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RECEIVED 22 November 2025

REVISED 25 January 2026

ACCEPTED 02 February 2026

PUBLISHED 18 February 2026

CITATION

Liu CZ, Deng K, Fu K and Liu H (2026) *In-Situ* resource utilization-derived iron perchlorate redox flow battery for Mars: electrolyte characterization and extreme cold performance validation. *Front. Space Technol.* 7:1751787. doi: 10.3389/frspt.2026.1751787

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In-Situ resource utilization-derived iron perchlorate redox flow battery for Mars: electrolyte characterization and extreme cold performance validation

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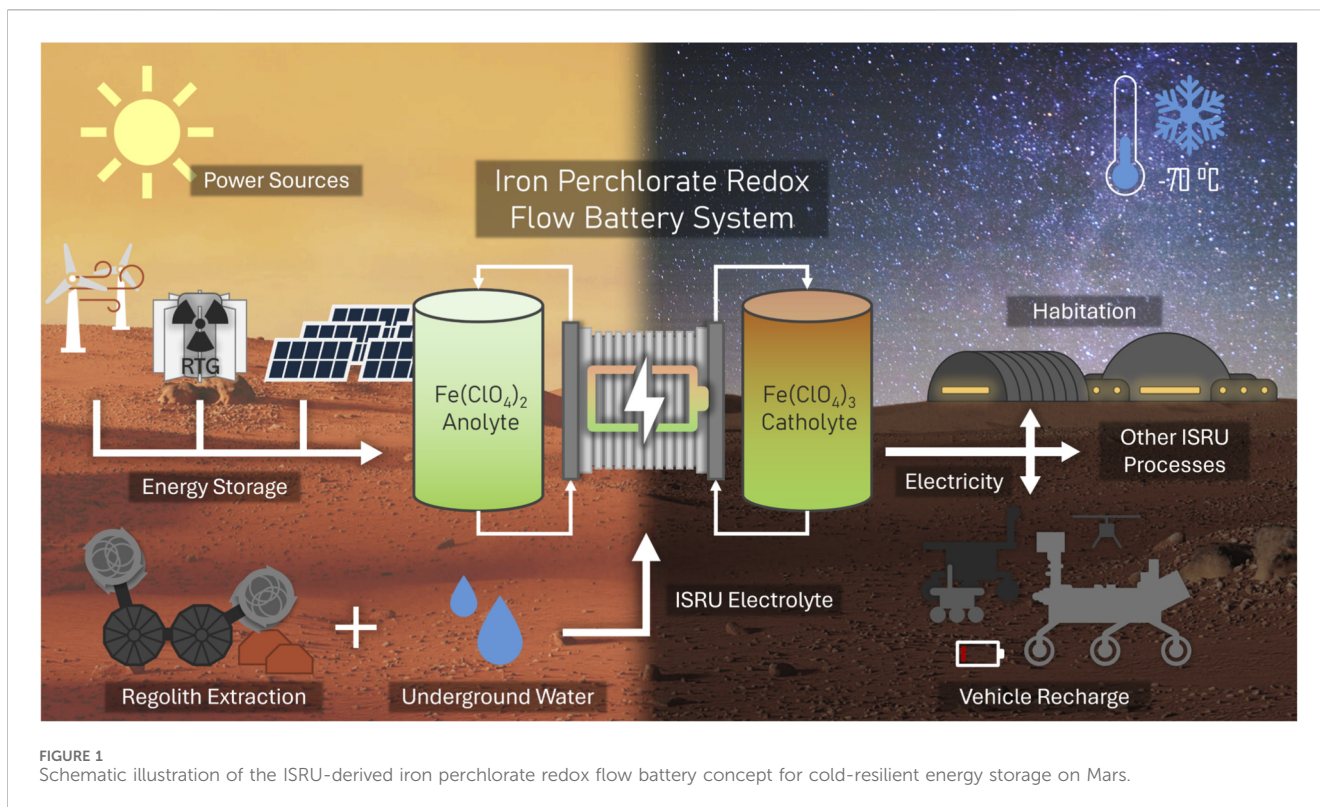
Sustained habitation on Mars demands robust energy storage systems capable of reliable operation under extreme cold, especially during night and dust storm periods that render conventional lithium-ion batteries ineffective. This work introduces an *in-situ* resource utilization (ISRU) strategy for constructing iron perchlorate redox flow batteries, fully leveraging Martian-available materials to achieve extreme cold resilience. Eutectic freezing points and ionic conductivities of three Martian-available electrolytes (iron sulfate, iron chloride, and iron perchlorate) were systematically characterized. Iron perchlorate aqueous solution at 45 wt% displayed a eutectic freezing point of -78°C , outperforming iron chloride (-55°C) and iron sulfate (-10°C). Laboratory-scale single cells were developed via computer-aided design and 3D printing, then tested under simulated Martian low-temperature conditions. The iron perchlorate system maintained 56% of its room-temperature capacity at -50°C and remained operational at -70°C , while iron chloride cells retained only 25% at -50°C and lost functionality at lower temperatures. Electrochemical impedance measurements revealed that, although electrolyte resistance increases at lower temperature, charge transfer resistance becomes the dominant limiting factor under extreme cold. The results establish that ISRU-derived iron perchlorate flow batteries offer a feasible, cold-resilient solution for reliable energy storage in future Mars surface operations and settlement, with further performance gains likely through advanced perchlorate brine formulation.

