



## Review

## Research progress in preparation of electrolyte for all-vanadium redox flow battery

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## ABSTRACT

All-vanadium redox flow battery (VRFB), as a large energy storage battery, has aroused great concern of scholars at home and abroad. The electrolyte, as the active material of VRFB, has been the research focus. The preparation technology of electrolyte is an extremely important part of VRFB, and it is the key to commercial application of VRFB. In this work, the preparation methods of VRFB electrolyte are reviewed, with emphasis on chemical reduction, electrolysis, solvent extraction and ion exchange resin. The principles, technological processes, advantages and disadvantages of each method are briefly described. The effects of different additives on high concentration electrolyte are also introduced. Finally, the development of vanadium electrolyte preparation technology is prospected.

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## Introduction

With the decrease of fossil energy and strict requirements for environmental protection, renewable energy such as solar energy and wind energy has attracted great attention [1–3]. However, renewable energy is inherently unstable and intermittent because of its climate change. Therefore, a stable energy storage system is

urgently needed to smooth the fluctuation of renewable energy [4–6]. Among all the energy storage technologies, redox flow battery is regarded as the most promising one with large capacity, flexibility and safety in design. While all-vanadium flow battery (VRFB) is regarded as a large-scale energy storage technology with great application potential because of its advantages of long life, high reliability, fast response speed, large capacity, and high efficiency [7,8].

VRFB is a kind of energy storage battery with different valence vanadium ions as positive and negative electrode active materials

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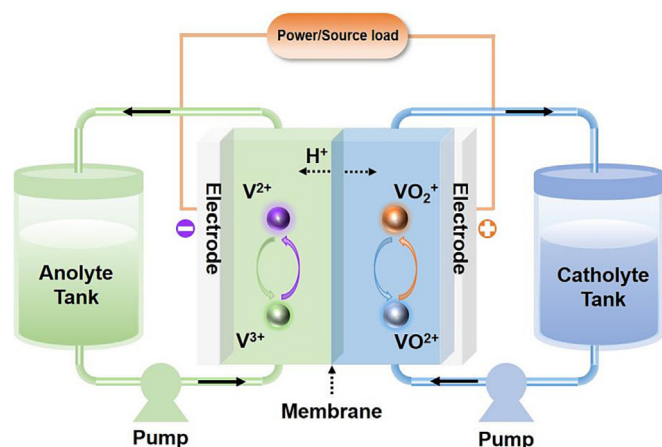


Fig. 1. Schematic of an all-vanadium redox flow battery on charge–discharge reaction.

and liquid active materials circulating through pump. The outermost electronic structure of the vanadium element is  $3d^34s^2$ , and its five electrons could participate in bonding to form four valence vanadium ions [9]. According to the potential of the four valence states of vanadium ions in the acidic solution environment, vanadium ions can form three pairs. The potential difference between  $V(II)/V(III)$  and  $V(IV)/V(V)$  is about 1.25 V, which can be used as the positive and negative electrodes of VRFB [10]. The VRFB is charged and discharged by the conversion of the valence state of the positive and negative vanadium ions. During the charging process, the positive vanadium ions are converted from  $V(IV)$  to  $V(V)$ , and the negative vanadium ions are changed from  $V(III)$  to  $V(II)$  [11]. When discharged, it is the opposite of charging process. The charging and discharging principle of VRFB is shown in Fig. 1 [12].

The VRFB system is mainly composed of stack, electrolyte, battery management system (BMS), conveying system (pump, pipeline) and energy storage converter (PCS). The stack determines the power of the VRFB, and the electrolyte determines the energy storage capacity of the VRFB. When the VRFB is working (Fig. 1), the electrolyte is pumped into the stack from the liquid storage tank. After the electrochemical reaction through the electrode, the electrolyte returns to the liquid storage tank and circulates in turn to realize the charge and discharge of the battery [13]. The stack of VRFB according to the power design by several single cells in series, and each single cell is composed of end plate, current collector, bipolar plate, flow frame, electrode and proton exchange membrane, positive and negative half battery separated by proton exchange membrane. Among them, the flow frame is designed through a special flow field to ensure that the electrolyte is uniformly electrochemically reacted through the electrode surface, and the current is imported or exported through the bipolar plate and the current collector [14]. Proton exchange membrane separates positive and negative electrolyte vanadium ions, while hydrogen ions through to ensure that the battery positive and negative charge balance [15].

The VRFB as an excellent green large-scale energy storage technology, in the wind and solar energy storage grid, power grid peaking, military storage, transportation, municipal, communications

base stations, UPS power supply and other fields have good application prospects [8,16–19]. The VRFB was originally proposed by Skyllas-Kazacos et al. from the University of New South Wales (UNSW), and the assembly of a 1 kW stack was completed in 1991 [20]. Subsequently, many research institutions began to develop VRFB systems and complete the assembly of VRFB of different sizes. At present, the functional and technical application of VRFB energy storage technology in large-scale power field has been verified in worldwide. Low cost, high efficiency and long life are the future development trend of VRFB technology.

The system cost determines the development prospect and technology development direction of VRFB. At present, there is less cost analysis for commercial VRFB. The vanadium electrolyte produced by Dalian Borong New Materials Co., Ltd. occupies more than 80 % of the global market share [21–25]. Due to technological advances, the cost of VRFB energy storage system has also dropped significantly. Due to technological advances, the cost of VRFB energy storage system has also dropped significantly. The actual prices of VRFB energy storage systems with different energy storage durations according to the price of the megawatt–level VRFB energy storage system of Rongke Energy Storage in the third quarter of 2021 and when the price of the electrolyte raw material vanadium pentoxide ( $V_2O_5$ ) at 100,000 yuan·t<sup>−1</sup> is shown in Table 1. When the price of  $V_2O_5$  is 100,000 yuan·t<sup>−1</sup>, the price of vanadium electrolyte is about 1500 yuan·kWh<sup>−1</sup>. When the energy storage time is 1 h, excluding the electrolyte energy storage system price of 6000 yuan·kW<sup>−1</sup>, plus the electrolyte price of 1500 yuan·kW<sup>−1</sup>, the total price of energy storage system is 7500 yuan·kWh<sup>−1</sup>. When the energy storage time is 4 h, the price of the energy storage system excluding the electrolyte is 6000 yuan·kW<sup>−1</sup>, which is apportioned by 4 h, 1500 yuan per hour, and the electrolyte is 1500 yuan·kWh<sup>−1</sup>, the total price of the energy storage system is 3000 yuan·kWh<sup>−1</sup>. Similarly, for a system with an energy storage time of 10 h, the total price of the energy storage system is 2100 yuan·kWh<sup>−1</sup>. It can be clearly seen that since the output power and energy storage capacity of the vanadium flow battery can be independent of each other, the longer the energy storage time, the cheaper the price. The longer the storage time, the higher the total cost of electrolyte accounted for VRFB. For the system with energy storage time of 10 h, the cost of electrolyte vehicle accounts for more than 71% of the total cost. Therefore, reducing the cost of electrolyte is an urgent problem to be solved in the promotion and application of VRFB.

