) electrolytes in the vanadium redox cell. *J. Electrochem. Soc.* **1996**, *143*, L86. [CrossRef]
- Huang, F.; Zhao, Q.; Luo, C.; Wang, G.; Yan, K.; Luo, D. Influence of Cr<sup>3+</sup> concentration on the electrochemical behavior of the anolyte for vanadium redox flow batteries. *Chin. Sci. Bull.* 2012, *57*, 4237–4243. [CrossRef]
- 29. Bard, A.J.; Faulkner, L.R.; White, H.S. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, NY, USA, 2022.
- 30. Xue, F.; Wang, Y.; Wang, W.; Wang, X. Investigation on the electrode process of the Mn (II)/Mn (III) couple in redox flow battery. *Electrochim. Acta* 2008, *53*, 6636–6642. [CrossRef]
- 31. Gao, C.; Wang, N.; Peng, S.; Liu, S.; Lei, Y.; Liang, X.; Zeng, S.; Zi, H. Influence of Fenton's reagent treatment on electrochemical properties of graphite felt for all vanadium redox flow battery. *Electrochim. Acta* **2013**, *88*, 193–202. [CrossRef]