KEYWORDS

energy storage, eutectic freezing point, extreme low temperature, iron perchlorate, ISRU, Martian resources, redox flow battery

1 Introduction

As humanity prepares to set foot on Mars, the challenge shifts from simply landing to sustaining long-term habitation. Mar's environment is characterized by severe energy unpredictability: radioisotope thermoelectric generators (RTGs) provide steady but limited electrical power, while solar and wind sources are highly intermittent due to long nights, frequent dust storms, and seasonally variable weather patterns (NASA, 2025; Marspedia,

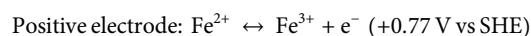
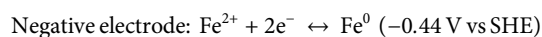


2024). To ensure continuous operation of life-support systems, scientific research, habitat infrastructure, and *in-situ* resource utilization (ISRU) processes, a robust and scalable energy storage system is indispensable (NASA, 2024; Handmer, 2024). Such a system must efficiently capture surplus energy during periods of abundance and deliver it reliably during outages or peak demand, bridging the gap between fluctuating generation and constant consumption. Without advanced, ISRU-compatible energy storage, settlements would remain vulnerable to dangerous power shortages, threatening both mission continuity and crew survival (Marspedia, 2024). Reliable, self-sustaining energy storage solutions are therefore fundamental for sustaining, growing, and safeguarding future human activities on Mars.

The thermal and environmental extremes of Mars pose formidable challenges to energy system design. Surface temperatures regularly fluctuate between approximately -13°C during the day and below -83°C at night, with winter and polar temperatures reaching down to -123°C (Barnett, 2023; Hartono, 2023). The thin carbon-dioxide-dominated atmosphere prevents effective heat retention, creating wide diurnal swings that drive thermal stress in energy systems. Traditional lithium-ion batteries (LIBs), which were used in several previous NASA missions, including Spirit, Opportunity, and Perseverance, experience substantial reductions in efficiency and capacity under such conditions because of electrolyte freezing and limited ionic mobility at low temperatures (Smart et al., 1999; Sun et al., 2023; NASA, 2025). To counter those limitations, mission designs have relied heavily on active thermal management systems, which maintain batteries above critical freezing temperatures but with significant penalties in complexity, mass, and continuous parasitic power consumption (Smart et al., 1999; NASA, 2025). These

challenges underscore the need for an intrinsically cold-resilient storage technology capable of operating without energy-intensive heating measures.

Herein, an innovative Iron Perchlorate Redox Flow Battery (IPRFB) system is meticulously conceptualized and designed to address the unique and formidable challenges of energy storage on Mars. The IPRFB concept leverages *in-situ* resource utilization (ISRU) of iron, perchlorate and water, which are abundantly available in the Martian regolith and subsurface brines (Davila et al., 2013; Rzymiski et al., 2024; Maurel et al., 2023). By producing both the anolyte and catholyte locally, the IPRFB establishes a sustainable and scalable energy storage approach inherently adapted to the Martian environment. The system architecture, illustrated in Figure 1, integrates power sources such as solar arrays, wind turbines, and RTGs with regolith extraction units to harvest both energy and chemical feedstocks. Extracted or synthesized iron perchlorates, combined with subsurface water, are processed to form ISRU-based electrolytes. At the system core lies the iron redox flow battery, a technology that decouples stored energy (held in external tanks) from power generation (within the electrochemical cell stack). The cell operates on the well-established $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple, following two half-reactions:



yielding an overall potential of approximately 1.21 V, a voltage suitable for robust and modular energy storage (Hruska and Savinell, 1981; Noack et al., 2015). During charge, surplus power from renewable sources or RTGs drives these redox reactions, storing energy chemically; during discharge, this process reverses

to supply electricity for habitats, vehicles, and ISRU operations (Figure 1).

A key innovation of this concept is the use of iron perchlorate as an electrolyte. On Mars, perchlorate salts are naturally pervasive within the regolith and polar brines and can be co-extracted with iron salts and water (Davila et al., 2013; Rzymiski et al., 2024). When dissolved near eutectic concentrations, perchlorate ions act as potent freezing-point depressants, enabling electrolytes to remain liquid at temperatures as low as -78°C (Nair and Unnikrishnan, 2020). Although laboratory data for iron perchlorate are limited, thermodynamic modeling and analogy to calcium perchlorate indicate an expected eutectic temperature below -70°C (Nair and Unnikrishnan, 2020; Nikolakakos and Whiteway, 2015). Binary or ternary magnesium-sodium perchlorate brines have been reported to remain liquid even at -93°C under Martian pressures (Nair and Unnikrishnan, 2020), emphasizing the profound anti-freeze properties of perchlorate systems. Such freeze resistance is vital for Mars operations, where equatorial surface temperatures frequently fall below -70°C during nocturnal or dust storm conditions. Implementing perchlorate-based electrolytes would therefore eliminate the need for energy-intensive heating or insulation, greatly enhancing system efficiency, reducing mass, and lowering parasitic power demand. Additionally, iron perchlorate exhibits high solubility and excellent ionic conductivity, supporting elevated energy densities and efficient charge-discharge cycling. Unlike chloride-based electrolytes commonly used in terrestrial iron flow batteries, perchlorate ions do not form complex species with iron ions, simplifying the chemistry and improving conductivity. While perchlorate's oxidative nature and toxicity pose safety challenges on Earth, these concerns are largely irrelevant on Mars, where perchlorate occurs naturally and ecological impacts differ fundamentally from terrestrial environments.

This study examines the thermophysical and electrochemical feasibility of an ISRU-derived iron perchlorate redox flow battery designed to sustain operation under Martian extreme cold. The central hypothesis posits that iron perchlorate electrolytes, formed from native Martian materials, maintain fluidity and conductivity at subfreezing temperatures and thus serve as a robust, cold-resilient medium for long-duration energy storage on Mars. To evaluate this hypothesis, the research investigates the eutectic freezing properties and ionic conductivities of potential Martian iron salts, develops a 3D-printed experimental flow battery prototype, and assesses cell performance under simulated Martian thermal conditions, validating the technical feasibility of IPRFB systems for future surface power infrastructure.

