

Multielectron Transfer in Halogen Batteries

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Multielectron transfer in halogen batteries is a promising solution in pursuing high-energy-density and affordable energy storage systems. Interest in rich chemistries derived from unique valence electron structures of halogens is surging in electrode material design. However, deploying multielectron transfer chemistry comes with challenges, including limited redox reactivity and degrees of electrochemical irreversibility, which contribute to poor charging and cycling. To address these challenges, researchers explore physical/chemical strat-

egies to activate high valence reactions and more electron transfer numbers and fix unstable valence state species through electrolyte and electrode regulation. This Concept presents the basic understanding of multielectron transfer electrochemistry concerning theoretical energy capabilities and electronic configuration evolutions. We divide multielectron transfer into two types: single and multi-redox centers, providing an overview of the current development of multielectron transfer and hoping it will spur more intensive efforts towards a diverse energy future.

1. Introduction

Halogen-based batteries are emerging as a promising candidate in the pursuit of efficient and sustainable energy storage technologies.^[1–7] With a natural abundance and potential for high energy density, halogen-based batteries offer competitive alternatives to traditional lithium-ion technologies.^[8–11] At the heart of their electrochemical performance lies rich multielectron transfer chemistry, wherein multiple electrons are gained/lost during redox reactions, thus enabling high-capacity and high-voltage energy storage.

Unlike conventional single-electron transfer batteries, rechargeable halogen-based batteries feature multielectron conversion involving diverse halogen species and complex redox reactions.^[12] Besides, the wide adaptability of halogen cathode reactions renders them appealing across aqueous, organic, and ionic-liquid electrolytes, suitable for both static and flow batteries.^[13–19] However, whether in aqueous or non-aqueous electrolytes, challenges of thermodynamic instability, low conductivity, shuttling effect and poor reversibility of multielectron conversion remain to be overcome. Compared with other transition metal ions and sulfur that transfer more than one electron, halogen can exhibit higher reactive activity both in aqueous and non-aqueous electrolytes, higher capacity and voltage than the former due to more multielectron transfer number, higher voltage and rate performance than the latter. All that results in wider application and attention in the field of energy storage. At a fundamental level, it is important to

understand the dynamics of the multiple redox reactions and associated structural evolutions during the redox reactions to determine the maximum number of electrons transferred during battery operations. All those are crucial for designing electrode materials, electrolytes, and cell architectures tailored to exploit the full potential of halogen-based energy storage.^[20–23]

Despite the great promise of multielectron transfer in halogen batteries, activating halogen-based multielectron reactions in electrodes presents a challenge regarding stability and reversibility. In this Concept, we summarize the multielectron chemistry of halogen and aim to clarify its mechanism and objective by analyzing electronic structures and theoretical energy storage capabilities. Furthermore, we highlight recent advances in halogen-containing multielectron reactions with single or multi-redox centers and strategies proposed to stabilize high-valence species, enhance electron transfer kinetics, and maximize energy density. Through a comprehensive understanding of multielectron transfer chemistry, we strive to unlock the full potential of halogen batteries and accelerate the transition toward a sustainable energy future.

2. Multielectron Chemistry

2.1. Specific Capacity of a Material Corresponding to One Mole Electron Storage

The following equation expresses the theoretical discharge capacity of electrode materials:

$$C = \frac{nF}{3.6 \cdot M} = \frac{26800n}{M} \quad (1)$$

where n is the electron transfer number of electrode materials per formula unit, M is the molar mass of active material, F is the Faraday constant, and C is the specific capacity with a unit of mAh g^{-1} . One mole electron transfer can deliver $\frac{26800}{M} \text{mAh g}^{-1}$ capacity in theory, and increasing the electron transfer number

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of an electrode material can improve capacity. For example, a single electron transfer reaction of $\text{I}^{0/-}$, $\text{Br}^{0/-}$, and $\text{Cl}^{0/-}$, can provide a theoretical capacity of 211, 335, and 756 mAh g^{-1} at 0.54, 1.07 and 1.36 V vs. SHE respectively.^[24]

2.2. What is the Target of Multielectron Transfer?

In addition to pursuing high capacity, the multielectron transfer also provides high voltage output. Every electron transfer brings about a discharge plateau (Figure 1), and normally, higher valence conversions occur at higher potential during charging/discharging. The specific gravimetric energy of full cells (E) is calculated by Equation (1) as following derivation process:

$$E (\text{Wh kg}^{-1}) = \int V (\text{V}) dC (\text{mAh g}^{-1}) \quad (2)$$

Energy density is the amount of energy stored in a given system per unit mass/volume, indicating the battery performance comprehensively as a key index.^[25,26] V is the voltage with a unit of V. As shown in Figure 1, the area of the polygon corresponds to the energy density, and the area increases as redox reactions change from one to three electron transfers. The high capacity and high voltage that multielectron transfer provides are promising in developing a high-energy-density battery.

