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Research Highlight

Powerful qua-functional electrolyte additive for lithium metal batteries

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Abstract

Lithium metal batteries (LMBs) have attracted tremendous research attention because of the high theoretical capacity (3860 mAh g^{-1}) and the lowest electrochemical potential (−3.04 V vs. standard hydrogen electrode). However, the Lithium dendrites, forming from plating/stripping processes, cause the excessive consumption of electrolyte and active Li and the puncture on the separator. This limits the commercialization of LMBs. Recently, Ma's group proposed heptafluorobutyric anhydride (HFA) as qua-functional electrolyte additive and verified the protection mechanism from the structure and electrochemical properties. Such results creatively put forward qua-functional electrolyte additive for the improvement of LMBs and provides good experience for the exploration of multi-functional additive, inspiring researchers to explore new multi-functional electrolyte additives in future.

Keywords: Lithium metal batteries (LMBs); Heptafluorobutyric anhydride (HFA); Qua-functional electrolyte

With the rapid development of electronic equipment, lithium-ion batteries (LIBs) have become increasingly difficult to meet higher capacity requirements [1,2]. The energy storages are facing the need for further upgrade. Among the numerous candidates, lithium metal batteries (LMBs) have attracted tremendous research attention because of the high theoretical capacity (3860 mAh g^{-1}) and the lowest electrochemical potential (−3.04 V vs. standard hydrogen electrode) [3–7]. Unfortunately, the commercialization of LMBs is limited by the wanton growth of Li dendrites during plating/stripping processes, which will cause the excessive consumption of electrolyte and active Li and the puncture on the separator [8]. In addition, too many side reactions can lead to low Coulombic efficiency (CE), resulting in poor cycle life of LMBs. Thus, the suppression of Li dendrites is the key point to solve the safety problem of LMBs [9,10]. Adding electrolyte additive is a very efficient and accessible strategy to improve the battery performance and has been extensively studied and reported. But most of electrolyte additives only have a single function and can not solve the issues from all sides. Finding an electrolyte additive with multiple functions become increasingly desired for researchers [11,12].

Inspired by this, Ma's group proposed heptafluorobutyric anhydride (HFA) as qua-functional electrolyte additive and verified the protection mechanism from the structure and electrochemical properties [13]. As shown in Fig. 1a, HFA can optimize electrode/electrolyte interphases and Li-ion flux/solvation simultaneously. At the side of anode, HFA has a more preferred reduction trend than based electrolyte due to the lower energy values of the lowest unoccupied molecular orbital (LUMO) (Fig. 1b), resulting in the formation of a dense and uniform inorganic-rich solid electrolyte interphase (SEI). The high fluoride content of HFA not only generates LiF which is conducive to the conduction of Li-ions in inner SEI, but also forms a C-F-rich surface of SEI that can facilitate the adsorption of Li-ions (Fig. 1c). On the cathode side, HFA can help to the formation of a thinner and compact cathode electrolyte interphase (CEI) which can protect the structure of active material and reduce the transition-metal-ion dissolution