2 Materials and methods

2.1 Electrolyte characterization

Three iron salts representative of resources available on Mars, i.e., iron (II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), iron (II) chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), and iron (II) perchlorate hydrate ($\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$), were chosen for comparative analysis. All reagents were reagent-grade and handled in a dry atmosphere until use. Electrolyte solutions of varying concentrations were prepared by dissolving each salt in deionized

water pre-acidified to pH 3 with the addition of ascorbic acid, minimizing iron (II) oxidation.

Eutectic freezing points and concentrations were determined for each salt by a cooling curve method using a stainless-steel Dewar filled with a dry ice-ethanol bath (-78°C). Glass vials (20 mL) containing 10 mL of the test electrolyte were submerged and continuously monitored with a digital thermocouple until initial ice formation was visually observed, recording the corresponding temperature (Figure 2A). Concentration-dependent freezing points were established empirically to identify the eutectic for each electrolyte.

Thermal and transport properties were characterized by ionic conductivity measurement using symmetrical coin cells. Each coin cell consisted of two identical stainless-steel electrodes sandwiching a glass microfiber separator saturated with 100 μL of electrolyte. The assembled coin cells were suspended within a programmable ultra-cold freezer (USA LAB, -85°C). Conductivity was extracted via electrochemical impedance spectroscopy (EIS) employing a Gamry Interface 1010E potentiostat, sweeping 2 MHz to 1 Hz at a 10 mV excitation amplitude.

For eutectic iron perchlorate solutions, differential scanning calorimetry (Discovery DSC 250, TA Instruments) was performed to further verify phase transition behavior at extreme low temperatures. Samples were sealed in hermetic pans and scanned from 25°C to -85°C and reversal back to 25°C at a $5^{\circ}\text{C}/\text{min}$ ramp under a nitrogen atmosphere.

2.2 Cell engineering

A laboratory-scale flow battery cell was engineered using a modular design approach. Computer-aided design (CAD) was performed with Onshape software to define the geometry of major cell components, including endplates and flow frames. These cell parts were fabricated using a stereolithography (SLA) 3D printer (Anycubic Photon M3) with high-strength acrylonitrile butadiene styrene (ABS) resin.

Cell stacks were assembled in the following order: 3D-printed ABS endplates and flow frames, graphite sheet current collectors (MTI Corporation), carbon felt electrodes (MSE Supplies), Celgard 3,501 microporous polypropylene separator, and custom-cut silicone gaskets (Fuel Cell Store) for sealing. Electrical connection was achieved through graphite sheets in direct contact with external leads. All seals, gaskets, and tubing (high-purity silicone) were chosen for compatibility with concentrated perchlorate and chloride electrolytes.

The assembled single cell was integrated into a laboratory-scale flow system comprising a peristaltic pump (Gikfun), silicone tubing, and borosilicate glass electrolyte reservoirs (250 mL). After assembly, the complete system was tested for leakage by recirculating deionized water at operational flow rates. Cells demonstrating no leakage or mechanical failure proceeded to electrolyte addition and electrochemical evaluation.

2.3 Flow battery testing protocol

All electrochemical measurements were conducted using a Gamry Interface 1010E potentiostat. Prior to each test, the required iron

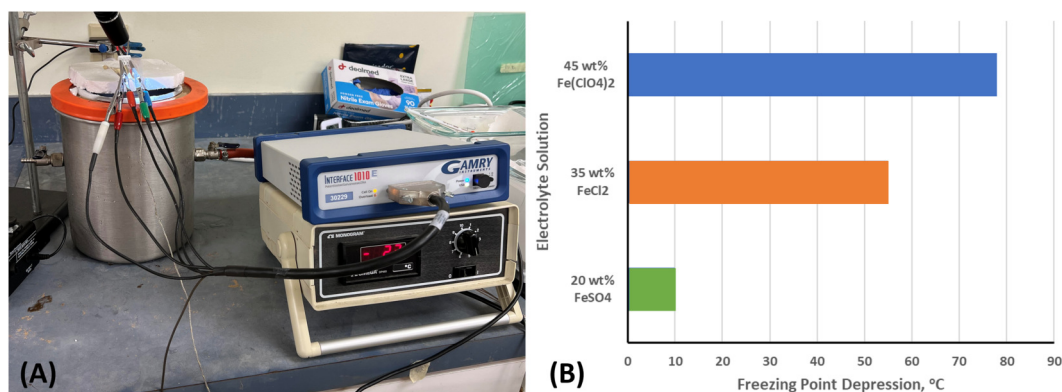


FIGURE 2 (A) Experimental setup for freezing point screening using a dry ice-ethanol bath and temperature monitoring. (B) Bar chart of empirically observed freezing point depression for 20 wt% FeSO₄, 35 wt% FeCl₂, and 45 wt% Fe(ClO₄)₂ aqueous solutions.

electrolyte (either chloride or perchlorate formulation at the experimentally determined eutectic concentration) was circulated through the cell at room temperature for 30 min to ensure complete wetting of the electrode surfaces and separator. Open-circuit voltage (OCV) was recorded following circulation/equilibration.