2.3. Why Can Halogen Achieve Multielectron Transfer?

Unique electronic structures of halogen elements support multielectron transfer chemistry in halogen batteries. The halogen atoms carry seven valence electrons in their outermost electron shell (Figure 2). They own the second maximum valence electron number after the noble gas next to it in the periodic table, but the electron configurations of the latter are exceptionally stable and thus lack redox activity.^[27–30] Therefore, halogen elements own the maximum active valence electrons. These seven outermost electrons are in two different kinds of orbitals, designated s (with two electrons) and p (with five).



Chunyi ZHI obtained a B.S. in Physics from Shandong University and a Ph.D. in condensed matter physics from the Institute of Physics, Chinese Academy of Sciences. After two years as a postdoctoral fellow at the National Institute for Materials Science (NIMS) in Japan, he was promoted to ICYS researcher, researcher, and senior researcher at NIMS. Dr. Zhi is now a chair professor at MSE, CityU. Dr. Zhi has extensive experience in aqueous electrolyte batteries and zinc ion batteries. He is a Clarivate Analytics Global highly cited researcher (2019–2023, Materials Science), RSC fellow, member of The Hong Kong Young Academy of Sciences, and RGC senior research fellow.

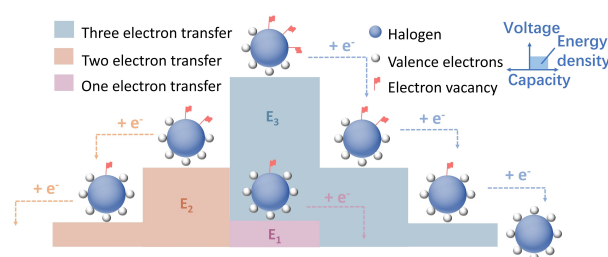


Figure 1. Multielectron transfer-boosted high-energy-density batteries. Schematic illustration of multielectron transfer along with enhanced voltage and capacity, leading to an enhanced energy-density battery. The schematic describes three discharging processes when the electron transfer number of the halogen-based redox reaction is one (purple area), two (orange area), and three (blue area), respectively. The area corresponds to the energy density.

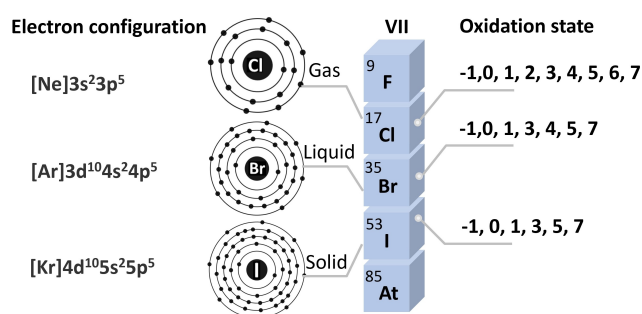


Figure 2. Redox chemistry of halogen multielectron transfer. Electron configuration and multi oxidation states of halogen. The oxidation state refers to the theoretical electrons that a halogen atom either gains (–) or loses (+) when forming a chemical bond with another atom. The number in the cube is the nuclear charge number.

Potentially, a halogen atom could hold one more electron (in a p orbital) to a stable structure (1- valence state), or lose one to seven valence electrons to form a high valence state from 1+ to 7+, resulting in multielectron transfer in halogen batteries. In theory, a maximum electron transfer number is eight with a corresponding maximum energy density of up to 26 k/9 k/5 kWh kg^{-1} based on $\text{Cl}^{-/+7}/\text{Br}^{-/+7}/\text{I}^{-/+7}$ redox reactions vs. $\text{Li}^{0/+}$.

3. Multielectron Transfer in Halogen Batteries

There are two types of multielectron transfer reactions in halogen batteries: one is related to a single redox center with the multivalent transformation of one halogen, and the other is multi-redox centers involving multiple halogens or a halogen combined with different kinds of active centers such as selenium (Se) and copper (Cu).

