High-energy and low-cost membrane-free chlorine flow battery

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Grid-scale energy storage is essential for reliable electricity transmission and renewable energy integration. Redox flow batteries (RFB) provide affordable and scalable solutions for stationary energy storage. However, most of the current RFB chemistries are based on expensive transition metal ions or synthetic organics. Here, we report a reversible chlorine redox flow battery starting from the electrolysis of aqueous NaCl electrolyte and the as-produced Cl2 is extracted and stored in the carbon tetrachloride (CCl4) or mineral spirit flow. The immiscibility between the CCl4 or mineral spirit and NaCl electrolyte enables a membrane-free design with an energy efficiency of >91% at 10 mA/cm2 and an energy density of 125.7 Wh/L. The chlorine flow battery can meet the stringent price and reliability target for stationary energy storage with the inherently low-cost active materials (~$5/kWh) and the highly reversible Cl2/CI− redox reaction.
Incorporating renewable energy, such as solar and wind power, is essential to reducing carbon emissions for sustainable development. However, large-scale utilization is hindered by the intermittence and uneven distribution of these power sources. Implementation of grid-scale energy storage is essential to mitigating the mismatch between electricity production and consumption. Different technologies are developed for this purpose, including supercapacitors, sodium–sulfur batteries, pump hydro, flywheels, and superconducting magnetic energy storage systems for large-scale applications due to the lower capital cost, higher energy conversion efficiency, and facile modularity. The cores of flow cells are the circulating electrolytes that carry the redox-active materials for energy storage and release.

Currently, the all-vanadium RFB is the most researched and developed RFB chemistry; however, the market adoption of this system has been hampered by high-cost chemicals (material cost close to 60% of the overall system cost) and low energy density. Although aqueous solvents organic redox species offer a potential option for low-cost materials, the synthetic processes required to customize the molecular structure for high solubility and optimal potential will again limit the material cost and availability. Also, they rely on the costly ion-permeable membranes to reduce cross-over, further increasing capital and maintenance costs.

Recently, polymer redox couples were developed to circumvent ion-permeable membranes, and the semi-solid Li-ion (suspensions of Li-ion battery active materials in nonaqueous electrolytes) systems have been explored for higher energy density and efficiency. However, high viscosity, lower peak power operation time, and high material cost emerged with these systems. To meet the needs of RFB chemistries with the naturally abundant and low-cost redox-active materials, we report a new RFB system that capitalizes the electrolysis of saltwater or aqueous NaCl electrolyte using the Cl2/Cl− redox couple as the active material for the positive electrode. The Cl2/Cl− has a theoretical capacity of 755 mAh/g, more than two times that of vanadium oxides (VO2+/VO2++ versus 226 mAh/g) used in current RFBs. Cl2/Cl− redox chemistry is a fast single-electron transferred reaction with an activation energy of 35.5 kJ/mol, which is comparable to or even smaller than that of VO2+/VO2++ versus normal hydrogen electrode (NHE). During charge, the Cl2 was generated from oxidizing the Cl−/Cl2 redox couple using the Cl2/Cl− redox reaction to be a promising candidate for RFB.

Rarely heard in the battery history is that Cl2/Cl− redox couple was used in the RFB to power the first fully controlled airship La France in 1884. The Cl2/Cl− based batteries are often typified by low Coulombic efficiency (CE) of 40–70% due to Cl2 dissolution in the electrolytes and large voltage hysteresis (0.7 V at 32 mA/cm²) due to non-wettability between electrolytes and electrodes, which limits the energy efficiency to around 60%. Graphite was reported as chlorine storage host via intercalation. However, the instability of Cl− intercalated graphite at room temperature results in low storage capacity (35–40 mAh/g) and limited cycle life. After that, no other materials with appropriate stability, storage capacity, and reaction kinetics have been reported to enable reversible Cl2 electrochemical reaction.

