

A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage

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The all-vanadium redox flow battery is a promising technology for large-scale renewable and grid energy storage, but is limited by the low energy density and poor stability of the vanadium electrolyte solutions. A new vanadium redox flow battery with a significant improvement over the current technology is reported in this paper. This battery uses sulfate-chloride mixed electrolytes, which are capable of dissolving 2.5 M vanadium, representing about a 70% increase in energy capacity over the current sulfate system. More importantly, the new electrolyte remains stable over a wide temperature range of -5 to 50 °C, potentially eliminating the need for electrolyte temperature control in practical applications. This development would lead to a significant reduction in the cost of energy storage, thus accelerating its market penetration.

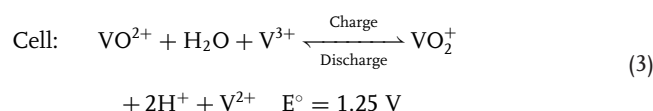
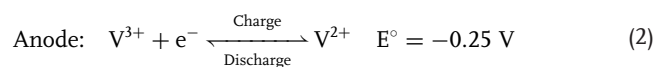
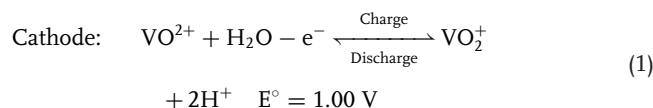
response time, low self discharge, long lifetime, and most importantly, independent tunable power and storage capacity, which make it possible to independently scale up the electricity storage capacity and power generation capacity as needed.

Of the many reported redox-flow battery systems,^[6–11] the all-vanadium sulfate RFB system (or VRB) demonstrates excellent electrochemical activity and reversibility.^[9,10] A VRB uses a V^{2+}/V^{3+} sulfate solution at the anode side and a V^{4+}/V^{5+} sulfate solution at the cathode side, eliminating the cross-contamination effect between the electrolytes through the ion-exchange membrane. A standard voltage of 1.25 V is produced by

1. Introduction

Concerns over the environmental consequences of burning fossil fuels and their remaining reserves have led to an increasing use of renewable energy generated from sources such as solar radiation and wind. However, the intermittent, varied nature of such renewable resources makes it difficult to integrate these valuable energies into electrical supply grids. One solution to this problem would be to employ large-scale electrical energy storage (EES), widely considered to be an effective approach to improve the reliability, power quality, and economy of these renewable energies.^[1–3] Among the most promising large-scale EES technologies are redox-flow batteries (RFBs). RFBs are special electrochemical systems that can repeatedly convert and store multi-megawatt-hours (MWhs) of electrical energy to chemical energy and convert the chemical energy back to electricity energy when needed.^[4,5] As shown in **Figure 1**, a RFB cell consists of two electrodes and two circulating electrolyte solutions (positive electrolyte and negative electrolyte) separated by an ion-exchange membrane or a separator. The energy conversion between electrical energy and chemical potential occurs instantly at the electrodes once the liquid electrolytes are flowing through the cell. The advantages of RFBs include high energy efficiency, short

the VRB system through the following reactions:



Multi-MWh VRB systems have been demonstrated,^[12] however, the current technology is still not ready for broad market penetration because of significant limitations on vanadium solubility and the stability of the electrolyte solutions. The precipitation of V_2O_5 at elevated temperatures^[13–15] and the low solubility (<1.7 M) of $(\text{VO})\text{SO}_4$ at low temperatures limit the energy capacity to <25 Wh.L⁻¹ and the operating temperature range to $10 \sim 40$ °C.^[10,14–16] This narrow operational temperature window, in particular its upper limit (40 °C), often necessitates electrolyte temperature control in practical applications. Such heat management can cause as much as 20% additional energy loss and significantly increases the overall operating costs.^[12] In the last decade, there have been great efforts to improve the solubility and stability of the electrolyte solutions with a wide range of organic and inorganic additives.^[17] Still, overall improvement of the VRB systems in terms of energy capacity and stability has been quite limited. As with all other