3.1. Single Redox Center

Based on the I redox center, Liang et al.^[13] reported a four-electron aqueous Zn-iodine battery by activating the highly reversible $\text{I}^{+/0}$ couple (0.99 V vs. SHE) in concentrated electrolyte besides $\text{I}^{0/-}$ conversion at 0.54 V vs. SHE. Usually, I^{+} is unstable

in electrolytes, so it isn't easy to realize the high voltage reaction of $I^{-/0}$ (Figure 3a). Concentrated electrolytes are important to suppress water activity and provide sufficient chloride ions to stabilize the I^+ during charging. Finally, the multivalent redox chemistry of iodine ($I^{-/0}/I^+$) was achieved.

Li et al.^[32] reported an acidic aqueous battery that can create a two-electron-transfer process from Br^- to Br^+ (Figure 3b). A new redox pair $BrCl_2^-/Br_2$ could be observed after the introduction of HCl into the HBr electrolyte; the two-electron-transfer product Br^+ could be stabilized by Cl^- via a bromine-chlorine interaction. The redox potential of $BrCl_2^-/Br_2$ was about 1.30 V vs SHE, which was between the redox potential of Br_2/Br^- (1.07 V vs SHE) and Cl_2/Cl^- (1.36 V vs SHE). Benefiting from the multielectron transfer of $Br^-/Br^0/Br^+$, a discharge capacity of 95 Ah L^{-1} can be obtained in flow batteries, among the highest discharge capacity and cycling stability compared with other reported aqueous flow battery systems (Figure 3c)

3.2. Multi redox Centers

3.2.1. Interhalogen

Halogen chemistry typically involves interhalogen bond formation, which can stabilize high-valence species mutually and remain redox active of multiple halogens. Wang et al.^[11] report a halogen conversion-intercalation chemistry in graphite using the anionic-redox reaction of halide anions Br^- and Cl^- (Figure 4a), realizing a capacity of 243 milliampere-hours per gram (for the total weight of the electrode) at an average potential of 4.2 volts versus Li/Li^+ . Experimental characterization

and modeling attribute this high specific capacity to a densely packed graphite intercalation compound, $C_{3.5}[Br_{0.5}Cl_{0.5}]$, which can form reversibly in water-in-bisalt electrolyte. Zhi et al.^[2] report an interhalogen compound, iodine trichloride (ICl_3), as a cathode for a $Li-Cl_2$ battery (Figure 4b and c). The Cl^0 is efficiently and chemically anchored by forming interhalogen bonds with I, which allows for the $Cl^{-/0}$ reaction in a highly reversible manner. First-principle density functional theory calculations were employed to predict the conversion path and structural evolution of the ICl_3 (Figure 4d). The rich chemistry of ICl_3 makes it possible to achieve multiple electron reactions and, therefore, high capacity. The rechargeable $Li-Cl_2$ battery delivers a capacity of 302 mAh g^{-1} at 425 mA g^{-1} .

3.2.2. Multi Redox Center Containing Halogen

Rich chemistry exists when combining active halogen redox centers with other types of redox centers, which is a flexible and effective method to construct a multiple-transfer cathode that can afford high-capacity storage. Zhi et al.^[33] utilized a Se-based organic molecule, diphenyl diselenide ($di-Ph-Se$), as the Cl anchoring agent and realized a Cl^0 fixation through chalcogen-halogen coordinating chemistry (Figure 5a). A desirable six-electron transfer process (two electrons from Cl^0 to Cl^- and four electrons from Se^{3+} to Se^-) is realized in the cell, resulting in remarkable electrochemical performance (Figure 5b). Niu et al.^[34] reported six-electron redox chemistry via the synergistic effect of redox-ion charge carriers and halide ions in electrolytes in contrast to conventional two-electron redox (Figure 5c and d). The redox-active Cu^{2+} ions in electro-