Before introducing the vanadium electrolyte preparation method, it is necessary to clarify the requirements of commercial vanadium electrolyte. Table 2 and Table 3 show the national standard GB/T 37204-2018 standard for the concentration of vanadium,  $SO_4^{2-}$  and impurities in vanadium electrolyte [26]. The total vanadium concentration of these three electrolytes is  $\geq 1.50$  M. The stability of different valence vanadium ions limits the operating temperature range of the electrolyte to 10–40 °C. To ensure the stable operation of VRFB, the vanadium concentration of electrolyte is generally lower than 1.6 M in practical application [27]. Xiao et al. found that  $V(II)$ ,  $V(III)$ ,  $V(IV)$  and  $V(V)$  electrolytes could be stable in the temperature range of −25 °C to 30 °C when the vanadium concentration was 1.50 M and the sulfate concentration was 3.875 M [28]. In conclusion, the concentration of vanadium, sulfuric acid and impurities in the vanadium electrolyte are very

Table 1  
Price of VRFB energy storage system with different storage duration.

Storage duration (h)	1	2	4	6	8	10
Price (yuan·kW <sup>−1</sup> )	7500	4500	3000	2500	2250	2100

**Table 2**The concentration of vanadium and  $\text{SO}_4^{2-}$  in vanadium electrolyte.

Product type	Component		Allowable deviation
$\text{V}^{3+}$ electrolyte	V	$\geq 1.50 \text{ M}$	$\pm 0.05 \text{ M}$
	$\text{SO}_4^{2-}$	$\geq 2.30 \text{ M}$	$\pm 0.10 \text{ M}$
	$\text{V}^{3+} : \text{V}$	$\geq 0.95$	—
$\text{V}^{3.5+}$ electrolyte	V	$\geq 1.50 \text{ M}$	$\pm 0.05 \text{ M}$
	$\text{SO}_4^{2-}$	$\geq 2.30 \text{ M}$	$\pm 0.10 \text{ M}$
	$\text{V}^{3+} : \text{VO}^{2+}$	$\geq 1.0$	$\pm 0.10$
$\text{V}^{4+}$ electrolyte	V	$\geq 1.50 \text{ M}$	$\pm 0.05 \text{ M}$
	$\text{SO}_4^{2-}$	$\geq 2.30 \text{ M}$	$\pm 0.10 \text{ M}$
	$\text{VO}^{2+} : \text{V}$	$\geq 0.95$	—

**Table 3**

The concentration of impurity elements in vanadium electrolyte.

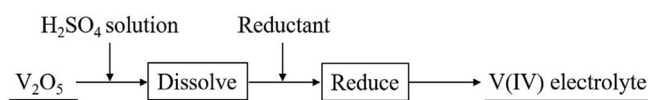
Impurity elements	The first grade ( $\text{mg}\cdot\text{L}^{-1}$ )	The second grade ( $\text{mg}\cdot\text{L}^{-1}$ )
Al	$\leq 50$	$\leq 80$
As	$\leq 1$	$\leq 1$
Au	$\leq 1$	$\leq 1$
Ca	$\leq 30$	$\leq 70$
Cl	$\leq 100$	—
Cr	$\leq 15$	$\leq 30$
Cu	$\leq 1$	$\leq 5$
Fe	$\leq 50$	$\leq 200$
K	$\leq 100$	$\leq 200$
Mg	$\leq 30$	$\leq 50$
Mn	$\leq 5$	$\leq 30$
Mo	$\leq 20$	$\leq 30$
$\text{NH}_4^+$	$\leq 20$	$\leq 50$
Na	$\leq 80$	$\leq 200$
Ni	$\leq 20$	$\leq 60$
Pd	$\leq 1$	$\leq 1$
Pt	$\leq 1$	$\leq 1$
Si	$\leq 10$	—

important for the operation of the VRFB. Therefore, the vanadium electrolyte preparation process needs to be continuously optimized to meet the requirements of the VRFB.

In the initial development of VRFB at the UNSW, the electrolyte was made by dissolving vanadyl sulfate ( $\text{VOSO}_4$ ) in sulfuric acid. The high cost of  $\text{VOSO}_4$  has led to efforts to replace it with cheaper  $\text{V}_2\text{O}_5$ . Therefore, two methods for producing VRFB electrolyte from  $\text{V}_2\text{O}_5$  powder were developed for the first time in the UNSW. The first method is to chemically dissolve the  $\text{V}_2\text{O}_5$  powder by reacting with sulfur dioxide to form a V(IV) sulfuric acid solution. The second process involves the suspended powder electrolysis of  $\text{V}_2\text{O}_5$  powder to produce a V(III)/V(VI) mixture. They also studied the chemical reduction method by adding reducing agents (Organic compounds,  $\text{H}_2$ ,  $\text{SO}_2$ , and ammonium compounds) to reduce  $\text{V}_2\text{O}_5$  in the solution to prepare a V(IV) electrolyte. In summary, the preparation of the electrolyte is mainly based on commercial vanadium oxide, which makes the cost of the electrolyte too high and limits the development of VRFB, so it is necessary to find a new method of preparing electrolyte with lower cost. In this work, the preparation methods of VRFB electrolyte are summarized, and the future development direction is prospected in combination with the problems existing in the preparation methods of vanadium electrolyte.

## Electrolyte preparation

As mentioned previously, one of the major challenges for VRFB development and commercialization is the relatively high cost of the vanadium electrolyte. The electrolyte initially used in VRFB is produced by dissolving vanadyl sulfate,  $\text{VOSO}_4$ , in sulfuric acid solution [29]. Because of the high price of  $\text{VOSO}_4$  crystal, the cost

**Fig. 2.** Technological process of preparing V(IV) electrolyte from  $\text{V}_2\text{O}_5$ .

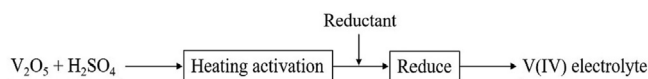
of preparing electrolyte is too high, so scholars began to look for a cheaper method to prepare electrolyte.  $\text{V}_2\text{O}_5$  is used as a substitute for  $\text{VOSO}_4$  in the process of vanadium electrolyte preparation [30,31]. It is common practice among VRFB developers to utilize vanadium electrolyte of high purity to eliminate any potential detrimental effects of impurities on VRFB performance [32–34]. However, high-purity  $\text{V}_2\text{O}_5$  (the purity of  $\text{V}_2\text{O}_5 \geq 99.5\%$ , the mass fractions of impurity elements chromium and iron below 0.1% and 0.07%) is associated with higher cost; therefore, to make the VRFB more price-competitive, producers are currently considering the use of low-grade vanadium from recycled products. To date, researchers have developed various methods to reduce the cost of vanadium electrolyte. The preparation methods of vanadium electrolyte including chemical reduction, electrolysis, solvent extraction, and ion exchange are summarized below.

## Chemical reduction

Chemical reduction method is the most mature method and the most frequently used method for preparing vanadium electrolyte [30,35]. Different raw materials are used to prepare electrolyte by chemical reduction method, and their preparation processes are also different [36–39]. There are many raw materials that can be used to prepare electrolyte, such as vanadium oxide, vanadate, vanadium extraction leaching solution, vanadium-containing waste residue, waste catalyst and so on [32,40]. The preparation process of electrolyte is explained from the perspective of different raw materials.