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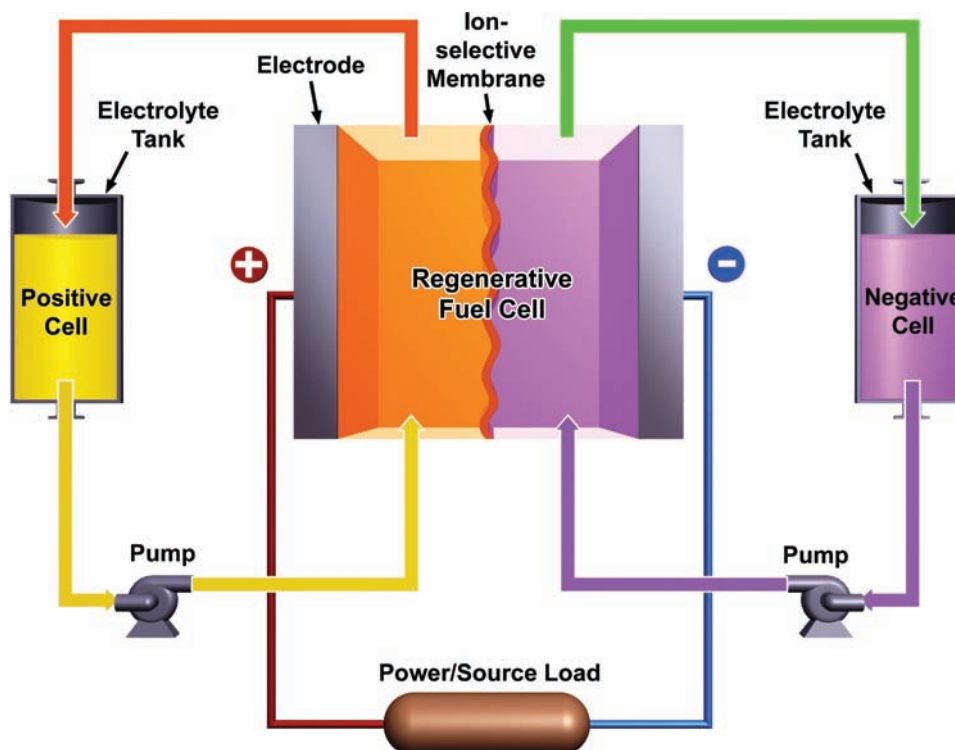


Figure 1. A schematic illustration of the structure of a redox flow battery.

large-scale energy storage systems, without technological breakthroughs, it will be difficult to rely on VBRs for efficient usage of intermittent renewables.

Here we report a new VRB system that uses mixed sulfate and chloride electrolytes based on a careful evaluation and understanding of the electrolyte chemistry. The mixed electrolyte VRB system allows for a more than 70% increase in the energy capacity over the current sulfate system and broadens the operational temperature range from 10–40 °C to –5–50 °C, which essentially eliminates the need for electrolyte temperature control.

2. Results and Discussion

2.1. Stability of the Mixed Acid Vanadium Electrolytes

First, we systematically evaluated the stability of V^{2+} , V^{3+} , V^{4+} , and V^{5+} sulfates in H_2SO_4 solutions. We found that the limited stability of the vanadium sulfate solutions (<1.7 M V) was determined by the low solubility of VO_2SO_4 at low temperatures (–5 °C) and the precipitation of V_2O_5 at high temperatures (40 °C), which is consistent with previous studies.^[13–16] We also studied the effect of a wide range of organic and inorganic additives. We were not able to identify any agent that could simultaneously stabilize all the four different vanadium cations at both the high and low temperature boundaries.

Such conclusions led us to explore mixed electrolyte systems in which different anions can help stabilize different cations. To achieve this goal, we studied the stability of V^{2+} , V^{3+} , V^{4+} , and

V^{5+} chlorides in HCl solutions in a temperature range of –5 to 40 °C. Up to 2.3 M V^{2+} , V^{4+} , and V^{5+} chlorides were stable (i.e., without crystallization or precipitation) in 6 M HCl over 10 days at all the designated temperatures. The overall stability of the chloride solutions was determined by the solubility of V^{3+} at low temperatures. At –5 °C, a mixture of $VOCl$ and VCl_3 precipitated out from 6 M HCl solutions with > 1.5 M V^{3+} .

These observations suggested that Cl^- anions help stabilize V^{4+} and V^{5+} , whereas SO_4^{2-} anions help stabilize V^{3+} . About 2 M or higher V^{2+} was found stable in both solutions. It is therefore likely that all the four V^{2+} , V^{3+} , V^{4+} , and V^{5+} cations can be stabilized in mixed sulfate and chloride electrolyte solutions.

To prove this hypothesis, the stability of V^{2+} , V^{3+} , V^{4+} , and V^{5+} sulfate and chloride mixtures was evaluated from –5 to 40 °C. All four valence states of vanadium were stable up to 2.5 M in a mixed solution containing 2.5 M SO_4^{2-} and 6 M Cl^- . When the vanadium concentration was increased to 3 M, a mixture of $VOCl$ and $V_2(SO_4)_3$ started to precipitate out in the V^{3+} -containing solution after 8 days at –5 °C. Nonetheless, the 2.5 M stability from the preliminary work represents a significant improvement in energy capacity over the current sulfate electrolytes. A systematic effort is underway to further optimize this newly discovered VRB electrolyte system.

Given that there is more concern about the stability of electrolytes at high temperatures, the V^{5+} mixed solutions were further investigated at 50 °C. After 10 days, no precipitation was observable in a mixture of 2.7 M V^{5+} and 0.3 M V^{4+} (corresponding to 90% of state-of-charge of a 3 M VRB system), indicating excellent V^{5+} stability in the mixed electrolytes. The extension of operational temperatures from 10 to 40 °C to –5 to

50 °C would significantly ease or potentially eliminate the need for the electrolyte temperature control in most areas in the world, leading to much improved energy storage efficiency and reduced energy storage cost. The related stability test results are given in Table 1 and 2.