Charge-discharge experiments were performed at varying current densities, while charging was conducted at 25 °C and discharging was proceeded at the studied temperatures: 25 °C, 0 °C, -25 °C, -50 °C, and -70 °C. The charge-discharge temperatures are intended to approximate Martian natural diurnal temperature cycle. A set of current densities (from 10 to 100 mA/cm²) were explored in preliminary tests to determine appropriate operating conditions for performance comparison. Charging was terminated at cut-off capacities (as per electrolyte volume) or a maximum set voltage of 2.0V. 2 wt% ascorbic acid was added to the electrolytes as a sacrificial hydrogen evolution suppressor, intended to limit losses from the hydrogen evolution side reaction (HER) and stabilize the cell's pH. At the fully charged state, AC impedance spectroscopy was carried out (10 mV perturbation, 2 MHz-1 Hz) to quantify system resistance and charge transfer kinetics. Discharging was then initiated at specific current densities down to a terminal voltage of 0.4 V at reference temperatures.

Experimental data, including temperature, voltage profiles, cell resistance, and discharge capacity, were rigorously logged and later analyzed for cold-performance assessment. This protocol was conducted in both the iron chloride and iron perchlorate battery systems to ensure a direct, controlled comparison.

3 Results

3.1 Electrolyte characterization

3.1.1 Eutectic freezing point and concentration screening

A series of freezing point depression experiments was conducted using iron (II) sulfate, iron (II) chloride, and iron (II) perchlorate

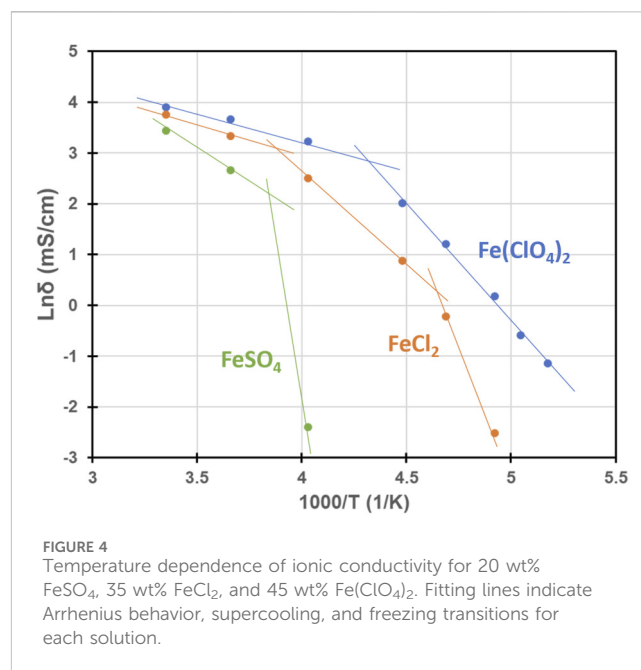
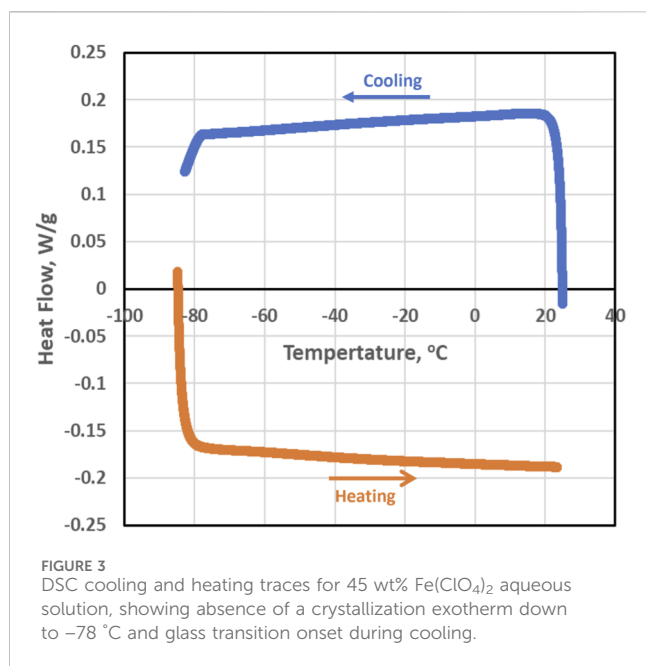
solutions, each tested near their respective solubility limits. Solutions were prepared at 20 wt% for FeSO₄, 30 wt%, 35 wt%, and 40 wt% for FeCl₂, and 40 wt%, 45 wt%, and 50 wt% for Fe(ClO₄)₂. Each solution was placed in a glass vial and rapidly cooled using a dry ice-ethanol bath, while temperature was monitored with a digital thermocouple.

For 20 wt% FeSO₄, crystallization appeared at -10 °C and the solution completely froze at -20 °C. Lower temperatures or higher concentrations led to incomplete dissolution and immediate freezing. FeCl₂ solutions exhibited a more significant freezing point depression as concentration increased. The 30 wt% FeCl₂ solution began to crystallize at approximately -50 °C, the 35 wt% solution at -55 °C, and the 40 wt% solution at -57 °C. However, precipitation was evident in the 40 wt% solution, indicating the practical eutectic is near 35 wt%. For Fe(ClO₄)₂, the 40 wt% solution started to freeze at -69 °C, while both 45 wt% and 50 wt% concentrations remained liquid at -78 °C; precipitation was observed in the 50 wt% solution.

Based on these results, the eutectic concentrations and corresponding freezing points were determined to be 20 wt% FeSO₄ at -10 °C, 35 wt% FeCl₂ at -55 °C, and 45 wt% Fe(ClO₄)₂ at -78 °C (Figure 2B). These findings closely align with values reported in earlier studies for FeSO₄ and FeCl₂ (Chevrier, et al., 2009; Nair and Unnikrishnan, 2020), and with the known cryoprotective behavior of Martian perchlorate brines such as Mg(ClO₄)₂ solutions (Nair and Unnikrishnan, 2020; Davila et al., 2013; Marion et al., 2010; Bishop et al., 2014). The results clearly show that iron perchlorate electrolytes enable the lowest temperature liquid operation among the iron salts tested.