The preparation of vanadium electrolyte from  $\text{V}_2\text{O}_5$  by chemical reduction is the most widely used method [41,42]. The purity of  $\text{V}_2\text{O}_5$  used as raw material is more than 99.5%, and the mass fractions of impurity elements chromium and iron are below 0.1% and 0.07%, respectively. The general implementation method is to dissolve  $\text{V}_2\text{O}_5$  into sulfuric acid solution first, and then add a reducing agent to reduce V(V) to V(IV) or V(III), the process flow is shown in Fig. 2. The other way is to mix  $\text{V}_2\text{O}_5$ , reducing agent and  $\text{H}_2\text{SO}_4$  solution, and reduce them while dissolving, to prepare different kinds of electrolytes [30,31,39,43–58]. Due to 3 M  $\text{H}_2\text{SO}_4$  used to dissolve  $\text{V}_2\text{O}_5$ , the equilibrium concentration of V(V) at 30 °C is only 0.6 M, which is not meet the vanadium concentration of electrolyte requirements [59]. Scholars explore the preparation methods of high concentration electrolyte. Maria Skyllas-Kazacos group mixed sulfuric acid with  $\text{V}_2\text{O}_5$  powder, introduced  $\text{SO}_2$  gas for reduction, and  $\text{V}_2\text{O}_5$  powder accelerated to dissolve in the reducing atmosphere, which increased the concentration of vanadium in the electrolyte, thus obtaining the electrolyte meeting the requirements of the battery [60].

Another method to increase the concentration of  $\text{V}_2\text{O}_5$  in sulfuric acid is heating and activation. According to the research on the dissolution of  $\text{V}_2\text{O}_5$  in  $\text{H}_2\text{SO}_4$  solution at different temperatures (0–40 °C) by El Hage et al., when the dissolving temperature

**Fig. 3.** Technological process of preparing V(IV) electrolyte by heating and dissolving  $\text{V}_2\text{O}_5$ .

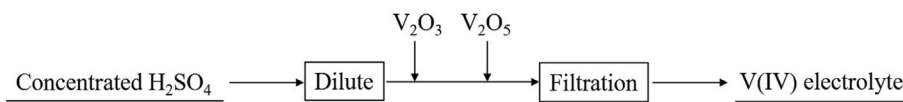


Fig. 4. Technological process of preparing electrolyte from  $V_2O_5$  and  $V_2O_3$ .

increases from 0 °C to 40 °C, the kinetic constant ( $k$ ) rapidly increases from  $0.9 \times 10^{-4}$  to  $7 \times 10^{-4} \text{ mol}^{-2} \cdot \text{s}^{-1} \cdot \text{L} \cdot \text{g}$ , which is fully explained that the increase of temperature is helpful to the dissolution of  $V_2O_5$  [59]. Therefore, in the process of dissolving  $V_2O_5$ , it is necessary to increase the temperature to increase the dissolution rate and vanadium concentration. Then, a reducing agent is added to the solution of  $V_2O_5$  powder to reduce V(V) to V(IV). After filtration, dehydration and drying, the product  $VOSO_4$  crystal is obtained, and then dissolved in sulfuric acid solution to obtain V(IV) electrolyte meeting the needs of batteries. The process flow is shown in Fig. 3 [61]. Because of its simple principle and operation, this process is the most used process for preparing electrolyte. When  $V_2O_5$  is used as raw material to prepare electrolyte, it is usually dissolved first and then reduced, or dissolved and reduced simultaneously. The difference lies in the different kinds of reducing agents [62]. At present, there are many kinds of reducing agents used, such as oxalic acid, sodium oxalate, potassium oxalate,  $SO_2$ ,  $H_2SO_4$ ,  $NH_4HSO_3$ ,  $(NH_4)_2SO_3$ ,  $N_2H_4$ ,  $MgH_2$ , primary and secondary tertiary alkyl alcohol, carboxylic acid, amine and so on. Organic compounds,  $H_2$ ,  $SO_2$  and amine compounds are particularly advantageous, because their reaction products are either sulfuric acid or gaseous compounds, which will not introduce impurities into the electrolyte [63].

There is a special reductant ( $V_2O_3$ ) among the reductants used to prepare electrolyte from  $V_2O_5$ . Actually, V(IV) electrolyte is prepared by reducing V(III) with low valence of  $V_2O_3$  to V(V) with oxidation–reduction reaction (Eq. (1)). The process flow is shown in Fig. 4.  $V_2O_3$  used in this method is not only a reducing agent but also a raw material, which will not introduce impurity elements into the electrolyte [37,64–67]. In addition to changing the valence state of vanadium in aqueous solution,  $V_2O_5$  and  $V_2O_3$  can be directly mixed and roasted to obtain multivalent vanadium compounds, which can be dissolved in sulfuric acid solution to obtain vanadium electrolyte. This method firstly directly obtains tetravalent vanadium through solid–phase reaction, and then dissolves to obtain electrolyte, without adding any additional reducing agent, but the mixed roasting conditions need to be strictly controlled [68].



The above process is aimed at preparing vanadium electrolyte with vanadium oxide as raw material. For the crude vanadium compound used in the preparation of electrolyte, it is necessary to remove impurities, purify and dissolve it to obtain the electrolyte meeting the requirements. The process flow is shown in Fig. 5 [69]. Compared with using industrial vanadium compounds as raw materials to prepare electrolyte, the process of impurity removal and purification is increased. From the cost point of view, it is almost the same as directly using vanadium compounds,

because purification links are added [70]. Similarly, vanadium titanomagnetite is used as raw material with oxidizing roasting additive (sodium sulfate or sodium carbonate) to get roasting clincker, which is leached by water to obtain leaching solution. The ammonium polyvanadate (APV) is obtained by acid ammonium salt precipitation, and it is dissolved in deionized water under the condition of introducing ammonia gas, and ammonium metavanadate (AMV) is obtained after reaction for a certain time.  $V_2O_5$  with purity above 99.55% can be obtained after calcination, and the electrolyte meeting the concentration requirement can be prepared by using oxalic acid as reducing agent. The process is shown in Fig. 6 [71]. The starting material of this method is vanadium titanomagnetite. Actually, the  $V_2O_5$  product is prepared first, and then the electrolyte is prepared by chemical reduction method. It has also gone through the process of preparing high–purity  $V_2O_5$ , and there is no obvious difference from the above–mentioned direct preparation of electrolyte with high–purity  $V_2O_5$  as raw material.

The cost of preparing electrolyte from high–purity vanadium compounds is still high because these vanadium compounds themselves have gone through the purification process, which makes the preparation cost too high [72–74]. In order to reduce the preparation cost, vanadium extraction leaching solution is selected as raw material to prepare electrolyte, and its preparation method is not unique [75–77]. Liang Chen et al. solidified the vanadium in the leaching solution into calcium vanadate with water–soluble calcium salt as precipitant, then introduced sulfur dioxide for reduction through pulping, and obtained V(IV) electrolyte through solid–liquid separation (Eq. (2)~Eq. (5)). The process flow is shown in Fig. 7 [78]. The method takes the low–priced vanadium extraction leaching solution as raw material, which can reduce the production cost and has the potential of expanding production. However, the calcium content in the finally obtained V(IV) electrolyte is high because of the large solubility product constant of calcium sulfate, which requires ball milling in the calcification precipitation process. Bo Liu et al. adjusted the pH of vanadium extraction leaching solution to below 1 with sulfuric acid, added reducing agent to reduce V(V) to V(IV), and then adjusted its pH to 7~9 with alkaline solution. At this time, all vanadium in the solution was precipitated, filtered and dried, and then dissolved in sulfuric acid solution to obtain V(IV) electrolyte. Its preparation process is shown in Fig. 8 [79]. This process also uses vanadium extraction leachate as raw material to obtain V(IV) electrolyte through chemical precipitation purification and reduction process. Its principle and operation are simple, and it is also suitable for large–scale production and the current production line. However, the impurity content of the electrolyte obtained by this process is high and fluctuates with the change of the impurity content of raw materials, so the stability of the final product electrolyte needs to be improved.