Table 1. Stability of Vⁿ⁺ sulfate solutions.*

V ⁿ⁺ species	V ⁿ⁺ , M	Total sulfate, M	T, °C	Time for precipitation
V ²⁺	2.0	5.0	-5	Stable (>10 d)
	2.0	5.0	25	Stable (>10 d)
	2.0	5.0	40	Stable (>10 d)
V ³⁺	2.0	5.0	-5	Stable (>10 d)
	2.0	5.0	25	Stable (>10 d)
	2.0	5.0	40	Stable (>10 d)
V ⁴⁺ (VO ²⁺)	2.0	5.0	-5	18 hr
	2.0	5.0	25	95 hr
	2.0	5.0	40	Stable (>10 d)
V ⁵⁺ (VO ₂ ⁺)	2.0	5.0	-5	Stable (>10 d)
	2.0	5.0	25	Stable (>10 d)
	2.0	5.0	40	95 hr

* The ions concentrations are estimated value based on electrolyte preparation.

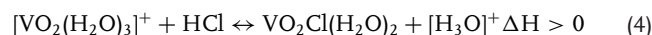
Table 2. Stability of Vⁿ⁺ sulfate-chloride mixed solutions.*

V ⁿ⁺ species	V ⁿ⁺ , M	Total sulfate, M	Cl ⁻ , M	T, °C	Time for precipitation
V ²⁺	3.0	3.0	6.0	-5	Stable (>10 d)
	2.5	2.5	6.0	-5	Stable (>10 d)
	2.5	2.5	6.0	25	Stable (>10 d)
	2.5	2.5	6.0	40	Stable (>10 d)
	3.0	3.0	6.0	40	Stable (>10 d)
V ³⁺	3.0	3.0	6.0	-5	192 hr (8 d)
	2.5	2.5	6.0	-5	Stable (>10 d)
	2.5	2.5	6.0	25	Stable (>10 d)
	2.5	2.5	6.0	40	Stable (>10 d)
	3.0	3.0	6.0	40	Stable (>10 d)
V ⁴⁺ (VO ²⁺)	3.0	3.0	6.0	-5	Stable (>10 d)
	2.5	2.5	6.0	-5	Stable (>10 d)
	2.5	2.5	6.0	25	Stable (>10 d)
	2.5	2.5	6.0	40	Stable (>10 d)
	3.0	3.0	6.0	40	Stable (>10 d)
V ⁵⁺	3.0	3.0	6.0	-5	Stable (>10 d)
	2.5	2.5	6.0	-5	Stable (>10 d)
	2.5	2.5	6.0	25	Stable (>10 d)
	2.5	2.5	6.0	40	Stable (>10 d)
	3.0	3.0	6.0	40	Stable (>10 d)
	2.7 V ⁵⁺ + 0.3 V ⁴⁺	3.0	6.0	50	Stable (>10 d)

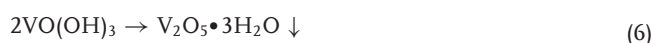
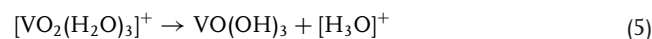
* The ions concentrations are estimated value based on electrolyte preparation.

2.2. Solution Chemistry of the Mixed Acid Vanadium Electrolytes

The improved stability of V⁵⁺ in the mixed electrolytes at elevated temperatures is attributed to the formation of a soluble neutral species, VO₂Cl(H₂O)₂ (see Figure 2a). Its formation was first predicted using the Amsterdam Density Functional (ADF) program, possibly via the following endothermic reaction:



The quantum calculation also indicated that in sulfate solutions, V⁵⁺ exists as a positively charged species, [VO₂(H₂O)₃]⁺ (also see Figure 2a). At elevated temperatures, this positively charged species would be converted to insoluble V₂O₅·3H₂O by the following de-protonation and condensation reactions:^[18]



Unlike V⁵⁺ cations, V²⁺, V³⁺, and V⁴⁺ were predicted to form [V(H₂O)₆]²⁺, [V(H₂O)₆]³⁺, and [VO(H₂O)₅]²⁺, respectively, in both the sulfate and the mixed sulfate-chloride solutions. It was observed in our stability tests that, in the mixed systems, the stability of V⁴⁺ is determined by the solubility of VOSO₄, and that of V³⁺ by the solubility of V₂(SO₄)₃ and VOCl. Therefore, the improvement of V³⁺ and V⁴⁺ stability in the mixed systems over the sulfate systems and the chloride systems is quite possibly due to the decrease of SO₄²⁻ and Cl⁻ concentration in the solutions. As mentioned before, high concentrations of V²⁺ are stable in both sulfate and mixed solutions.