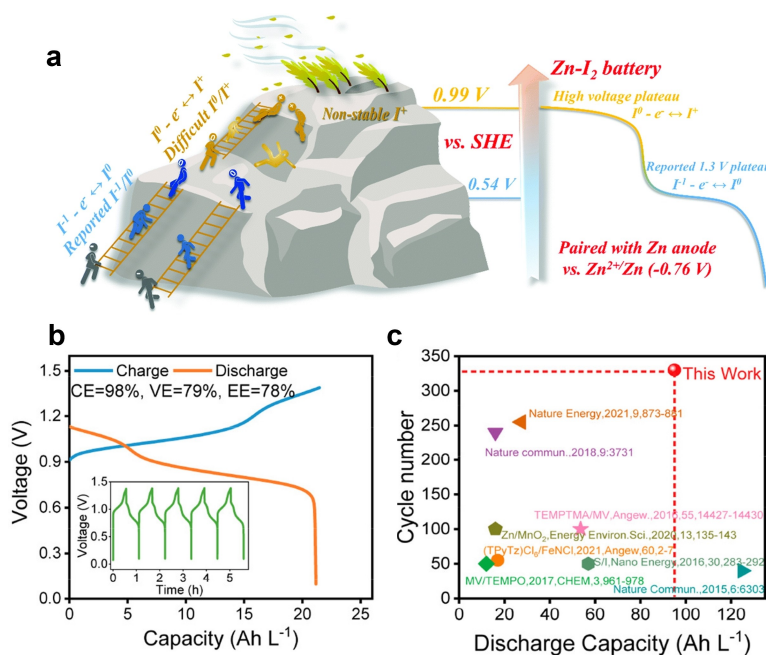


Figure 3. Multivalent transformation of iodine and bromine-based batteries. (a) Illustration of the iodine-based batteries with reversible $I^{-/0}$ conversion at 0.54 V vs. SHE and I^0/I^+ redox at high 0.99 V vs. SHE. Produced from Ref.^[31] Copyright (2021), with permission from Royal Society of Chemistry. (b) Charge-discharge plots of a bromine-based flow battery with the two-electron transfer of positive bromine electrode. (c) Performance of bromine-based multielectron transfer flow batteries compared with those based on other redox pairs. Produced from Ref.^[32] Copyright (2023), with permission from Elsevier.

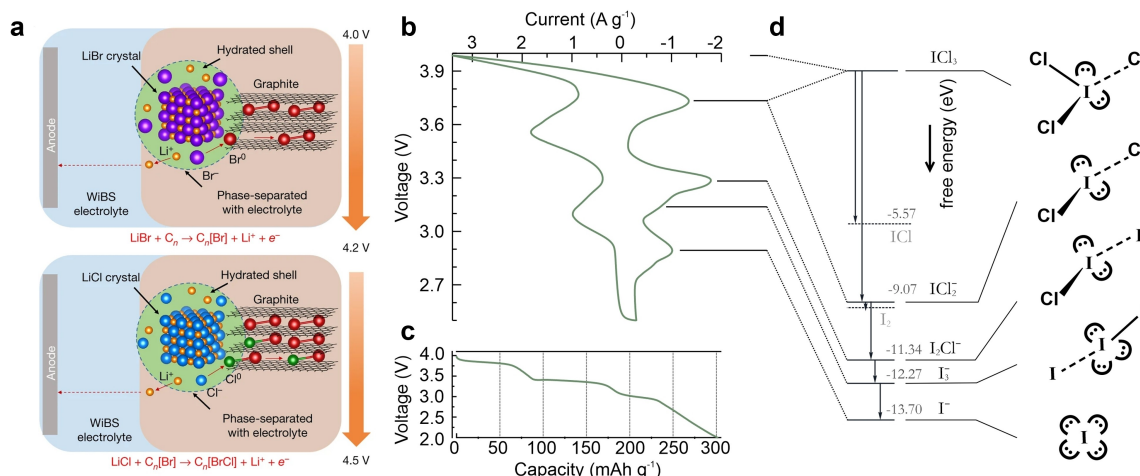


Figure 4. Interhalogen chemistry. Two or more halogens as multi-redox centers gain/lose electrons. (a) Schematic of the conversion-intercalation mechanism occurring in the (LiBr)_{0.5}(LiCl)_{0.5}-graphite cathode with anionic-redox reaction of halide anions (Br⁻ and Cl⁻) in a water-in-salt aqueous gel electrolyte. Produced from Ref.^[1] Copyright (2019), with permission from Springer Nature. (b) CV curve showing a redox process of Li-ICl₃ cell showing the redox activity of both I and Cl in 1 M LiTFSI in DOL/DME electrolyte at 1 mV s⁻¹. (c) The discharge behavior of a Li-ICl₃ cell with three plateaus at 3.85, 3.40, and 3.00 V, respectively. (d) Calculated Gibbs free energy and the optimized reaction path (left panel) of the ICl₃ redox process. The right panel shows Lewis structures of reaction products. Produced from Ref.^[2] Copyright (2024), with permission from Cell Press.