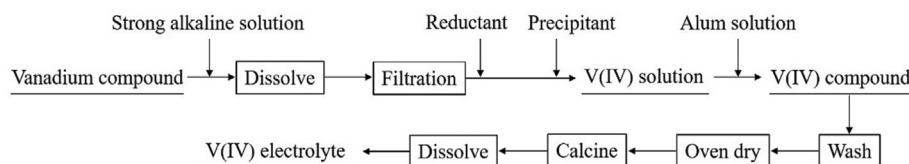


Fig. 5. Technological process of preparing electrolyte from vanadium compound.



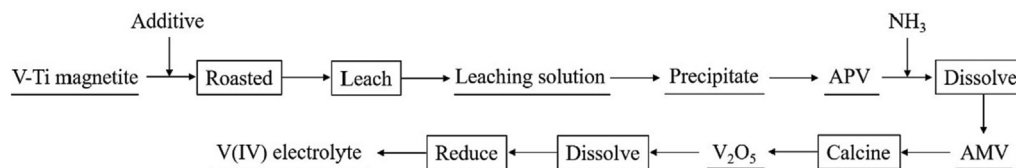


Fig. 6. Technological process of preparing electrolyte from V-Ti magnetite.

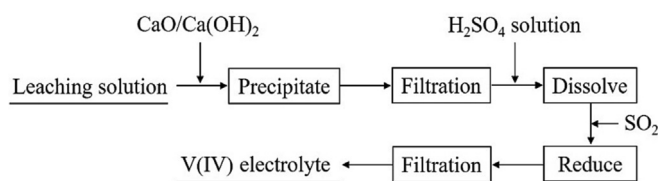


Fig. 7. Technological process of preparing electrolyte by calcified precipitation method.

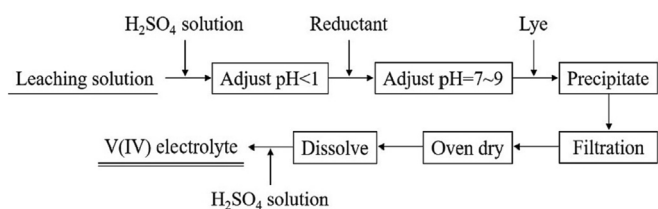
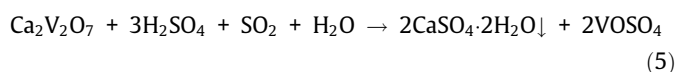
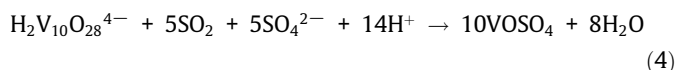
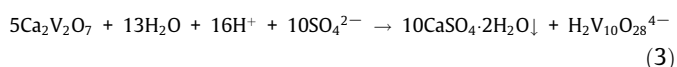
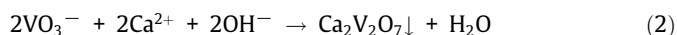


Fig. 8. Technological process of preparing electrolyte by alkaline precipitation method.

Chemical precipitation is also used to prepare V(IV) electrolyte from crude  $\text{VOSO}_4$  solution, which provided that the impurity content of crude  $\text{VOSO}_4$  solution itself is relatively low, and the preparation of V(IV) electrolyte can be realized by this method [80–82].



In addition to the traditional vanadium raw materials, there are some deactivated vanadium-containing catalysts, so vanadium, a valuable element, should be extracted from the perspective of comprehensive utilization of resources [83]. After the vanadium catalyst used in sulfuric acid industry is deactivated, vanadium is transferred to the solution in the form of vanadyl oxalate by soak-

ing in oxalic acid solution. After adding polyacid for full reaction, impurities removed and filtered, and the mother solution of vanadyl oxalate is obtained by concentration. V(IV) electrolyte is obtained by adding sulfuric acid. The process flow is shown in Fig. 9 [84]. This method realizes the recovery of vanadium from waste vanadium catalyst, and obtains the electrolyte required by battery level. However, the whole process takes too long and the production cost is high, so it needs further optimization.

There are many ways to prepare vanadium electrolyte by chemical reduction, and there are different preparation processes for different raw materials, even for the same raw material. The principle and operation of chemical reduction method are simple, which is very friendly to industrial production and highly matched with the existing production line equipment. However, there are still some problems in these methods, which have not been applied on a large scale. Only by continuous exploration can we seek a process with simple operation and lower cost.

### Electrolysis

The electrolysis raw materials are mainly  $\text{V}_2\text{O}_5$  and vanadate, which are added to the negative electrode of the electrolytic cell with diaphragm, and the sulfuric acid solution is added to the positive electrode. In the process of electrolysis, V(V) is reduced to V(III) and V(II), which can promote the dissolution of  $\text{V}_2\text{O}_5$  and vanadate and accelerate the preparation of electrolyte [42]. Skyllas-Kazacos group dissolved  $\text{V}_2\text{O}_5$  in sulfuric acid solution, and then assembled it with the stack to form VRFB, which was charged at a constant current until bright yellow V(V) solution and bright purple V(II) solution were produced in the positive and negative half cells, respectively [15]. According to the requirements, part of the electrolyte was taken out of the battery, and the remaining electrolyte was discharged in the battery, producing V(IV) blue solution and V(III) green solution in the positive half battery and the negative half battery respectively, thus completing a complete charging and discharging process. The process flow is shown in Fig. 10 [85,86]. In order to reduce the production cost of electrolyte,  $\text{NH}_4\text{VO}_3$  is selected as the raw material, and the preparation process of electrolyte is similar to  $\text{V}_2\text{O}_5$ . Xiuli Feng used  $\text{VOSO}_4$  solution as the initial electrolyte, which was placed at the two poles of the battery to charge. The positive pole generated V(V) electrolyte and the negative pole generated V(II) electrolyte. Then the battery discharges, and the vanadium in the positive and negative electrodes becomes V(IV) and V(III) respectively.

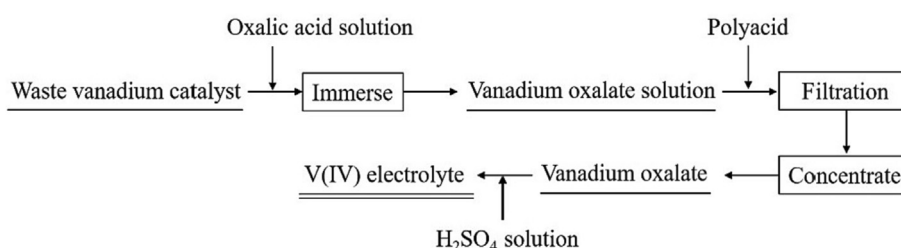


Fig. 9. Technological process of preparing electrolyte from waste vanadium catalyst.