The formation of soluble VO₂Cl(H₂O)₂ was supported by our nuclear magnetic resonance (NMR) study. Figure 2b shows a ⁵¹V spectrum of the mixed solution, along with that of the sulfate solution. The chemical shift and width of ⁵¹V in the mixed solution is quite different from that in the sulfate solution, indicating the different chemical environment between these two solutions. The ³⁵Cl spectrum (see Figure 2c) of the mixed solution further reveals the existence of two different Cl⁻ bonding environments, one in the bulk aqueous solution and the other in the V-containing complexes, supporting the predicted VO₂Cl(H₂O)₂ structure. Our NMR study on the solutions at varied temperatures (see Figure 2d) indicated that the formation of the new vanadium species is strongly dependant on temperature. It appeared that the VO₂Cl(H₂O)₂ complex started to form in the mixed solutions when the temperature approaches 20 °C. This is evidenced by a quick rise in the chemical shift and the line width of ⁵¹V spectra in the mixed solution at around 20 °C.

2.3. Performance of a Vanadium Redox-Flow Cell Using the Mixed Acid Electrolytes

The mixed solutions were further investigated for their electrochemical properties. Figure 3 shows the cyclic voltammogram (CV) of a mixed solution containing 2.5 M V⁴⁺, 2.5 M SO₄²⁻, and 6 M Cl⁻, along with that of a solution containing 1.5 M V⁴⁺

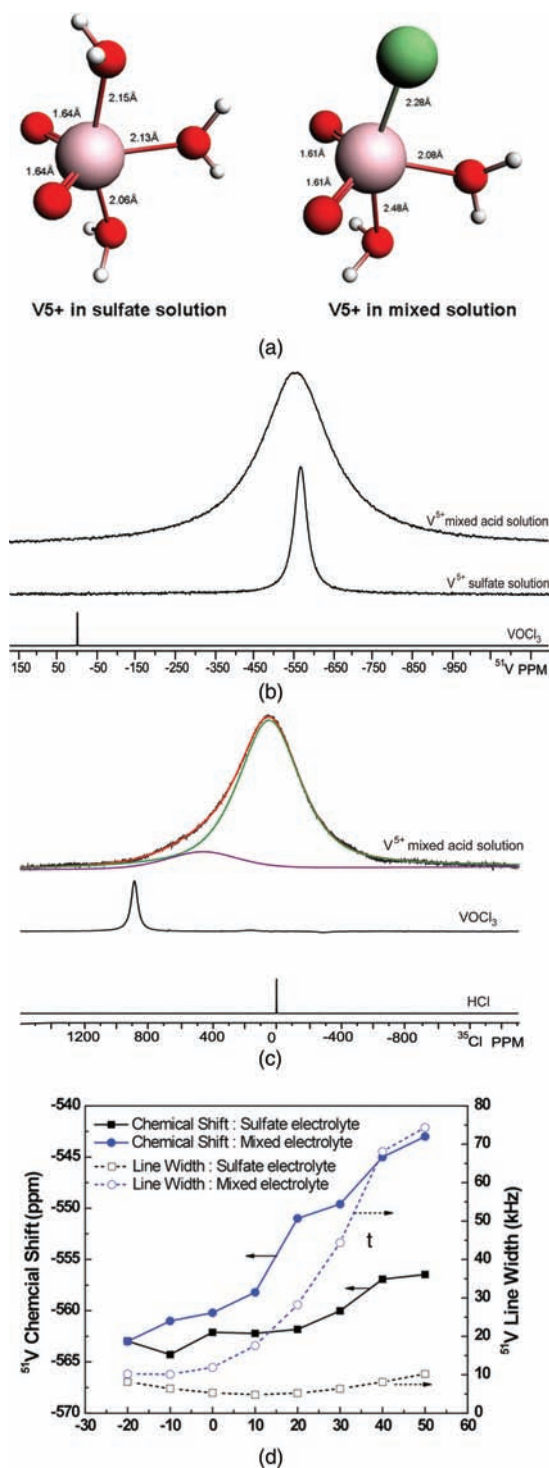


Figure 2. Structures of vanadium sulfate-chloride mixed electrolyte. a) The structures of V^{5+} complexes in the sulfate and the sulfate-chloride mixed solutions, as predicted by quantum calculation. The pink, green, red, and white spheres represent vanadium, chloride, oxygen, and proton ions, respectively. The numbers are the calculated bond lengths. b) ^{51}V NMR spectra of a mixed sulfate-chloride solution (20 °C, 2.5 M V^{5+} , 2.5 M SO_4^{2-} , 6 M Cl^- , and 7.25 M H^+) and a sulfate solution (20 °C, 2 M V^{5+} , 5 M SO_4^{2-} , and 9 M H^+). c) ^{35}Cl NMR spectra of the mixed solution in (b). d) The chemical shift and line width of ^{51}V NMR as a function of temperature of the sulfate and the mixed solutions in (b).