Our objective is to develop a new RFB with the highly reversible Cl2/Cl− redox species through electrolyzing the saturated NaCl aqueous electrolyte (NaCl/H2O) and storing the as-produced Cl2 in water-immiscible organic phases such as carbon tetrachloride (CCl4) or mineral spirits. These organic phases provide several desirable properties: (1) Cl2 in CCl4 (Cl2-CCl4) delivers a volumetric capacity of 97 Ah/L due to high solubility of Cl2 in CCl4 (0.184 mole/mole CCl4), which is a 2 to 4 times improvement over the current vanadium-based catholyte (22.6–43.1 Ah/L). (2) The Cl2-CCl4 is immiscible to NaCl/H2O, thus requires no membrane to prevent cross-over, further reducing costs; (3) The Cl2-CCl4 has low and constant viscosity of 0.819 mPa.s, in contrast to high and varying viscosity of aqueous vanadium-based catholyte (1.4–3.2 mPa.s), thus is easy to flow; (4) Cl2-CCl4 can wet carbon porous electrodes easily, which significantly enhances the surface area for Cl2 storage and reaction; (5) Cl2 has high diffusivity in CCl4, minimizing energy dissipation for mass transport.

Results
Storage and electrochemical performance of Cl2-CCl4. The Cl2/Cl− redox reaction in NaCl/H2O was evaluated in a concentric cell with RuO2-TiO2 coated porous carbon (RuO2-TiO2@C) as a working electrode, activated carbon as a counter electrode (Fig. S1), and Ag/AgCl as the reference electrode (Fig. 1A). The RuO2-TiO2 catalysts on porous carbon (Figs. S2, S3) are used to promote the oxidation kinetics of chloride and Cl2 electrochemistry. CCl4 was pumped through the working electrode, and the NaCl/H2O through the interstitial space between the working and counter electrodes to ensure adequate Cl2 supply. While CCl4 and NaCl/H2O entered the RuO2-TiO2@C electrode as separate flows, they both wet the carbon electrode, demonstrated by <90° contact angles (CAs) on a graphite plate electrode (Fig. 1B, C). The liquid CCl4 and NaCl/H2O volume in the RuO2-TiO2@C electrode, respectively (see the determination of percentage volume in Supplementary Note 1). The ion-permeable membrane used in traditional RFBs to prevent cross-contamination is not required here since the Cl2-CCl4 and NaCl/H2O are phase separated.

During charge, the Cl2 was generated from oxidizing the Cl− in the RuO2-TiO2@C electrode. The reaction shows a potential at 1.2 V versus Ag/AgCl reference electrode (1.36 V versus normal hydrogen electrode (NHE)). During discharge, the Cl2 in CCl4 was reduced to Cl− in the working electrode and entered the NaCl/H2O (see the formulation for positive electrode reaction). The presence of CCl4 flow significantly enhances the coulombic efficiency (CE) from 8 to 97% (Fig. 1D). Because the solubility of Cl2 in CCl4 is three orders of magnitude higher than that in NaCl/H2O (0.184 mole/mole CCl4 versus 0.0005 mole/mole NaCl/H2O), the Cl2 generated during the charging process can be stored in CCl4, which prevents Cl2 diffusion into NaCl/H2O as supported by Raman spectroscopy (Fig. S5) and the positive Gibbs free energy to transfer Cl2 from CCl4 to NaCl/H2O (Fig. S6). When 60 mL CCl4 was used, a maximum reversible capacity for Cl2/Cl− conversion is 600 mAh (Fig. S7), rendering the capacity of 97 Ah/L for the Cl2-CCl4.

Positive electrode reaction.

\[ \text{Cl}_2^- - 2e^- \rightarrow \text{Cl}_2 \quad E^0 = 1.36 \text{V (versus NHE)} \]

The Cl2-CCl4 positive electrode has a low and almost consistent viscosity. The current of Cl2 increases from 0 to 0.184 mole/mole CCl4 (saturation), the viscosity even slightly decreases from 0.894 to 0.819 mPa.s (Fig. 1P) in accord to Eyring's absolute reaction rate theory for gas–liquid mixtures. On the other hand, the viscosity of common catholyte could increase by several or even dozen times as the concentration of solute increases. The low viscosity of Cl2-CCl4 reduces the pumping loss, and the steady viscosity minimizes the
volumetric transfer between catholyte and anolyte at different SOCs\textsuperscript{50,51}.