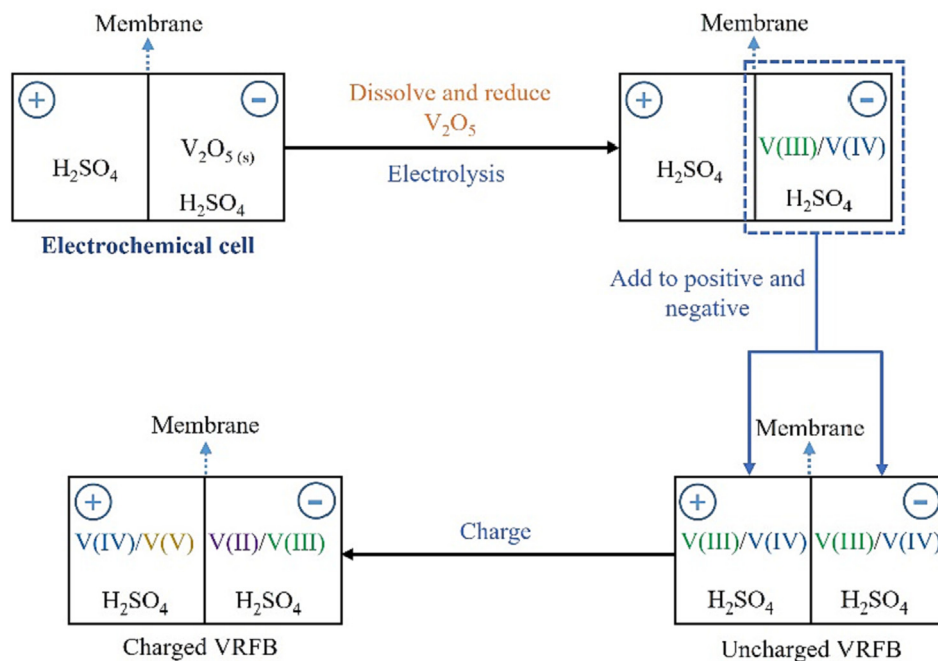


Fig. 10. Process flow of electrolytic preparation of vanadium electrolyte.

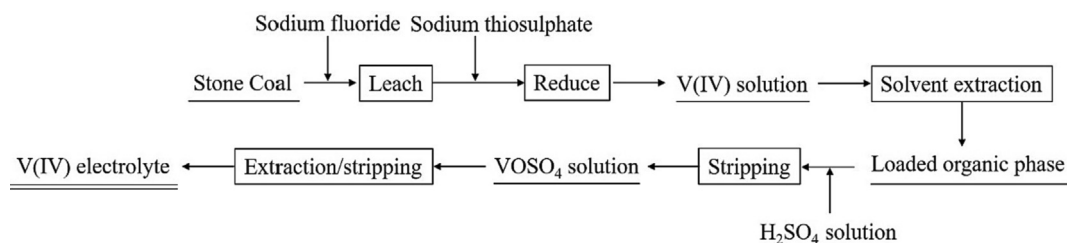


Fig. 11. Technological process of preparing electrolyte from stone coal.

Repeat the above process to realize charge and discharge cycle [87]. Compared with the chemical reduction method, electrolysis method has the biggest advantage that it can prepare a large amount of electrolyte on a large scale, its principle and operation are simple, and it is easy to realize industrial production. However, this method has high requirements for equipment, low production efficiency and high energy consumption, which leads to high final production cost.

#### Solvent extraction

Because the prices of vanadium oxide and vanadate as raw materials for electrolyte preparation are high, scholars began to explore the preparation of  $\text{VOSO}_4$  solution by solvent extraction with vanadium leaching solution as raw material substitute. Gang

Fan et al. used stone coal as raw material,  $\text{H}_2\text{SO}_4$  as leaching solution and sodium fluoride as additive, and obtained  $\text{V(IV)}$ -containing leaching solution by solid–liquid separation. Adding sodium thiosulphate into the leaching solution, reducing  $\text{Fe(III)}$  into  $\text{Fe(II)}$ , the pH of the leaching solution after treatment was adjusted to 2.2 with ammonia water. The mixture of bis(2-ethylhexyl) phosphoric acid and sulfonated kerosene used as the extraction system, and the mixture was extracted with water phase. After the separation of the two phases, the loaded organic phase is stripped with  $\text{H}_2\text{SO}_4$  solution, and the pH of the  $\text{VOSO}_4$  solution obtained by stripping extraction is adjusted to 2.2 with sodium hydroxide, and the second repeated extraction is carried out with di-isooctyl phosphate and sulfonated kerosene system, and the loaded phase is stripped with sulfuric acid to obtain high-purity  $\text{VOSO}_4$  solution. The main technical route is shown in Fig. 11 [88]. The  $\text{V(IV)}$  elec-

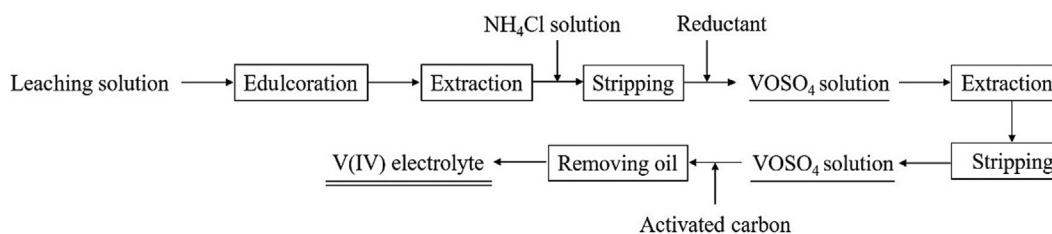


Fig. 12. Technological process of preparing electrolyte from vanadium leaching solution.

trolite can be obtained by two stages of extraction and stripping extraction, and stone coal is used as raw material. Compared with the above methods, the preparation and dissolution of  $V_2O_5$  are omitted, and the  $VOSO_4$  solution can be directly extracted from the leaching solution. However, this method has gone through two extraction and stripping processes, in which the consumption of acid, alkali and water is large. If the waste can be recycled internally, it is a good method to prepare  $VOSO_4$  solution.

Yan Xu et al. put forward a two-stage extraction method for preparing V(IV) electrolyte, the main process of which is shown in Fig. 12 [89]. The pentavalent qualified vanadium liquid produced by the vanadium factory, which is purified by adding impurity remover. Then pentavalent vanadium is extracted by amine extractant (quaternary ammonium salt), ammonium chloride is used as stripping solvent  $\rightarrow$  reducing agent (hydroxylamine hydrazine or oxalic acid) is added to reduce to tetravalent vanadium  $\rightarrow$  acid extractant (di-isooctyl phosphate and tributyl phosphate) extracts tetravalent vanadium, sulfuric acid stripping  $\rightarrow$  activated carbon adsorption degreasing. It is directly prepared from pentavalent sodium vanadate solution without precipitation process. In this method, qualified pentavalent vanadium solution used as raw material, and all commonly consumed reagents in the preparation process, so the price is low. The extractant used in the preparation process also can be reused. There are some advantages including simple preparation steps, mild reaction condition, no need of high temperature and high purity of the obtained vanadium electrolyte product. However, the preliminary impurity removal process is tedious and difficult to filter, and the extraction of vanadium ions with different valence states by two systems will inevitably pollute each other, which is not conducive to the recycling of extractant. Moreover, the process flow is lengthy, so it places hope that industrial application will have a long way to go.

