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Research Highlight

Halogen conversion-intercalation chemistry promises high energy density Li-ion battery

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The state-of-art lithium-ion batteries (LIBs) have achieved great commercial success during the past decades. The intercalation mechanisms in graphite anode and lithium transition metal oxide enabled its long-term stability in organic electrolytes. The classic electrolyte formula of lithium hexafluorophosphate ($LiPF_6$) in carbonate solvents provided a benign solid electrolyte interphase (SEI) on the electrode surface. Subsequent researches on materials and electrolytes have improved the electrochemical stability and energy density for LIBs. Nevertheless, their adoptions, especially in electric vehicles and power grid have been obstructed owing to the safety concerns and environmental impact. The flammable carbonate solvents are easy to trigger fire and cause cell failure. The common used $LiPF_6$ is sensitive to moisture which increases much difficulty to eliminate trace water in practical application.

An effective strategy to address the security and environmental concerns is the introduction of aqueous electrolyte. However, the limited electrochemical stability window (1.23 V) negatively restricts the choice of electrodes. Hydrogen evolution at the anode and oxygen evolution at the cathode would happen and destruct the electrode structure. Previous work of "water-in-salt" electrolyte and series of modification works have greatly expanded the electrochemical windows of aqueous electrolyte (>3 V) and choices for electrochemical couples [1–3]. Higher energy density would be achieved in a well-designed electrochemical system with high capacity electrodes and high output voltage. For example, the success utilization of graphite anode via an interphase precursor coating largely extended the electrochemical window to 4 V [2]. However, the intrinsic intercalation chemistry into layered graphite or lithium transition metal oxide severely limited the Li storage capacity. Recently, Chunsheng Wang and co-authors [4] introduced a halogen conversion-intercalation mechanism in graphite to improve capacity. Graphite and layered oxide have been proved to be effective to de(intercalate) anions and present a high platform [5–8]. Nonetheless, the capacity is hindered by the concentrations of anions in electrolyte and the intrinsic intercalation mechanism. Herein, Wang and co-authors [4] overcame this problem and fully exploited the Li^+ storage capacity without shuttle of anions. This promising result exhibits a 4 V Li-ion cell with an energy density of 460 Wh kg^{-1} in aqueous electrolyte.

Wang and co-workers [5] introduced a halogen conversion-intercalation mechanism in layered graphite to improve Li storage capacity. A composite $(LiBr)_{0.5}$-$(LiCl)_{0.5}$-graphite exhibited an enhanced chemistry and electrochemistry stability in "water-in-bisalt" electrolyte. The Li halogen in composite cannot leak in the saturated electrolyte and was confined partially within the solid cathode matrix. Graphite served as host for reversible anionic-redox reaction of halide anions (Br^- or Cl^-). As shown in Fig. 1a, LiBr and LiCl crystals remain stable in the hydrated shell with a slight amount of water absorption from WiBS gel electrolyte. Graphite presents a host to form a graphite intercalation compound (GIC). It is different from most reports of using GIC to reversibly absorb anions [6]. Firstly, anions experience a conversion process, which promises more capacity. Secondly, anions do not need to shuttle in the bulk of electrolyte. The cyclic voltammogram in Fig. 1b indicated a distinct two step reactions involving the oxidation of Br^- (about 4.0 V) and Cl^- (about 4.2 V) and their later intercalation into the layered graphite. During the charge process, each halogen involves a one-electron transfer reaction and their theoretical capacities are 309 mAh g^{-1} for LiBr, and 632 mAh g^{-1} for LiCl, respectively. It should be noted that the individual intercalation of Cl^0 in graphite is thermodynamically unfavorable at ambient temperature, unless it is coupled with a Br^0. Although the neat LiBr-LiCl composite without graphite host delivered a high charge capacity (oxidation process), its discharge capacity is very low owing to the absence of graphite host to accommodate the gaseous halogens.