Full chlorine flow battery (CFB). To fabricate a full CFB, the activated carbon counter electrode was replaced by NaTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} negative electrode (Fig. 2A). NaTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (Figs. S8, S9) was chosen as the negative electrode due to low potential (−0.5 V (versus NHE)), rapid and reversible Na-ion insertion/extraction in NaCl/H\textsubscript{2}O, demonstrated by the symmetric anodic and cathodic peaks with 60 mV separation in the cyclic voltammetry (negative electrode reaction and Fig. S10A)\textsuperscript{52}. The NaTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} shows a 65% capacity retention even at the C-rate of 315 C (1 C = fully discharge/charge within 1 hour, Fig. S10) and long cycle life of 1000 cycles (Fig. S11).

Negative electrode reaction.

$$\text{Na}_3\text{Ti}_2(\text{PO}_4)_3 - 2e^- - 2\text{Na}^+ \leftrightarrow \text{NaTi}_2(\text{PO}_4)_3$$

E\textsubscript{0} = −0.5 V (versus NHE)

While the overpotentials enhanced (orange dash lines in Fig. 2B, C) as the current density increased, the discharge capacities did not vary (Fig. 2B, C), which could be attributed to the large reaction surface area endowed by the wetting between carbon electrode and Cl\textsubscript{2}-CCl\textsubscript{4} (Fig. 1B, C). Fig. 2D demonstrates cell voltage efficiency (defined as the potential ratio of discharge to charge) of 93.6% at 10 mA/cm\textsuperscript{2} and ~77% at 100 mA/cm\textsuperscript{2}. The multiplications of discharge capacity and voltage gives the cell power density that peaks at 325 mW/cm\textsuperscript{2} when operated at 350 mA/cm\textsuperscript{2} (Fig. 2E). It is worth noting that polarizations for discharge are more significant than those for discharge (Fig. 2B, C). In the CFB, overpotentials are caused by redox reactions and concentration gradient. Since the symmetric factors for Cl\textsuperscript{−}/Cl\textsubscript{2} redox reactions are equal\textsuperscript{17,25} the overpotentials needed to drive the reduction and oxidation reaction are the same, the different overpotentials for charge and discharge observed here could only be attributed to the concentration gradient.

A steady-state model was developed to understand the species distribution and controlling steps in the CFB. The Nernst-Plank equation was applied to the porous RuO\textsubscript{2}-TiO\textsubscript{2}@C electrode (cell width = 0–1.0 mm in Fig. 2A), and NaCl/H\textsubscript{2}O (cell width = 1.0–4.0 mm in Fig. 2A), Fick’s equation was applied to the Cl\textsubscript{2}-CCl\textsubscript{4} phase (cell width = 2.0–0 mm in Fig. 2A). The negative electrode was involved implicitly at the boundary of the NaCl/H\textsubscript{2}O (cell width = 4.0 mm in Fig. 2A) (see model description and Tables S1–S4 in Supplementary Note 1). The model was validated by the agreement between the simulated and experimental cell voltages (black lines and dots in Fig. 3A, B, experimental potential retrieved from Fig. 2B, C) at the same flow rates and current densities.
The model was then used to visualize the species distribution in the NaCl/H2O and in Cl2–CCl4. During charge, the Cl− in NaCl/H2O was consumed inside the porous carbon electrode (Fig. 3C) and limits the reaction kinetics; during discharge, Cl2 in CCl4 is consumed and limits the reaction kinetics. The Cl− concentration gradients are more significant than the Cl2 concentration gradient in the porous electrode for both charge and discharge (Fig. 3C, D), which is the result of a smaller diffusivity of Cl− (1.5 × 10−5 cm2/s) for Cl−, 2.0 × 10−5 cm2/s for Cl2 in NaCl/H2O and 3 × 10−5 cm2/s for Cl2 in CCl4 and lower volume percentage of NaCl/H2O than CCl4 in the porous carbon electrode. The distinct species that control charge and discharge kinetics thus generate the asymmetric charge and discharge overpotentials (Fig. 2B, C). Since Cl− and Cl2 are in different phases, increasing the flow rate of NaCl/H2O during charge and that of the Cl2–CCl4 during discharge enhance the mass transport of the limiting species accordingly, in which not only the overpotentials reduce, but the current density range allowing steady cell voltage extends (inset of Fig. 3A, B). At the highest flow rate examined, the voltage efficiency could be postulated to >93% at 20 mA/cm2.