Qiusong Guo et al. used vanadium-containing solution obtained by leaching stone coal with sulfuric acid as raw material, D2EHPA–TBP– sulfonated kerosene as synergistic extraction system, and adopted three-stage countercurrent extraction and two-stage countercurrent stripping extraction to remove iron, manganese and chromium impurities to prepare  $VOSO_4$  solution ( $21.8 \text{ g}\cdot\text{L}^{-1}$  V(IV) with impurities of  $0.43 \text{ mg}\cdot\text{L}^{-1}$  Fe and  $0.2 \text{ mg}\cdot\text{L}^{-1}$  Cr), the main process of which is shown in Fig. 13 [90]. After countercurrent extraction and stripping, the removal efficiency of iron, manganese and chromium impurities was 99.1%, and the direct recovery rate of vanadium was 41.3%. When two-stage combined synergistic extraction was used for deep impurity removal, the total impurity removal rate of iron, manganese and chromium was 99.87%, and the direct vanadium yield in the whole extraction process was 24.7%. The method verified the feasibility of preparing  $VOSO_4$  solution by directly removing impurities from vanadium-containing solution. However, the process of this method is too long, and the two-stage combined extraction deep impurity removal process has a high impurity removal efficiency and a low vanadium recovery efficiency, which is extremely unfavorable to industrial production.

Li et al. used EHEHPA as extractant and TBP as phase modifier to extract vanadium sulfate solution containing iron and aluminum impurities to prepare  $VOSO_4$  solution, the technological process is shown in Fig. 14 [91]. In the process of extraction, under the

optimum conditions, the extraction efficiencies of vanadium and iron are 68% and 53% respectively, while the extraction efficiency of aluminum is only 2%, which indicates that the separation effect of vanadium and aluminum is efficient. When  $3.8 \text{ mol}\cdot\text{L}^{-1}$  sulfuric acid is used for the stripping of the loaded organic phase, phase ratio A/O at 3:1 or 4:1, the stripping efficiencies of vanadium, aluminum and iron are 100%, 95% and 10% respectively. After five stages of extraction and stripping,  $VOSO_4$  solution was obtained, with V(IV) concentration of  $76.5 \text{ g}\cdot\text{L}^{-1}$ , Fe concentration of  $12 \text{ mg}\cdot\text{L}^{-1}$  and Al concentration of  $10 \text{ mg}\cdot\text{L}^{-1}$ , which met the requirements of vanadium electrolyte. After stripping, oxalic acid can be used to remove the existing iron in the organic phase, so as to achieve the purpose of recycling the organic phase. This method could prepare vanadium electrolyte meeting the requirements, but the process is lengthy, five-stage extraction and stripping–extraction, which requires a lot of water and reduces the production efficiency, and the extraction efficiency is not high enough, so the actual utilization rate of vanadium is too low.

Jian Zhang et al. prepared vanadium electrolyte by one-step purification of the leaching solution containing vanadium after sodium roasting of vanadium slag, the technological process is shown in Fig. 15 [92,93]. Firstly, the leaching solution containing vanadium is acidified to pH 0.5 by sulfuric acid, then reducing V (V) to V(IV) by adding reducing agent, adjusting the final pH of the solution to 1.0, and adding extractant for extraction, in which the concentration of extractant P507 is 30%. During the extraction process, the separation effect of vanadium from aluminum and silicon is good, and the extraction efficiency of vanadium can reach 98% after two-stage extraction. Through two-stage stripping,  $5 \text{ mol}\cdot\text{L}^{-1}$  sulfuric acid used as stripping agent, the ratio of O/A at 5: 1, the stripping efficiency can reach over 99.5%. Compared with the general extraction method for preparing  $VOSO_4$  solution, this method has a lower extraction order, which is of positive significance for large-scale production.

Ying Zhang et al. used V(IV)–containing converter vanadium slag as raw material, and obtained V(IV)–containing solution by direct acid leaching, the technological process is shown in Fig. 16 [94]. V(IV) in the leaching solution was extracted by extractant D2EHPA, and the extraction system had high selectivity to both Fe(III) and V(IV). After stripping extraction by  $H_2SO_4$  solution, the iron content in the stripping extraction solution was higher between  $0.2$  and  $0.7 \text{ g}\cdot\text{L}^{-1}$ . In order to improve the purity and remove Fe(III), EDTA was used to complex Fe(III), and the complex Fe(III)–EDTA was precipitated. After filtration,  $VOSO_4$  solution was obtained. In this work, the complexing effects of different complexing agents EDTA, 5-sulfosalicylic acid and citric acid on iron are also studied, and the number of ligands in each complex is calculated. The molar ratio of EDTA to Fe(III) is 1.5, and the complexation efficiency with Fe(III) is over 98%. At last, the impurity contents of Fe, Cr and Al in  $VOSO_4$  are all lower than 2 ppm. The method can successfully prepare  $VOSO_4$  solution, and directly take converter vanadium slag as raw material, thus skipping the preparation of  $V_2O_5$ , and providing an experimental basis for industrial application. The disadvantage is that the process is too long, which may lead to high cost.

The preparation of vanadium electrolyte by solvent extraction is shown in Table 4. V(IV) electrolyte is prepared by extraction, and

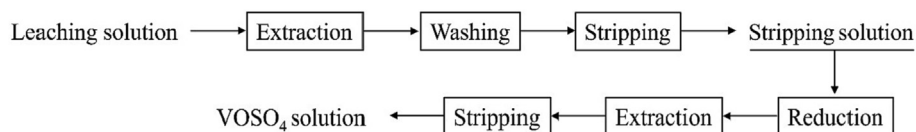


Fig. 13. Technological process of preparing  $VOSO_4$  solution by D2EHPA/TBP.

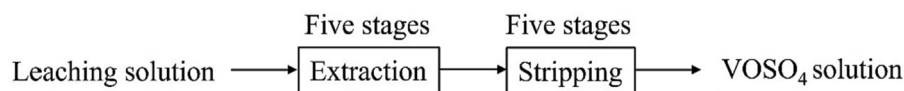
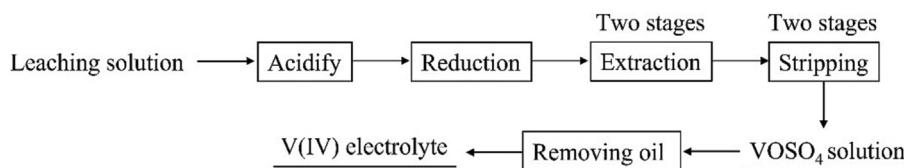
Fig. 14. Technological process of preparing  $\text{VOSO}_4$  solution by EHEHPA/TBP.

Fig. 15. Technological process of preparing V(IV) electrolyte by P507.