3.1.2 Differential scanning calorimetry validation

Differential scanning calorimetry (DSC) was used to validate the thermal behavior of 45 wt% Fe(ClO₄)₂ aqueous solution, supporting its suitability for low-temperature flow battery applications. Experiments were conducted with a TA Instruments Discovery DSC at a scan rate of 5 °C/min. The sample was cooled from 25 °C to -85 °C, held isothermally for 1 min, then heated back to 25 °C. Figure 3 shows the recorded cooling and heating curves. It



should be noted that this instrument uses a reversed heat flow convention, with exothermic transitions depicted as positive and endothermic as negative, opposite to the standard IUPAC convention. At the initial cooling and heating, spikes near 25°C (cooling) and near -85°C (heating) were observed, reflecting instrumental artifacts rather than sample phase transitions. After these transients, the cooling curve displayed a consistent slope with no exothermic peaks down to -78°C , indicating persistent supercooling and the absence of ice crystallization. A distinct downward shift in heat flow at approximately -78°C signaled the glass transition (T_g) of the concentrated brine, corresponding to a decrease in heat capacity as the sample entered a vitrified, glassy state. During the subsequent heating cycle, aside from the initial artifact, the thermogram retained a gradual slope, and no melting endotherm was detected up to 25°C .

These data confirm that the 45 wt% $\text{Fe}(\text{ClO}_4)_2$ solution exhibits extreme freezing suppression, with no evidence of ice crystallization within the accessible temperature range and stable formation of a glassy phase below -78°C . The observed behavior is consistent with prior studies of perchlorate-stabilized metastable brines on Mars, which also report persistent supercooling and vitrification in high-perchlorate systems (Toner et al., 2014; Cull et al., 2010).

3.1.3 Ionic conductivity vs. temperature

Ionic conductivity measurements were carried out on the three Mars-relevant iron salt electrolytes at their experimentally determined eutectic concentrations: 20 wt% FeSO_4 , 35 wt% FeCl_2 , and 45 wt% $\text{Fe}(\text{ClO}_4)_2$. Electrolyte samples were loaded into symmetric coin cells and equilibrated at controlled temperatures ranging from room temperature down to -70°C . Conductivity was determined via electrochemical impedance spectroscopy and plotted as the natural logarithm of conductivity ($\text{Ln } \sigma, \text{mS/cm}$) versus inverse temperature ($1,000/T, 1/\text{K}$) in Figure 4.

All three electrolytes showed Arrhenius-like conductivity behavior at higher temperatures, with conductivity decreasing

smoothly as temperature dropped. However, clear divergence occurred below the freezing onset of each solution. For FeSO_4 , a marked drop in conductivity was observed at -25°C , in agreement with its rapid crystallization in freezing point experiments. FeCl_2 followed a similar trend, maintaining conductivity down to about -50°C , after which values dropped sharply, consistent with the previously identified eutectic freezing point. Because its freezing point is too high, FeSO_4 electrolyte was screened out of the following electrochemical performance evaluation.

In contrast, 45 wt% $\text{Fe}(\text{ClO}_4)_2$ retained high ionic conductivity even at -70°C . The appearance of an extended supercooling regime and delayed conductivity decline reflects the suppression of ice crystallization and formation of a metastable glassy state, as observed in the DSC data. The persistence of measurable conductivity in $\text{Fe}(\text{ClO}_4)_2$ at temperatures where FeSO_4 and FeCl_2 have already transitioned to insulating solids further highlights perchlorate's unique advantage for subzero Martian battery operation.

These results are fully aligned with the findings from freezing point screening and DSC analysis, confirming that iron perchlorate solutions combine low freezing points with robust ionic transport, making them exceptionally well-suited for cold-resilient Mars flow battery electrolytes.

It is worth noting that the ionic transport in a supercooled phase is still through cooperative rearrangements of the liquid network. On further cooling through the glass transition, the electrolyte vitrifies and becomes a disordered solid-like matrix; ionic motion then occurs mainly via localized hopping with much lower mobility. This glassy conduction mechanism likely preserves an ion-conducting phase without crystallization below the T_g (-78°C), but constrains sustainable current density and only favors low-rate discharge for long-term stability in the vitrified regime. To further improve the cold resilience of this battery system, deep eutectic composite perchlorate electrolytes with lower glass transition temperatures and freezing points will be explored in future work.