The high voltage efficiency of the cell is attributed not only to the fast reaction kinetics but also the membrane-free configuration. The potential gradient in the NaCl/H2O was determined by the model (Fig. 4A, B), and the potential difference across the cell at half-cell height was plotted. The potential drop of ~20 mV at 10 mA/cm2 and ~250 mV at 100 mA/cm2 (Fig. 4C) are equivalent to proton transport but over 5 times smaller than Na+ and K+ transport in Nafion ion-permeable membranes in aqueous flow batteries with similar cell dimensions. Thus, removing the ion-selective membrane opens a range of chemistries to be investigated, as the charge carriers can be chosen arbitrarily.

The CFB demonstrates the round-trip energy efficiency of 91% (calculated by voltage efficiency × Coulombic efficiency) at 10 mA/cm2 and provides an energy density of 125.7 Wh/L (see Methods), which is among the highest of the flow battery systems reported in past 10 years (Table S5). It is worth noting that the Cl2–CCl4 is different from bromine used in flow batteries that faces the serious self-discharge due to the diffusion of Br2 to the negative electrodes in the form of polybromide. When ion-permeable membranes were used to decrease Br2 cross-over, voltage efficiency was significantly limited by the transport of ions in the membrane, resulting in <80% energy efficiency in overall performance. Figure 5A, B show the measured cell voltage profile and stable round-trip cycling for this battery at 20 mA/cm2 with a charge storage capacity of 600 mAh and the stable capacity retention for 500 cycles.

### Discussion

In this study, CCl4 was used as a proof of concept, it can be replaced by other liquids with high Cl2 solubility and are immiscible with NaCl/H2O. The candidates include heptane (chlorine solubility = 0.173 mole fraction at ambient temperature), octane (chlorine solubility = 0.168 mole fraction at ambient temperature), tetradeane (chlorine solubility = 0.254 mole fraction at ambient temperature), and mineral spirit. Mineral spirit demonstrates good wettability (CA = 9.1°) with carbon current collector (Fig. S12A), low viscosity (1.24 mPa.s), low toxicity, and is cheaper than CCl4. When CCl4 was replaced by mineral spirit in the CFB, a volumetric capacity of 91.6 Ah/L was delivered at 20 °C (Fig. S12B).

The removal of the ion-permeable membrane also allows multivalent ions as charge carriers. When ZnCl2 is added to the electrolyte, NaTi2(PO4)3 can be replaced by zinc metal electrode, increasing the cell operating voltage to 1.9 V (Fig. S13).

Cost is one of the significant concerns to implementing flow batteries on a large scale for stationary energy storage. Considering that the ion-permeable membrane (mainly fluorinated polymers) takes up more than 30% of the cost of flow batteries, significant cost reduction is expected with the membrane-free design. The total material cost for energy storage with the proposed CFB is estimated to be ~$5/kWh, which is the cheapest among all the current flow battery systems (Fig. 5C and Table S5). In addition, the RuO2 catalyst for chlorine evolution reaction (CER) can also be replaced by tin, zinc, cobalt, and other cheap metal oxides partially. Therefore, the proposed CFB design leaves significant space to meet the stringent target of ~$100/kWh for RFB applications.
Cl₂ is a reactive chemical commodity used in paper, plastic, dye, textile, medicine, antiseptics, insecticide, solvent, and paint industries. Administration and engineering controls for storage and transport are available to confine the incident rate to 0.019% of total chlorine shipments between 2007 and 2017. The Occupational Safety and Health Administration of the United States has set a permissible exposure limit at a time-weighted average of 0.1 ppm (0.68 mg/m³) for bromine, 0.05 mg/m³ for vanadium pentoxide dust, 0.1 ppm (0.4 mg/m³) for quinone, and 1.0 ppm (3 mg/m³) for chlorine. Thus, there is no apparent increase in chemical exposure risk when changing to chlorine redox reaction.

However, protections and cautions are still crucial. The CFB proposed here is a closed system in which the leakage of Cl₂ gas is minimized by the fluoropolymer gasket (see Supplementary Note 2 for evaluation of chlorine permeation). Strategies from the chloro-alkali industry can be applied to reduce the risk of exposure upon scaling up, such as external seal pipe, shutoff system, neutralization reagents (scrubber) and sensing systems.

In summary, the CFB proposed has demonstrated several unique advantages over current flow battery systems, including higher energy density, higher round-trip energy efficiency, and significantly lower prices. The membrane-free design enables both anionic and cationic charge carriers for a RFB, thus...
expanding the material and chemistry space of the redox flow technologies.