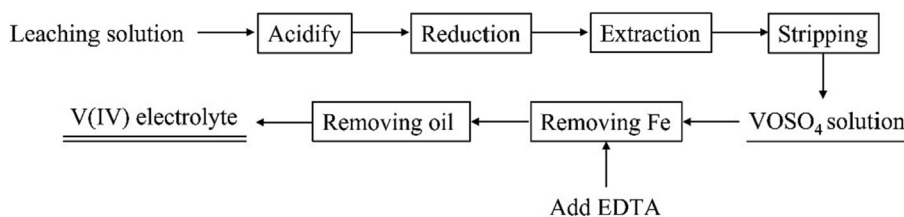


Fig. 16. Technological process of preparing V(IV) electrolyte by D2EHPA.

Table 4

Preparation of vanadium electrolyte by solvent extraction.

Serial number	Raw materials	Extractant	Extraction stages	Stripping stages	References
1	Stone coal	D2EHPA	2	2	[88]
2	V(V) leaching solution	Aliquat 336/ D2EHPA	2	1	[89]
3	Stone coal	D2EHPA	3	2	[90]
4	Vanadium-bearing titanomagnetite	EHEHPA	5	5	[91]
5	Vanadium slag	P507	2	2	[92,93]
6	Vanadium slag	D2EHPA	3	3	[94]

$\text{VOSO}_4$  solution is prepared by reduction–extraction–stripping or extraction–reduction–stripping with vanadium leaching solution as raw material. If the vanadium concentration is not up to standard, high concentration V(IV) electrolyte can be obtained by concentration [75–77,95–101]. Compared with vanadium oxide and vanadate, this method reduces the production cost, and has good selectivity, which could prepare vanadium electrolyte suitable for VRFB. However, the solvent extraction method has a long production process, and the multi-stage extraction, stripping extraction and washing process increase the operation cost. The extraction process is easy to produce emulsifying phenomenon or the third phase, which is not conducive to the separation of organic phase and water phase, resulting in serious loss of extractant and threatening the realization of closed cycle of the process.

#### Ion exchange

Longyun Bai et al. used vanadium-containing leaching solution to prepare  $\text{VOSO}_4$  solution [102]. The pentavalent vanadium in leaching solution from traditional vanadium slag or stone coal extraction process was absorbed and enriched by anion exchange resin (which can be any one of D816, D815, D201, D290 and D301) after sulfuric acid transformation.  $\text{VOSO}_4$  solution was obtained by reducing and desorbing pentavalent vanadium with reducing agent ( $\text{SO}_2$  gas, ascorbic acid or sulfuric acid aqueous solution containing  $\text{V}^{3+}$ ).

The method saves the technical processes of impurity removal, ammonium salt vanadium precipitation, drying, calcination deamination, vanadium powder dissolution and the like in the traditional process [74]. And it simplifies the production process, saves the production time, reduces the production cost, greatly improves the working environment, does not introduce other impurities in the preparation process, greatly improves the product purity, and the concentration of  $\text{V}^{4+}$  in the obtained  $\text{VOSO}_4$  solution is more than  $1 \text{ mol}\cdot\text{L}^{-1}$  [73]. However, the main problems of preparing  $\text{VOSO}_4$  solution by adsorbing and enriching vanadium with resin are that the adsorption capacity of resin is small, and a large amount of wastewater will be produced during desorption and regeneration. If the resin is poisoned, it can't be recycled. So far, no resin has been used in industrial production of  $\text{VOSO}_4$  solution.

Zhou Xiangyou et al. used vanadium solution prepared by sodium roasting vanadium-containing clinker through leaching process or ammonium vanadate dissolution as raw material, and adjusted its pH value to 8.0–10.0. The technical process is shown in Fig. 17 [103]. Ion exchange resin for selectively adsorbing vanadium is loaded into an ion exchange column to form a resin bed layer, and the vanadium solution flows through the resin bed layer downstream at a flow rate of 1–6 times the bed volume/hour. Then desorbing the loaded ion exchange column with a desorbent (the composition of desorbent: 2%–8%  $\text{H}_2\text{SO}_4$  + 4%–15%  $\text{H}_2\text{SO}_4$  mixed solution), the dosage of which is 2–6 times of the resin bed volume, and the desorption speed is 1–5 times of the resin bed volume/



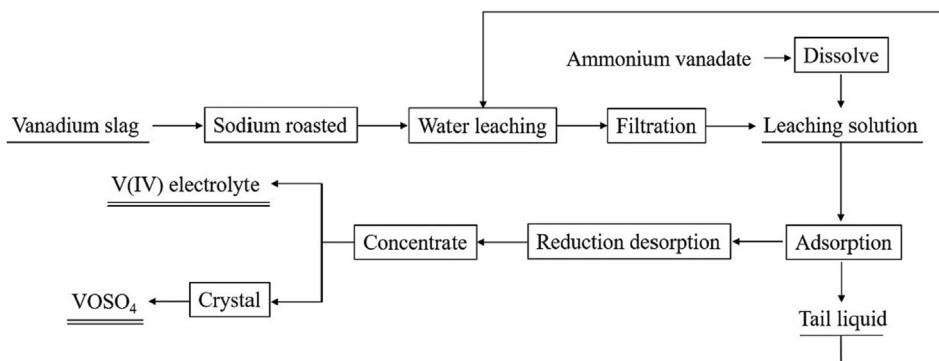


Fig. 17. Technological process of preparing electrolyte by ion exchange method.

hour. After desorption,  $\text{VOSO}_4$  solution was obtained. The process takes vanadium solution as raw material, which avoids the intermediate process of preparing  $\text{V}_2\text{O}_5$ . The operation is simple, energy-saving and environment-friendly. The recovery efficiency of vanadium over 92.8%, and the V(IV) content more than 99.9%, which meets the requirements of vanadium electrolyte. However, the adsorption capacity of resin is limited, and the conversion between adsorption and desorption will make some resins invalid. For industrial applications, it needs more comprehensive to research.

The method can separate and extract vanadium from the leaching solution to prepare V(IV) electrolyte. The ion exchange resin is used as the separation medium, so that vanadium in the aqueous solution is well selected, and vanadium electrolyte can be obtained. While, the adsorption capacity of ion resin exchange is limited, so evaporation and concentration are needed to obtain electrolyte with high concentration. The long adsorption and desorption time leads to low production efficiency. The adsorption and desorption process will also produce a large amount of wastewater, which will cause serious pollution to the environment and increase the environmental protection cost.