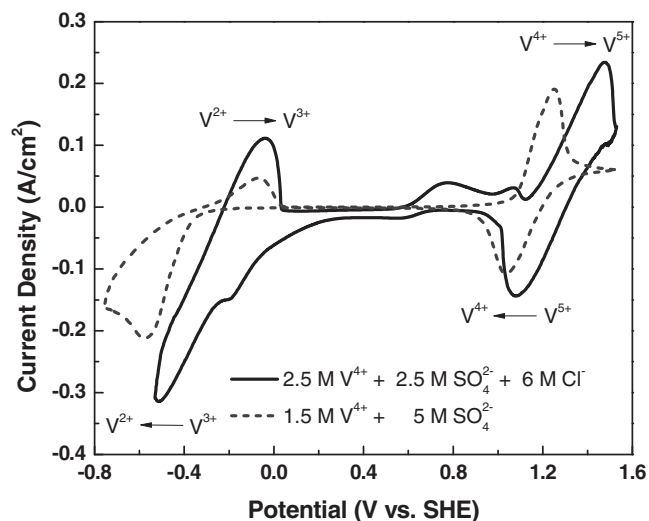
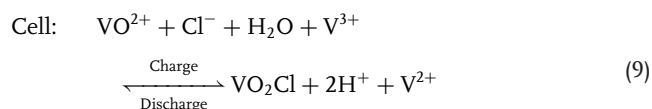
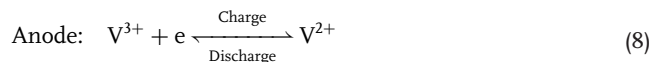
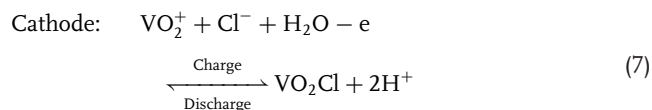


Figure 3. Cyclic voltammogram on a graphite felt electrode of a mixed electrolyte solution containing 2.5 M V^{4+} , 2.5 M SO_4^{2-} , and 6 M Cl^- , along with that of a solution containing 1.5 M V^{4+} and 5.0 M SO_4^{2-} (a standard electrolyte for a sulfate VRB system). The scan was carried out at room temperature at a scan rate of 0.5 mV/s.

and 5.0 M SO_4^{2-} (a standard electrolyte solution for sulfate VRB systems). The peak currents of vanadium redox reactions in the mixed solution are higher than those in the sulfate solution, indicating improved electrode reaction kinetics in the mixed solutions even with a 2.5 M vanadium concentration. These fast reaction kinetics are in part due to the good fluidity of the new electrolyte (see Experimental Section). In general, the electrochemical reversibility of the redox couples in the mixed solution is similar to that of the sulfate solution, except that there is a small shift towards higher potential for both V^{2+}/V^{3+} and V^{4+}/V^{5+} in the mixed acid system. Furthermore, the cyclic voltammetry test revealed no chlorine gas evolution until at least 1.5 V, which is consistent with the fact that the standard potential of reaction $2\text{Cl}^- - 2e = \text{Cl}_2(\text{g})$ is 1.36 V, and that of reaction $\text{VO}^{2+} + \text{H}_2\text{O} - e = \text{VO}_2^+ + 2\text{H}^+$ is 1.00 V. Under normal conditions, V^{4+} oxidation should happen before Cl^- oxidation. According to our thermodynamic analysis of reaction $2\text{VO}_2^+(\text{a}) + 4\text{H}^+(\text{a}) + 2\text{Cl}^-(\text{a}) = 2\text{VO}_2^+(\text{a}) + \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}$, under normal flow battery operation conditions (i.e., $T < 40^\circ\text{C}$ and $\text{SOC} < 80\%$), the equilibrium concentration of Cl_2 gas is less than 10 ppm. Due to the formation of $\text{VO}_2\text{Cl}(\text{H}_2\text{O})_2$ structure, the equilibrium concentration of Cl_2 gas in the positive electrolyte solution should be even lower. Even if formed in a small quantity, the Cl_2 gas would dissolve in the catholyte solutions, given its relatively high solubility in water (0.57 g Cl_2 per 100 g water at 30 °C). During the following discharging steps, Cl_2 can be reduced back to Cl^- anions, and the stored electrical energy is released. Because VRBs are commonly operated in a closed system, the small amount of chlorine evolution, if any, should not be a big issue. Nevertheless, sufficient safety controls are highly recommended for this new system. All these suggest that a VRB using mixed electrolytes would have similar voltage, improved reaction kinetics, and much higher energy density over the current sulfate system.

According to our quantum calculation and NMR studies (see Figure 2), the following electrode and cell reactions are proposed for a VRB using the mixed sulfate-chloride electrolytes:



Given that the formation of the neutral complex VO_2Cl starts at around 20 °C (see Figure 2d), reactions 7 to 9 should dominate only in the elevated temperature zone (>20 °C). On the other hand, in the low temperature zone (<20 °C), reactions 1 to 3 should still be the dominant reactions. The new reaction mechanism at the elevated temperatures is schematically illustrated in Figure 4 for charging and discharging, respectively.