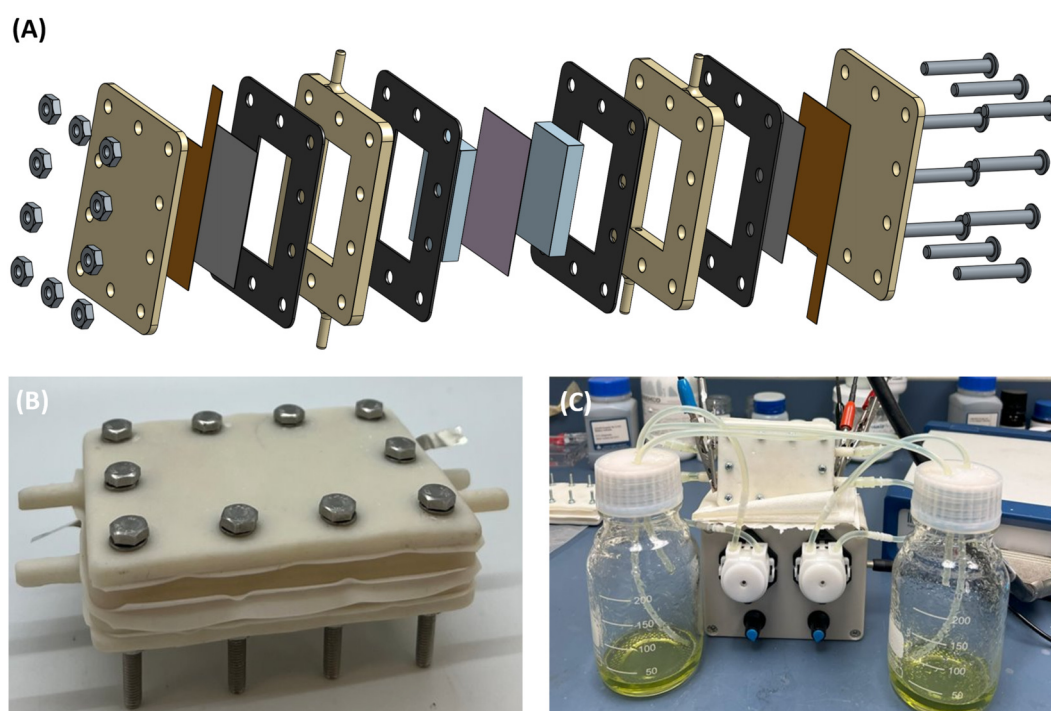


FIGURE 5
Flow cell assembly: (A) exploded-view CAD schematic, (B) assembled single cell, and (C) laboratory-scale flow battery system.

3.2 Flow cell design and fabrication

A modular flow cell was engineered to test the battery performance of iron perchlorate and iron chloride electrolytes under Martian-relevant conditions. The cell design was developed using computer-aided design (CAD), and an exploded-view schematic of the component assembly is shown in Figure 5A. The assembly is composed of a pair of ABS endplates, multiple flow frames and bipolar plates also 3D printed in ABS resin, graphite sheet current collectors, Celgard separator, carbon felt electrodes (width 2.4 cm x length 4.4 cm), and silicone rubber gaskets for sealing. Stainless steel bolts securely fasten the assembly and maintain compression during operation. Figure 5B presents a completed single cell after assembly and tightening. The cell features dual inlet and outlet ports for electrolyte circulation. For full-system operation, the flow cell was incorporated into a laboratory-scale flow battery system, illustrated in Figure 5C. The system consists of the flow cell, peristaltic pumps to drive electrolyte flow through the cell, and external glass reservoirs for the anolyte and catholyte. All components are connected using chemically resistant tubing and fitted for leak-tight operation. This setup enabled reliable charge-discharge testing and temperature-variable experiments under controlled laboratory conditions.

A critical aspect of cell engineering was the selection of an appropriate separator to balance ionic conductivity and redox species crossover. Four candidate materials were screened: Whatman Glass Microfiber Filters GF/F (pore size 0.7 μm), Nylon Membrane Filters (0.22 μm), Celgard 3,501 microporous polypropylene separator (pore size 64 nm), and PFSA D125-U dense

proton exchange membrane. Both the glass microfiber and nylon membrane separators exhibited high ionic conductivity but allowed significant crossover of iron and perchlorate species, which led to reduced Coulombic efficiency and limited cell lifetime. In contrast, the dense PFSA membrane effectively blocked crossover but introduced prohibitively high cell resistance, resulting in severe polarization losses. The Celgard 3,501 separator provided a favorable compromise, combining low area-specific resistance with adequately suppressed crossover, likely due to its fine pore structure and hydrophobic polypropylene matrix. This choice is consistent with recent studies that demonstrate Celgard 3,501 achieves low total cell resistance and stable operation in various aqueous flow battery applications (Yuan et al., 2019).

3.3 Electrochemical cell performance under cold conditions

To simulate Martian power scenarios, flow batteries were charged at room temperature and discharged at progressively colder conditions, reflecting day-night and dust storm thermal cycles on Mars. A critical element in these tests was balancing the catholyte and anolyte volumes to manage the freezing-point dynamics during discharge. Electrolyte volumes were configured so that the cathode reservoir contained three times the volume of the anode reservoir, each starting at 45 wt% $\text{Fe}(\text{ClO}_4)_2$ or 35 wt% FeCl_2 concentration. This volume ratio ensures, after discharge, that Fe^{2+} ions in the anolyte are replenished through controlled crossover from the catholyte, maintaining electrolyte concentrations above

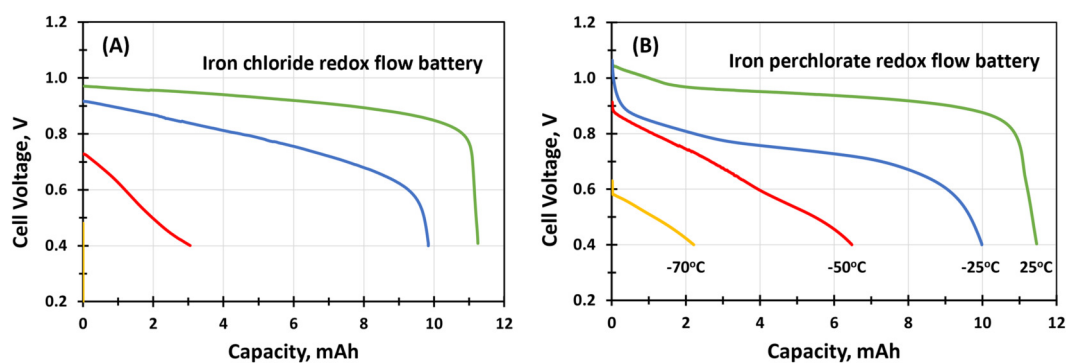


FIGURE 6 Discharge curves at 25 °C, -25 °C, -50 °C, and -70 °C for (A) iron chloride redox flow battery and (B) iron perchlorate redox flow battery.