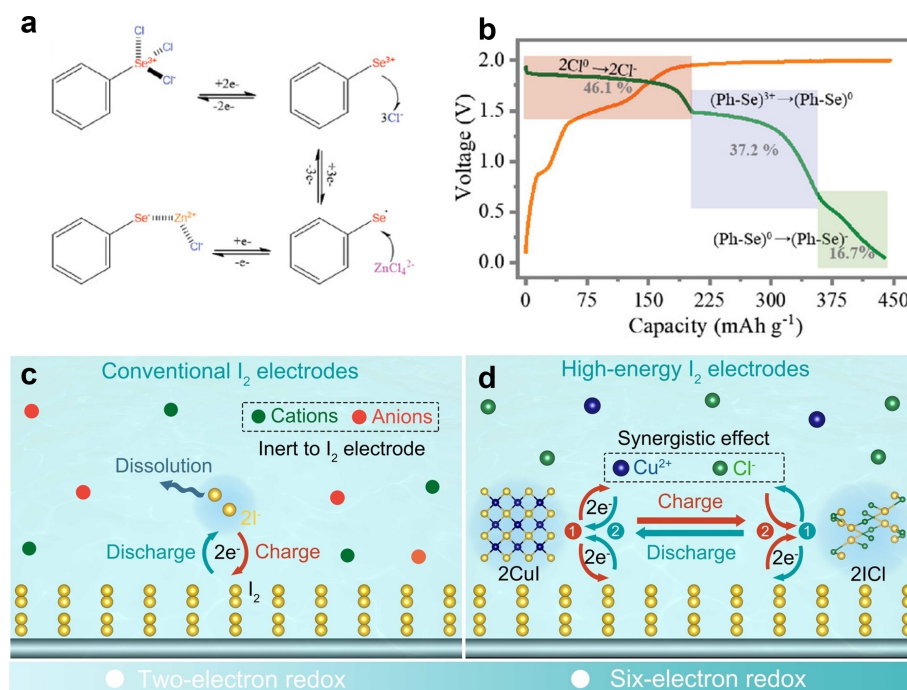


Figure 5. Multi redox center containing halogen. (a) Schematic representation for molecular structures transformation of diphenyl diselenide (*di*-Ph-Se) during charging, based on Se⁰/Se²⁺ and Cl⁻/Cl⁰ redox couples. (b) Galvanostatic charge-discharge profiles of a six-electron conversion process with two oxidized Cl⁰ anchoring on a single Ph-Se and the multivalence conversion of Se. Produced from Ref.^[33] Copyright (2023), with permission from Wiley-VCH. (c) Schematic diagram of conventional two-electron redox of I₂ to I⁻. (d) Schematic diagram of six-electron redox processes based on conversion between Cu²⁺ ions and I₂ to CuI in aqueous electrolytes. Produced from Ref.^[34] Copyright (2023), with permission from Wiley-VCH.

lytes induce the conversion between Cu²⁺ ions and I₂ to CuI at low potential. Simultaneously, the Cl⁻ ions in electrolytes activate the I₂/ICl redox couple at high potential. Based on I^{-/0/+} and Cu^{2+/+} six electron redox reaction, the I₂ electrodes deliver a discharge capacity of 560.4 mAh g⁻¹ at 1.0 A g⁻¹, adaptable in Zn || I₂, Mn || I₂ and Fe || I₂ aqueous hybrid batteries.

4. Summary and Outlook

In summary, multielectron transfer in halogen batteries significantly enriches cathode chemistry based on their unique electronic structure with maximum valence electrons, enabling high energy capabilities both in aqueous and non-aqueous electrolytes. The multielectron transfer involves single or multi-

redox centers. Interhalogen-type multi-redox centers, in theory, approach the ideal cathode model with the highest energy density, as all halogen components are redox active, contributing to a rich chemistry, and they can stabilize high valence species mutually. In this flourishing field, the biggest challenge and opportunity coexist in stabilizing the products of multi-electron transfer, allowing for reversible new reactions and stable cycling. In the future, more multielectron transfer chemistries deserve to be explored before achieving a practical redox couple with desired performance metrics beyond current technologies.

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Conflict of Interests

The authors declare no conflict of interest.

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