Both LiBr and LiCl are strong water-absorbing substance and squeeze water even from WiBS gel electrolyte. When the electrolyte/electrode weight ratio is low, water is concentrated in the hydrated shell and the ion transportation in WiBS electrolyte cannot sustain the discharge/charge process. One practical solution is using monohydrate Li halogen to lessen this effect although it would decrease the energy density. As shown in Fig. 2a, the $(LiBr)_{0.5}$-$(LiCl)_{0.5}$-graphite composite shows two typical charge–discharge platforms, which correspond to conversion-intercalation of LiBr and LiCl, respectively. A high discharge capacity of 127 mAh g^{-1} (based on the mass of anode and cathode) and an

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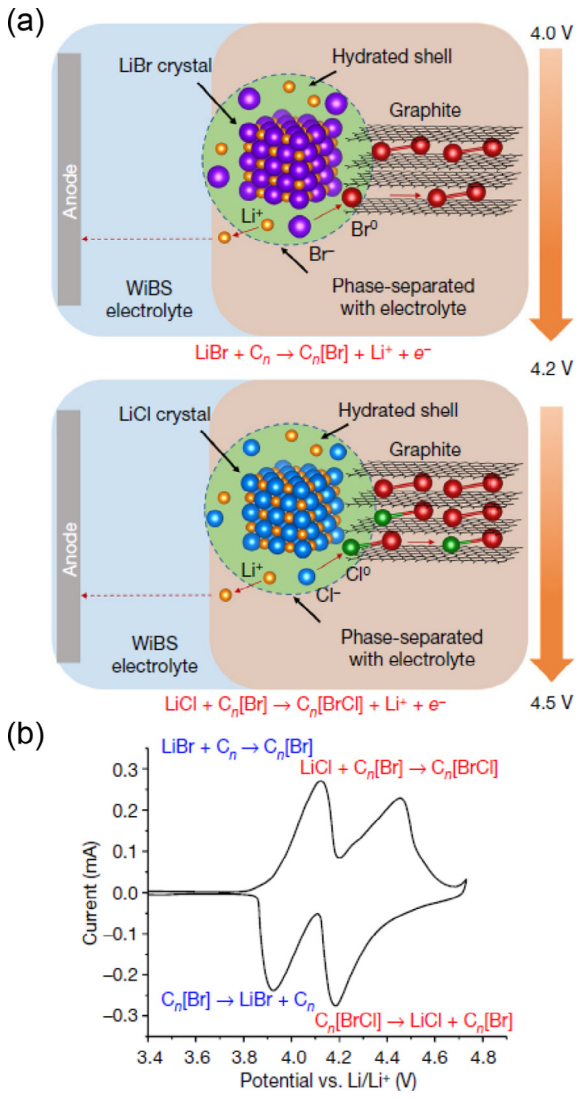


Fig. 1. (Color online) (a) Schematic of the conversion–intercalation mechanism in the $(LiBr)_{0.5}$-$(LiCl)_{0.5}$-graphite composite during its oxidation (charge) process in WiBS aqueous-gel electrolyte. The two step reactions involve the oxidation of Br^- (about 4.0 V) and Cl^- (about 4.2 V) and their subsequent intercalation into the graphitic structure. (b) Cyclic voltammogram of $(LiBr)_{0.5}$-$(LiCl)_{0.5}$-graphite composite between 3.2 and 4.9 V vs. Li/Li^+ at a scan rate of 0.05 mV s^{-1} [4]. Copyright © 2019, Springer Nature.