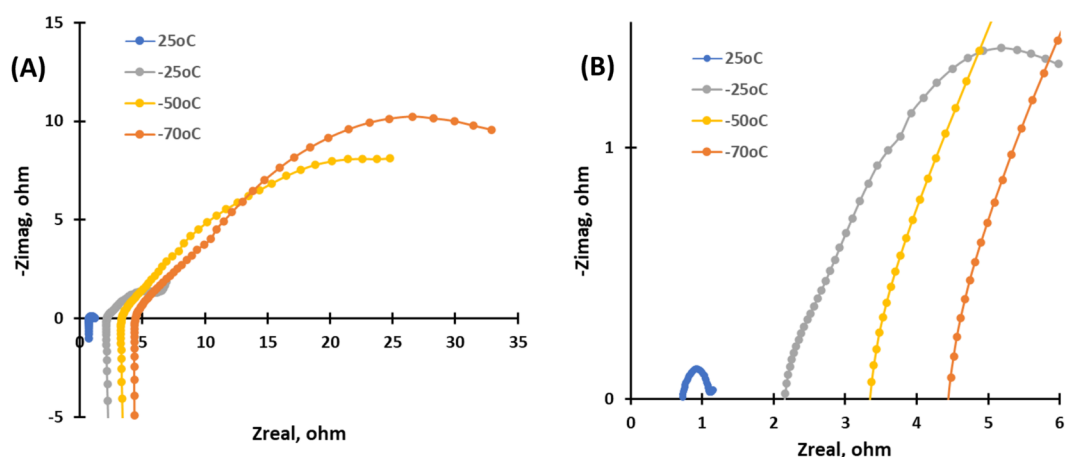


FIGURE 7 (A) Electrochemical impedance spectra of iron perchlorate redox flow battery at different discharge temperatures. (B) Zoomed spectra highlighting evolution in solution resistance and charge transfer resistance.

their eutectic freezing points and preventing localized freezing, despite Fe deposition at the anode.

The cells were pre-charged under pump circulation of electrolytes at 50 mA/cm² at room temperature, using stipulated capacity cutoffs, which were calculated for converting 2/3 of catholyte from Fe(II) to Fe(III). This ensured an excess charge capacity for the cold-temperature discharge test and minimized hydrogen evolution reactions (HER) effects on the comparison of discharge capacities. With charge capacity increase, the catholyte color changed from pale green to yellow eventually to brown, while the anolyte color initially changed to lighter green but eventually maintained pale green due to ion crossover. The charged cells with pump turn-off were placed in the freezer for temperature reduction and a 1-h hold at the target cold temperatures. Discharge was then performed with steady electrolytes at a consistent current of 10 mA/cm² to a cutoff voltage of 0.4 V.

Figures 6A,B display the discharge profiles for the iron chloride and iron perchlorate flow batteries across all tested temperatures. At 25 °C and -25 °C, both chemistries exhibited nearly identical

performance, indicating comparable kinetics and mobility in moderate conditions. Marked divergence emerged at -50 °C: the Fe(ClO₄)₂ cell retained 56% of its room-temperature capacity, whereas the FeCl₂ cell retained only 25%. At -70 °C, only the perchlorate flow battery remained operational, while the chloride-based cell failed to discharge. The observed larger IR drop in the iron perchlorate cell versus the iron chloride cell could be related to differences in concentration, viscosity and wettability, indicating the cell performance is not only impacted by bulk electrolyte conductivity but also by electrolyte/electrode interface resistance.

Impedance spectra (Figure 7), measured for the iron perchlorate battery at varied temperatures, reveal quantitatively the evolving cell resistance. Solution resistance increased modestly, from 0.7 Ω at 25 °C to 2.1, 3.3, and 4.4 Ω at -25, -50, and -70 °C, respectively. However, charge transfer resistance changed much more substantially, climbing from 0.4 Ω at 25 °C to 6, 33, and 42 Ω at colder setpoints. This indicates that as temperatures decrease, overall cell performance becomes increasingly limited by charge transfer processes rather than simple ionic conductivity. Perchlorate

ions are known to have weak complexation with iron ions, a significant contrast to the strong complexation observed with chloride ions. This weak interaction is advantageous at extreme cold temperatures because it reduces desolvation energy and promotes more favorable charge transfer kinetics.

This study demonstrates that iron perchlorate flow batteries retain 56% of room-temperature discharge capacity at -50°C and remain operational at -70°C , whereas comparable iron chloride systems retain only 25% at -50°C and entirely fail at lower temperatures. These results extend the operational temperature window of aqueous redox flow batteries for Mars applications by at least 20°C compared to prior terrestrial studies using chloride- and sulfate-based electrolytes, which are typically limited by electrolyte freezing or severe performance loss below -50°C .

4 Discussion

This work demonstrates that iron perchlorate electrolytes enable the lowest freezing points and functional stability at extreme cold, consistent with the fundamental properties of perchlorate brine. The strong freezing point depression arises from the high solubility and weak hydration shell of perchlorate ions, which disrupt water's hydrogen-bond network and allow solutions to remain liquid far below the eutectic limits of chloride or sulfate-based salts (Toner and Catling, 2016; Nair and Unnikrishnan, 2020; Cull et al., 2010; Marion et al., 2010). As observed in this study and corroborated by Martian brine modeling, concentrated perchlorate solutions exhibit glass transitions and supercooling that permit liquid or amorphous states down to -78°C and below, far outpacing alternative salts such as MgSO_4 , NaCl , or KCl (Cull et al., 2010; Bishop et al., 2014; Toner and Catling, 2016). The lack of strong perchlorate-iron complexation further benefits the system by lowering the desolvation and charge transfer barriers, maintaining favorable kinetics even under high viscosity at low temperature.