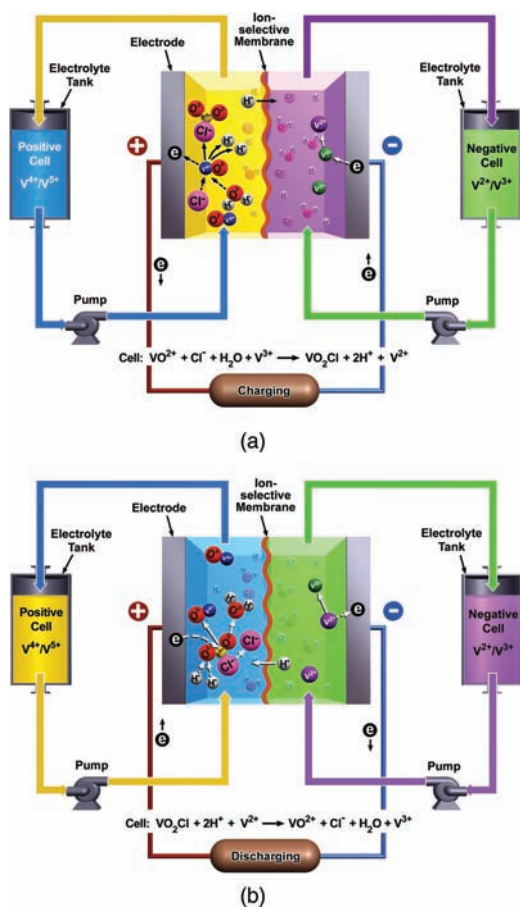


Figure 4. A schematic illustration of a vanadium redox flow battery using mixed sulfate-chloride electrolyte solutions at temperatures higher than 20 °C (top: charging; bottom: discharging)

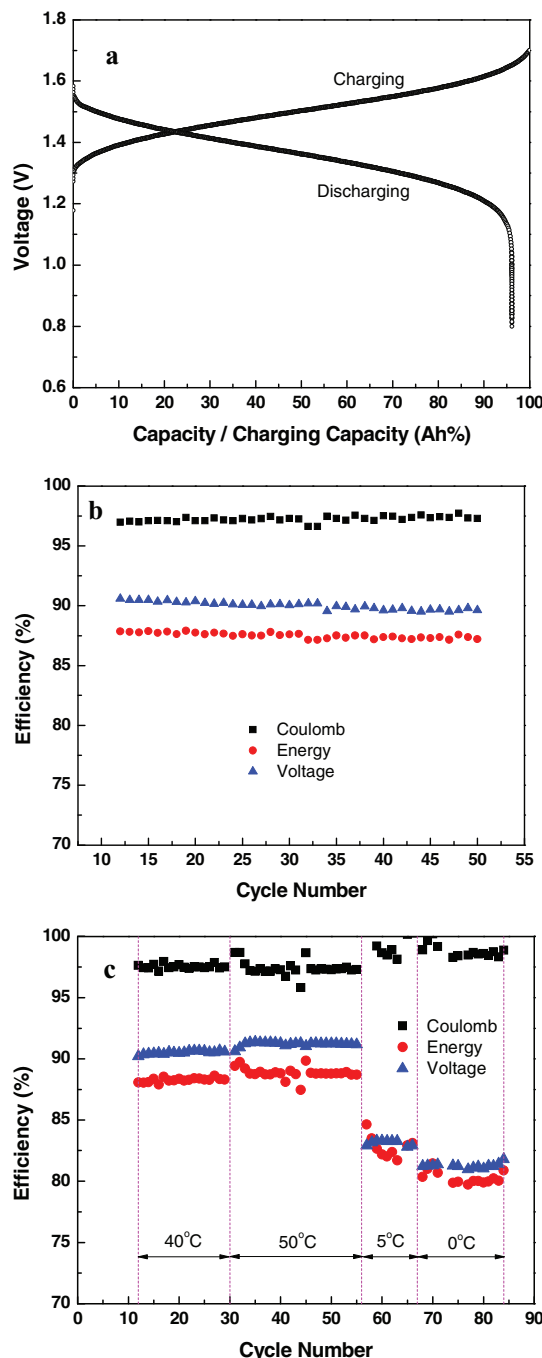


Figure 5. Electrochemical behavior of a VRB using mixed sulfate-chloride electrolyte. a) Performance of a VRB with a 2.5 M all-vanadium, sulfate-chloride, mixed electrolyte flow battery at room temperature (−25 °C). Charge and discharge voltage window: 1.27 to 1.6 V; discharge and charge current: 50 mA/cm². b) Cyclic performance of a VRB with a 2.5 M vanadium mixed solution at 25 °C. Same cell operation conditions as (a). c) Performance of a VRB with a 2.5 m vanadium mixed solution at 40, 50, 5, and 0 °C. Same cell operation conditions as (a).