Methods

Material synthesis. The activated carbon with RuO_2/TiO_2 particles was prepared by dissolving 0.69 mmol RuCl_3 and 1.622 mmol C_16H_36O_4Ti in 100 mL iso-propanol, then adding 2.0 g activated carbon into the solution. The mixture was stirred for 2 hours, and then the isopropanol was evaporated at 90 °C. Finally, the products were annealed at 500 °C for 1 hour under ambient conditions.

The carbon-coated NaTi_2(PO_4)_3 was synthesized from 0.002475 mol Na_2CO_3, 0.01485 mol NH_4H_2PO_4, and 0.0099 mol TiO_2 in 100 mL of a 2.0 wt% poly-vinyl-alcohol (PVA) aqueous solution. The mixture was stirred at 80 °C until the water evaporated and white solids formed. The white solids were placed in a porcelain boat and heated at 900 °C for 10 hours with an increasing rate of 5 °C/min under an N_2 flow in a tube furnace. To improve the cycling stability and electronic conductivity, thermal vapor deposition (TVD) was employed to prepare carbon-coated NaTi_2(PO_4)_3 after calcination. The as-prepared powder was transferred into a reaction tube to make a fluid-bed layer for the reaction at 700 °C for 2 hours where a toluene vapor was carried by N_2 through the reaction tube at a flow rate of...
Electrode preparation and electrochemical measurements. The working electrode was fabricated by pressing a mixture of the active materials (porous carbon or carbon-coated NaTi2(PO4)3), carbon black, and PTFE (polytetrafluoroethylene) binder at the weight ratio of 7:2:1 onto a titanium grid with a thickness of 10 MPA. The cylic voltamograms (CV) were obtained using a three-electrode cell with an active carbon counter electrode and Ag/AgCl reference electrode (0.197 V versus NHE). In the concentric cell, the inner diameter of the tube containing CCI4 and the RuO2-TiO2@c electrode is 2.0 mm, the thickness of the porous carbon electrode is 1.0 mm, the distance between the counter and working electrodes is 3.0 mm, and the thickness of the counter electrode is 3.0 mm. The height of the cell is 2.0 cm, and the volume capacity of the cell is around 2.0 mL. The total volume of the CCL4 reservoir is 6.0 mL and the total volume of the NaCl/H2O reservoir is 2.0 mL. The CV measurements were carried out on a CH660B electrochemical workstation. The galvanostatic charge and discharge profiles were obtained with an Arbin battery test station.

Material characterizations. Scanning electron microscopy (SEM) images were taken with Hitachi SU-70 analytical SEM (Japan). Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). Raman spectroscopy was performed on a Horiba Jobin Yvon Labram Aramis using a 532 nm diode-pumped solid-state laser, attenuated to give ~900 mW power at the sample surface. Viscosity Measurements were carried out using a CANNON-FENSKE viscometer.

Energy density calculations. The energy density of CFB was calculated based on the 600 mAh cell used in this study with Eq. (1). The average operating potential is 1.8 V at 10 mA/cm², the volume of CCl4 is 6.0 mL, the volume of NaCl/H2O is 2.0 mL, and the volume of NaTi2(PO4)3 is 0.592 mL. The working electrode is 2.0 mm, and the thickness of the counter electrode is 2.0 mm. The total volume of active materials is 8.592 mL. Based on these configurations, the cell-level energy density (based on active materials) is 125.7 Wh/L.

\[
\text{Energy density} = \frac{\text{Cell capacity} \times \text{average potential}}{\text{Total volume of active materials}} \quad (1)
\]

Data availability. The data that support the findings within this paper are available within the article and Supplementary Information. Additional data are available from the corresponding authors upon request. Source data are provided with this paper.

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Author contributions
S.H., L.C., and Xiu.F. contributed equally to this work. S.H. and L.C. conceived the idea of a membrane-free chlorine flow battery. S.H. performed the numerical simulations and physicochemical measurements. L.C., Xiu.F, and Xiaotong.F. did the material synthesis and electrochemical measurements. X.J. performs the DFT calculations. S.H. and L.C. analyzed the results and wrote the manuscript. B.W., C.C., J.C., W.W., and C.L. participated in the discussions. C.W. supervised all the studies.

Competing interests
The authors declare no competing interests.

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