From a system design perspective, these findings support iron perchlorate-based flow batteries as a highly promising option for Mars energy storage. The use of *in-situ* derived iron and perchlorate resources is directly aligned with ISRU strategies now prioritized for sustainable Martian infrastructure (Davila et al., 2013; Kleinhenz and Paz, 2017). Although iron perchlorates have not yet been directly detected in past Mars missions, established displacement reactions among known Martian salts, such as conversion of $\text{Ca}(\text{ClO}_4)_2$ and FeSO_4 to $\text{Fe}(\text{ClO}_4)_2$, relying on the low solubility of CaSO_4 , offer a realistic chemical pathway for ISRU synthesis of iron perchlorate. This scenario leverages both the energetic and practical benefits of utilizing locally available materials. Recent advances in engineering also promote additive manufacturing as a route for on-site production of battery hardware using 3D printing, which can further reduce landed mass and enable scalable deployment for future Mars settlements (Maurel et al., 2023). The specific ISRU protocols to obtain these battery materials will be explored in future work.

A challenge inherent to iron-based aqueous batteries, especially at low pH, is the hydrogen evolution reaction (HER) occurring at the charged negative electrode. HER reduces Coulombic efficiency and may cause pH drift, limiting long-term performance. In this work,

the use of ascorbic acid as a sacrificial additive partially suppressed HER by serving as an auxiliary redox sink. Other approaches from literature, such as pulsed charging, optimized electrolyte formulation, using organic or ionic additives and integration of a proton pump, provide sufficient avenues to suppress HER and extend battery lifetime (Zeng et al., 2021; Liu et al., 2025; ESSInc, 2025). The terrestrially commercial iron chloride redox flow battery system (EES, Inc., 2025) has demonstrated $>10,000$ cycles for a lifetime of 25 years. Due to the complexity of managing HER at low temperatures and the lengthy equilibration needed for freeze-thaw cycles, this study did not assess long-term cycling performance. Extended cycling at subzero conditions requires prolonged testing, which was beyond this work's practical scope. Evaluating durability, capacity retention, and degradation in cold-adaptive protocols will be a key focus for future work.

Future research should investigate even more deeply supercooled "complex perchlorate brines," including binary and ternary mixtures (e.g., with Mg^{2+} , Na^+ , Ca^{2+}), which according to Martian brine models may stay liquid to nearly -100°C (Cull et al., 2010; Bishop et al., 2014; Toner and Catling, 2016). By tuning composition and cooling protocols, the operational window for ISRU-derived Mars batteries may be extended throughout the coldest Martian environments, supporting round-the-clock operations even under the harshest conditions.

The present work is based on laboratory-scale prototypes and controlled, simulated Martian thermal cycling in Earth-based test chambers. While the results robustly demonstrate subfreezing operation and electrolyte resilience, limitations include the use of small cell formats and non-continuous cycling operation. In our system-level concept, the battery enclosure is assumed to follow the natural diurnal temperature cycle at an equatorial Mars site, without additional dedicated heaters or coolers. Charging occurs during the warmer daytime period, while discharge is scheduled as the system cools overnight. In realistic Mars mission scenarios, some level of integrated thermal management using waste heat or available power sources (e.g., RTGs, solar arrays, or the battery itself) would still be required to optimize overall energy efficiency and ensure reliable operation over long durations. Real Martian field conditions involve additional factors such as microgravity, radiation, and long-duration cycling, which may further influence flow battery performance. Additional validation in larger-scale cells and extended campaigns, including space or Mars-analog testbeds, will be necessary to confirm the full feasibility of this technology for planetary deployment.

5 Conclusion

This study establishes that iron perchlorate redox flow batteries, constructed from Martian-available resources, can retain substantial energy storage capability even under conditions of extreme cold relevant to Mars surface operations. Through experimental electrolyte screening, it was found that 45 wt% $\text{Fe}(\text{ClO}_4)_2$ solutions possess an exceptionally low freezing point and maintain high ionic conductivity, supporting functional discharge at temperatures down to -70°C . These attributes are unmatched by terrestrial existing (either iron sulfate or iron chloride) systems and are directly attributable to the unique cryoprotective properties of perchlorate ions.

The successful fabrication and laboratory testing of a modular flow battery cell, using ISRU-compatible engineering methods, demonstrates the practical viability of such technologies for Mars settlement. By carefully managing electrolyte composition, separator selection, and reservoir volumes, the proposed battery design avoids freezing-induced failures and maximizes operational robustness.

Limitations including hydrogen evolution at the negative electrode were mitigated using sacrificial additives, with further improvements possible through advanced electrolyte and system engineering. The results highlight iron perchlorate flow batteries as a leading candidate for sustainable, scalable, and cold-resilient energy storage on Mars. Future work should focus on optimization of electrolyte formulations, integration with Martian resource extraction processes, and long-duration cycling to further advance the readiness of this technology for planetary deployment.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

CL: Conceptualization, Methodology, Writing – original draft, Writing – review and editing, Formal Analysis, Visualization, Investigation, Validation, Data curation. KD: Writing – review and editing, Investigation, Data curation, Formal Analysis. KF: Supervision, Writing – review and editing, Resources. HL: Resources, Conceptualization, Project administration, Methodology, Writing – review and editing, Funding acquisition, Supervision.

Funding

The author(s) declared that financial support was not received for this work and/or its publication.

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Acknowledgements

CL gratefully acknowledges Michael Valenti of the Charter School of Wilmington for supporting and mentoring his science fair project. The work was sponsored by Talos Tech LLC and benefited from research facilities and resources provided by the University of Delaware. CL recognizes Talos Tech and the University of Delaware for offering formative internship experiences that enabled the completion of this study.

Conflict of interest

Authors CL and HL were employed by Talos Tech LLC.

The remaining author(s) declared that this work was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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