The performance of a VRB using mixed electrolyte solutions was evaluated in a single RFB cell. Figure 5a shows the charge-discharge curves of a 2.5 M vanadium sulfate-chloride

Table 3. Performance of all-vanadium redox flow cells using mixed sulfate-chloride electrolytes and sulfate-only electrolyte.^{a,b)}

Current of Discharge, (mA.cm ⁻²)	Energy Density (Wh.L ⁻¹)			Columbic Efficiency			Energy Efficiency		
	2.5 VS 6 Cl	3 VS 6 Cl	1.6 V 4.5 S	2.5 VS 6 Cl	3 VS 6 Cl	1.6 V 4.5 S	2.5 VS 6 Cl	3 VS 6 Cl	1.6 V 4.5 S
100	36.2	39.5	22.3	0.95	0.95	0.94	0.81	0.76	0.83
75	37.5	40.8	22.4	0.96	0.96	0.94	0.84	0.81	0.85
50	38.5	41.8	22.6	0.96	0.97	0.94	0.87	0.85	0.87
25	39.2	43.1	22.6	0.96	0.97	0.94	0.90	0.89	0.88

^{a)} Cell operation conditions: 10 cm² flow cell, Charged to 1.7 V by 50 mA/cm² current; ^{b)} 2.5VS 6Cl: 2.5 M V, 2.5 M SO₄²⁻, 6.0 M Cl⁻; 3VS6Cl: 3.0 M V, 3.0 M SO₄²⁻, 6.0 M Cl⁻; 1.6V4.5S: 1.6 M V, 4.5 M SO₄²⁻; ^{c)} Energy density is defined as discharge energy divided by electrolyte volume.

mixed system (containing 2.5 M SO₄²⁻ and 6 M Cl⁻) at ambient temperature. Figure 5b gives its columbic, voltage, and energy efficiency as a function of cycling number. Stable performance with an energy efficiency of 87% was observed during a course of 20 days. The change of gas-phase pressures of the positive and negative electrolytes containers was minimal, indicating no significant gas evolution in the system. Figure 5c shows the performance of this system at 0, 5, 40, and 50 °C, respectively. While higher at higher temperatures, an energy efficiency over 80% was obtainable at 0 °C. Again, negligible, if any, gas evolution was observed, even during the operation at 50 °C. **Table 3** compares the performance of the VRB cells using 2.5 M and 3.0 M vanadium mixed electrolytes with that using 1.6 M vanadium sulfate electrolyte. Overall, the cells using the mixed sulfate-chloride electrolytes were successfully demonstrated at much higher vanadium concentrations than the sulfate system while still being highly efficient.

3. Conclusions

A vanadium sulfate and chloride mixed electrolyte proved to be stable with a vanadium content of up to 2.5 M over a temperature range of -5~50 °C because of the formation of stable VO₂Cl(H₂O)₂ at elevated temperatures and reduction in SO₄²⁻ concentrations. The vanadium redox couples in mixed electrolytes demonstrated improved reaction kinetics while remaining as highly reversible as the sulfate system. The VRBs with the mixed electrolytes were successfully demonstrated with the same high efficiencies as those of the sulfate systems, but over a much broader temperature window. Our battery tests, along with thermodynamic calculations, concluded that there was no concern of chlorine gas evolution during the battery operation. The highly improved energy capacity and the excellent electrochemical performance over a broader operation temperature window would help to substantially reduce the cost of the VRB technologies. With cell, stack, and system engineering and optimization, this new RFB technology is of great potential to accelerate the market penetration of the renewable energy sources to the electrical grid.

4. Experimental Section

Electrochemical study: A Solartron 1287 potentiostat was employed for cyclic voltammetry (CV) experiments. Graphite felt (SGL, Germany)

was punched into round discs of 5mm in diameter and sealed onto a SS mesh current collector. Cyclic voltammetry was carried out in a 3-electrode electrochemical cell with a Pt wire as the counter electrode to ensure the area of working electrode is much larger than that of the counter electrode. The scan was carried out at room temperature at a scan rate of 0.5mV/s.

The flow cells consisted of two graphite felt electrodes, two gold-coated copper current collectors, two polytetrafluoroethylene (PTFE) gaskets, and a Nafion 117 membrane. The graphite felt (GFD5, SGL Carbon Group, Germany) was oxidized in air at 400 °C for 6 h to enhance electrochemical activity and hydrophilicity. The active area of the electrode and the membrane was about 10 cm². The details on the flow cell are described in previous work.^[19] An Arbin battery tester was used to evaluate the performance of flow cells and to control the charging and discharging of the electrolytes. The flow rate was fixed at 20 mL/min, which was controlled by a peristaltic pump. A balanced flow cell contained about 50 mL anolyte and 50 mL catholyte. An environmental chamber was used to control the temperatures during flow cell tests.

For cell performance evaluation and electrolyte solution preparation, the cell was normally charged at a current density of 50 mA/cm² to 1.7 V and discharged to 0.8 V with a current density of 25 to 100 mA/cm². Cell cycling tests were performed at 90% state-of-charge and state-of-discharge at a fixed charging and discharging current density of 50 mA/cm².