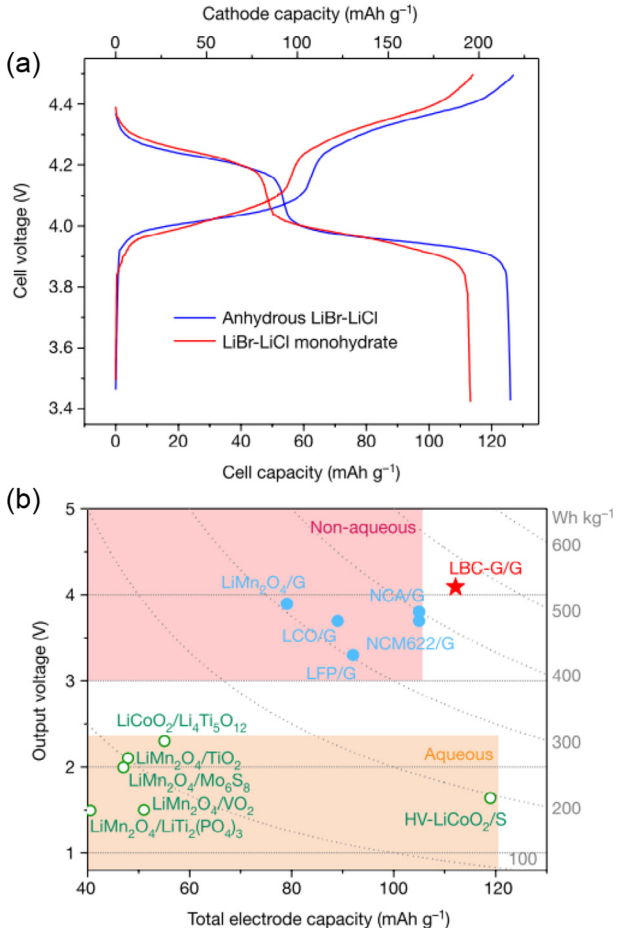


Fig. 2. (Color online) (a) Typical charge–discharge voltage profiles (the third cycles) of LBC-G cathodes consisting of anhydrous LiBr/LiCl (blue) or LiBr/LiCl monohydrates (red). The cell capacity was calculated on the basis of the cathode mass alone (top horizontal axis) or the total mass of the cathode and the anode, including the binder and protective coating (bottom horizontal axis). (b) Actual (red star) energy density of the LBC-G full cells (with LiBr/LiCl monohydrates), compared with various commercial and experimental Li-ion chemistries using both non-aqueous (blue circles) and aqueous (green circles) electrolytes. For comparison, all energy densities were calculated based on the total weight of the positive and negative electrodes (not containing the electrolyte and cell packaging) [4]. Copyright © 2019, Springer Nature.

average platform of 4.1 V were obtained. Given the electrochemical stability, the energy density of Li-ion full cell was calculated on monohydrate Li halogen to be around 460 Wh kg^{-1}. This value is very competitive even compared with commercial and reported Li-ion batteries (Fig. 2b).

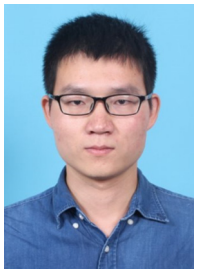
This work presents a new research direction to obtain high-energy and safe aqueous Li-ion batteries. The conversion-intercalation chemistry also sheds light for other types of batteries. However, the limited cycle life still hinders its further application and needs to improve in the subsequent research work. In the future, more attention should be paid on long-term stability and cost-effectiveness for the new aqueous Li-ion battery.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Suo L, Borodin O, Gao T, et al. "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. Science 2015;350:938–43.
[2] Yang C, Chen J, Qing T, et al. 4.0 V Aqueous Li-ion batteries. Joule 2017;1:122–32.
[3] Suo L, Borodin O, Sun W, et al. Advanced high-voltage aqueous lithium-ion battery enabled by "Water-in-Bisalt" electrolyte. Angew Chem 2016;55:7136–41.
[4] Yang C, Chen J, Ji X, et al. Aqueous Li-ion battery enabled by halogen conversion-intercalation chemistry in graphite. Nature 2019;569:245–50.
[5] Li Q, Qiao Y, Guo S, et al. Both cationic and anionic Co-(de)intercalation into a metal-oxide material. Joule 2018;2:1134–45.
[6] Zhou X, Liu Q, Jiang C, et al. Beyond conventional batteries: strategies towards low-cost dual-ion batteries with high performance. Angew Chem 2019. https://doi.org/10.1002/anie.201814294.
[7] Qiao Y, Jiang K, Li X, et al. A hybrid electrolytes design for capacity-equivalent dual-graphite battery with superior long-term cycle life. Adv Energy Mater 2018;8:1801120–28.
[8] Lin MC, Gong M, Lu B, et al. An ultrafast rechargeable aluminium-ion battery. Nature 2015;520:325–8.



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