#### Additives stabilize vanadium electrolyte

For commercial vanadium electrolytes, the vanadium concentration is in the range of 1.5–1.8 M [104]. When the vanadium concentration is greater than 1.5 M, the acid concentration in the electrolyte needs to be accurately controlled at 3 M, and the operating temperature is between 10 and 40 °C. At this time, the operation of the electrolyte is basically in a supersaturated or supercritical state. In order to maintain the stable operation of high concentration electrolyte, the research and development of additives has become a hot spot and focus of electrolyte research. The research scope also covers a large number of inorganic compounds and organic compounds [5,105]. The most studied is to stabilize V(V) at high temperature by additives, thereby broadening the temperature range of electrolyte application. Skyllas-Kazacos divided additives into dispersion, complexing, and threshold according to their mechanism of action [106]. Dispersed additives are some low-molecular-weight polymers with opposite charges to the nuclear colloidal particles formed by vanadium precipitation in the electrolyte, which can prevent the growth of nuclear particles, such as lignin and polyaniline sulfonic acid, etc. Complexing additives are some organic ligands, which coordinate with vanadium ions to reduce the precipitation activity of vanadium ions and improve the stability of electrolyte, such as EDTA, 8-hydroxyquinoline, etc. The threshold additive is different from the former two. It can be adsorbed to the surface of the precipitated particles to prevent the precipitation nucleus from growing. Its addition

amount has no fixed composition ratio with vanadium ions, such as pyrophosphate and sodium hexametaphosphate, etc. In addition to complexing additives, other types of additives can not increase the solubility of vanadium ions, but can only increase its supersaturation, so that the electrolyte can work in a high metastable state [105]. As early as the 1990s, researchers from UNSW extensively screened a variety of stabilizing additives, including surfactants, various carbon-chain multifunctional compounds such as compounds with alcoholic hydroxyl groups, amino groups, thiol groups, organic phosphoric acids, ammonium salts, phosphoric acids, and various salts, polysaccharide compounds, carboxylic acids, and chelates containing other functional groups. Since V(V) has strong catalytic oxidation in strong acid medium, most organic compounds can be oxidized by V(V), which are not suitable as stable additives [107].

When selecting additives, it is necessary to take into account the various valence ions of V in the electrolyte and the influence on the electrochemical performance. Researchers from UNSW screened a large number of inorganic compounds and determined that phosphoric acid and ammonium phosphate were the best stabilizing additives [104]. Gang et al. dissolved 1.8 M vanadium into 3 M sulfuric acid solution to obtain an electrolyte. The effects of organic- $\text{NH}_4^+$ , including chitosan, nonionic polyvinylamine, and inorganic- $\text{NH}_4^+$  salts, including ammonium thiocyanate, ammonium ferrous sulfate, and ammonium ferric sulfate, on the stability of the electrolyte were compared in detail. It was confirmed that the addition of 0.5% inorganic- $\text{NH}_4^+$  could stabilize the electrolyte well at -5 to 45 °C, while also enhancing the electrochemical performance. Skyllas-Kazacos et al. developed a composite cathode stabilizer KS11, which is composed of 1% potassium phosphate and 1% sodium hexametaphosphate. The stabilizer could adsorb on the surface of the initial particle core of V(V) to inhibit or even eliminate the growth or continuous formation of the precipitated particles, so that it could well stabilize 4 M V(V) in 5.7 M  $\text{SO}_4^{2-}/\text{HSO}_4^-$  solution to 50 °C, and could inhibit V(IV) precipitation at 5 °C [108].

Vijayakumar Murugesan et al. systematically studied the action mechanism of inorganic ionic additives and proposed two modes: (1) contact-ion pair based on anions; (2) barrier precipitation nucleus based on cation coordination complexation [109]. The stable temperature range of electrolyte containing 2.0 M vanadium and 5.5 M  $\text{SO}_4^{2-}$  was extended to 5–50 °C by using 0.1 M  $\text{MgCl}_2$  and  $(\text{NH}_4)_3\text{PO}_4$ , while the concentration of vanadium electrolyte without additives was only lower than 1.5 M. However, recent studies by Jianlu Zhang et al. have reported that  $\text{K}^+$ , phosphate and polyphosphate react with V(V) to form  $\text{KVO}_6$  and  $\text{VOPO}_4$ , which are not suitable as stabilizers [109]. Studies have shown that polyacrylic acid and methyl sulfonic acid can stabilize all four valence states of vanadium ions in a 1.8 M vanadium electrolyte solution,

**Table 5**

Preparation process of vanadium electrolyte.

Methods	Advantage	Disadvantage
Chemical reduction	Simple process; highly efficient and fast speed; easy to scale production	High cost of raw material (high-purity $V_2O_5$ ); High cost of production
Electrolysis	Do not use reducing agent or poison gas; Shortened vanadium electrolyte preparation process	High cost of raw material; difficult to scale up due to difficulties with maintaining the $V_2O_5$ powder in suspension; low produce efficiency; require complex filtering system
Solvent extraction	Suitable for both low and high concentration V-containing solution; high selectivity; high yield; easy to get vanadium electrolyte meeting to the standard; easy continuous and automatic control of the production process, recyclable extractant	Produce emulsification or the third phase in extraction process; extractant lose seriously; high price of extraction system; regeneration stability of extraction system needs to be improved; heavy odor of organic phase; poor operating conditions in the plant; hidden trouble in safety; lengthy process flow
Ion exchange	Suitable for low concentration V-containing solution; high selectivity; high yield; easy to get vanadium electrolyte meeting to the standard	Limited adsorption capacity; not suitable for high concentration V-containing solution; resin easy poisoning causing non-recyclability; large amount of wastewater; low production efficiencies; high cost of production

which is a very promising stabilizer. Stabilizing V(V) in a vanadium electrolyte solution greater than 1.8 M above 40 °C still needs further study.

## Summary and outlook

At present, there are four main preparation methods of vanadium electrolyte. Chemical reduction is the most mainstream preparation method, which is simple, highly efficient, fast speed, easy to scale production, but the production cost is too high due to high cost of  $V_2O_5$ . Electrolysis avoids the use of reducing agents and poison gases and shortens the preparation process, but there are also problems such as high cost of raw material, difficult to scale up due to difficulties with maintaining the  $V_2O_5$  powder in suspension, low produce efficiency and require complex filtering system. Solvent extraction is suitable for both low and high concentration V-containing solution, which has these advantages (high selectivity; high yield; easy to get vanadium electrolyte meeting to the standard). However, extraction system is easy to produce emulsification or the third phase in extraction process. Moreover, Solvent extraction is with a lengthy process flow. Ion exchange and solvent extraction have the same advantages, but it also has some limitations. Ion exchange is not suitable for high concentration V-containing solution due to limited adsorption capacity. In addition, ion exchange resin is difficult to recycle due to easy poisoning with low production efficiencies and high cost of production. The four methods for preparing vanadium electrolyte are summarized in Table 5.

The uppermost preparation method of the vanadium electrolyte of VRFB uses vanadium oxide or vanadate as raw materials to prepare the electrolyte by dissolving–reducing or reducing–dissolving. However, these vanadium compounds are industrial products, which have gone through the complicated process of multistage purification and impurity removal from vanadium extraction leaching solution, which greatly increases the operation cost, generates a large amount of wastewater and waste solids, threatens the ecological environment, increases the environmental protection cost, and leads to the high preparation cost of the electrolyte.

In order to reduce the cost of electrolyte preparation, vanadium extraction leaching solution was used as raw material to replace product–grade vanadium compounds. Electrolyte is directly prepared from vanadium extraction leaching solution by solvent extraction and ion exchange resin method. However, these two methods have their own problems, so they can't be industrialized. However, they provide a new idea for researchers—preparing electrolyte based on vanadium extraction leaching solution.

In the future, the preparation of electrolyte may take vanadium extraction leaching solution as raw material, select suitable separation medium, prepare electrolyte through short process, and develop a new process that can meet the concept of green, recycling, high efficiency and sustainable production. With the urgent demand for renewable energy utilization and the expectation of changing the national energy structure, VRFB will be ready to go, leading a new era of energy.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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