Electrolyte stability study: The electrolyte solutions of V²⁺, V³⁺, V⁴⁺, and V⁵⁺ used in this work were prepared electrochemically in flow cells using VOSO₄ (from Alfa Aesar) and VCl₃ as starting chemicals. VCl₃ solutions were prepared by dissolving V₂O₃ (from Alfa Aesar) in HCl solutions. The electrolyte stability tests were carried out in polypropylene tubes at -5 °C, ambient temperature, 40 °C, 50 °C, and 60 °C, using approximately 5 mL solution per sample. During the stability tests, the samples were kept static without any agitation and were monitored daily by naked eye for the formation of precipitation. Selected precipitates were separated out from the solution and analyzed with X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) to check their crystal structures, morphologies, and elemental compositions.

NMR study: The ambient and variable temperature ³⁵Cl and ⁵¹V NMR measurements were performed using a Varian 500 Inova spectrometer. The ³⁵Cl and ⁵¹V chemical shifts were externally referenced to H³⁵Cl and clear ⁵¹VOCl₃ solutions, respectively ($\delta_{\text{iso}} = 0$ ppm). The chemical shifts (error ± 0.5 ppm) and line width (error ± 100 Hz) at each temperature were obtained from fitting the line shapes of the resonance lines using the SpinWorks 3.1 program (K. Marat, University of Manitoba, Manitoba, Canada, 2009).

Others: Solution viscosity was measured using an Ubbelohde calibrated viscometer tube. Our measurement indicated a viscosity 6.1 cP and a density 1.40 g/mL for the 2.5 M V⁴⁺, 2.5 M SO₄²⁻, and 6.0 M Cl⁻ solution at 30 °C, in comparison with 6.4 cP and 1.45 g/mL for the 2.0 M V⁴⁺, 5.0 M SO₄²⁻ solution at the same temperature.

Thermodynamic calculations were carried out using HSC Chemistry[®] 6.1 program from Outotec Research Oy. Quantum chemistry calculations were carried out using the Amsterdam Density Functional (ADF) program.

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- [1] US Department of Energy, *Bottling Electricity: Storage as a Strategic Tool for Managing Variability and Capacity Concerns in the Modern Grid* (Electricity Advisory Committee Publication, 2008. http://www.oe.energy.gov/DocumentsandMedia/final-energy-storage_12--16-08.pdf). (Accessed Dec 2010)
- [2] B. S. Lee, D. E. Gushee, *Chem. Eng. Progr.* **2008**, *104*, S29.
- [3] Z. Yang, J. Liu, S. Baskaran, C. H. Imhoff, J. D. Holladay, *JOM*, **2010**, *9*, 14.
- [4] C. P. de León, A. Frías-Ferrer, J. González-García, D. A. Szánto, F. C. Walsh, *J. Power Sources*. **2006**, *160*, 716.
- [5] K. C. Divya, J. Østergaard, *Electr. Power Syst. Res.* **2009**, *79*, 511.
- [6] L. H. Thaller (NASA), *US Patent* 4159366, **1979**.
- [7] R. J. Remick, P. G. P. Ang (Institute of Gas Technology), *US Patent* 4485154, **1984**.
- [8] R. Zito Jr (Gel, Inc.), *US Patent* 4482614, **1984**.
- [9] M. Skyllas-Kazacos, M. Rychick, R. Robins (Unisearch Limited), *US Patent* 4786567, **1988**.
- [10] P. Zhao, H. M. Zhang, H. Zhou, J. Chan, S. Gao, B. L. Yi, *J. Power Sources* **2006**, *162*, 1416.
- [11] M. Skyllas-Kazacos, *J. Power Sources*. **2003**, *124*, 299.
- [12] S. Eckroad, "Vanadium redox flow batteries: An in-depth analysis". (Technical Report EPRI-1014836, Electric Power Research Institute, Palo Alto, CA, **2007**).
- [13] M. Skyllas-Kazacos, C. Menictas, M. Kazacos, *J. Electrochem. Soc.* **1996**, *143*(4), L86.
- [14] F. Rahman, M. Skyllas-Kazacos, *J. Power Sources* **2009**, *189*, 1212.
- [15] M. Kazacos, M. Cheng, M. Skyllas-Kazacos, *J. Appl. Electrochem.* **1990**, *20*, 463.
- [16] F. Rahman, M. Skyllas-Kazacos, *J. Power Sources* **1998**, *72*, 105.
- [17] M. Kazacos, M. Skyllas-Kazacos (VRB Power Systems, Inc.), *US Patent* 7078123 B2, **2006**.
- [18] M. Vijayakumar, L. Li, G. Graff, J. Liu, H. Zhang, Z. Yang, J. Hu, *J. Power Sources* **2010**, *196*, 3669.
- [19] S. Kim, J. Yan, B. Schwenzer, J. Zhang, L. Li, J. Liu, Z. G. Yang, M. A. Hickner, *Electrochem. Commun.* **2010**, *12*, 1650.