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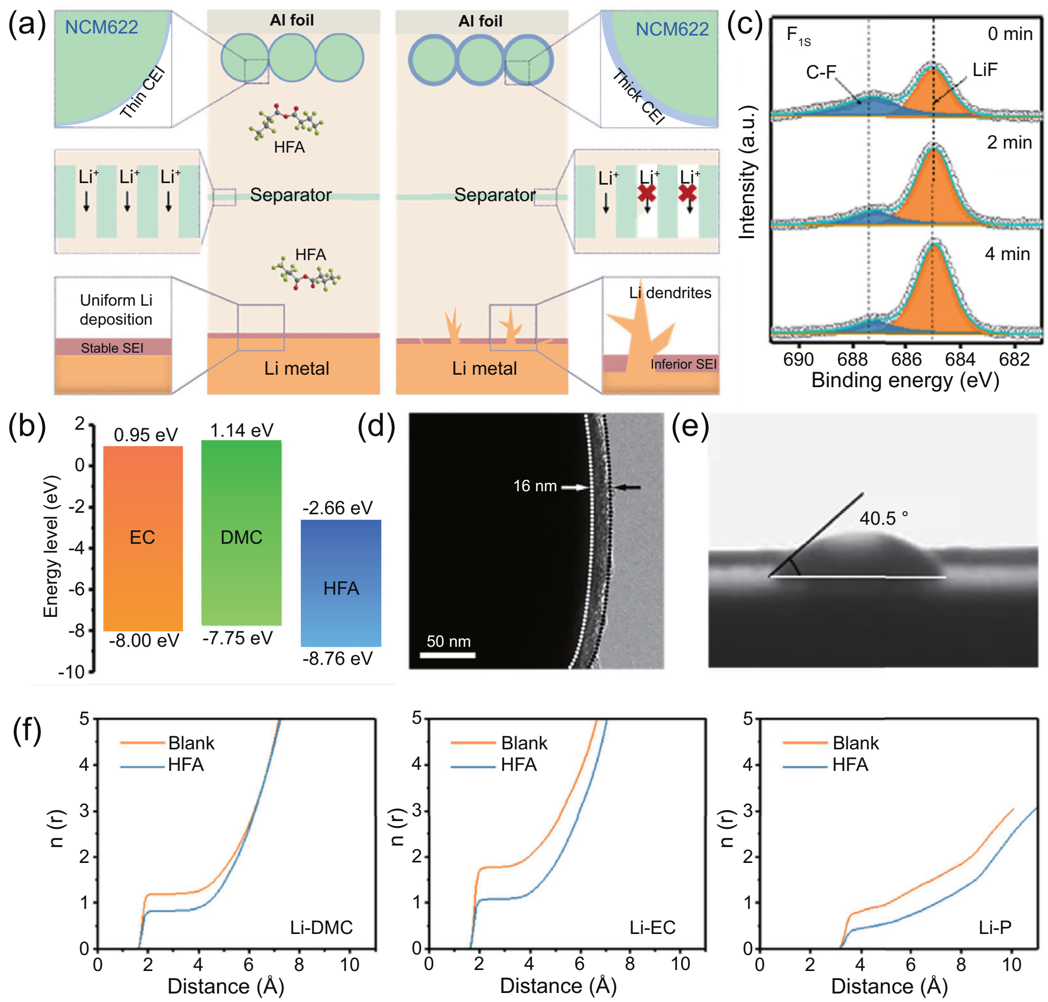

Fig. 1. (a) Schematic illustration of the effect of qua-functional HFA. (b) The LUMO and HOMO energy values of EC, DMC and HFA. (c) XPS spectra of F 1s of Li anode with HFA-contained electrolyte after 10 cycles in different depths. (d) The TEM image of cathode after 10 cycles in HFA-contained electrolyte. (e) The contact angles of HFA-contained electrolyte. (f) The cumulative coordination number of Li^+ with DMC, EC and PF_6^-. Reprinted with permission from Ref. [13]. Copyright (2021) Wiley.

(Fig. 1d). In addition, the increasing content of LiF in CEI can enhance fast Li-ion transportation. For the separator, HFA can serve as the surfactant to reduce the electrolyte surface tension and boost the wettability of separator to increase the Li-ion flux, as shown in Fig. 1e. The uniform Li-ion flux is conducive to the even deposition of Li. In the bulk electrolyte, the addition of HFA decreases the cumulative coordination number of the solvent molecules, facilitating the desolation of Li-ion (Fig. 1f).

Benefited by the addition of HFA, the growth of Li dendrite has been depressed remarkably. As the in situ optical images shown (Fig. 2a and b), there are continued growth of Li dendrites during the plating in blank electrolyte while no Li dendrites can be observed in HFA-contained electrolyte in 20 min. In addition, the surface of the Li anode cycled in HFA-contained electrolyte is smoother and neater than that in blank electrolyte, without any needly-like Li dendrites (Fig. 2c and d). As the result, the Li||Li symmetric cells contained 1.0 wt% HFA can steadily cycle more than 340 h with only mildly polarization while the overpotential increases rapidly in blank electrolyte after 100 h (Fig. 2e). The EIS result is shown in Fig. 2f and also reveals a lower impedance in HFA-contained electrolyte than that in blank electrolyte. For Li||NCM622 full cells, the cycling performance is greatly improved and the capacity retention increases observably after 250 cycles with the addition of HFA (Fig. 2f). Moreover, as shown in Fig. 2g, the concentration of transition metal ion in HFA-contained is much lower than that in blank electrolyte, which implies HFA can help to reduce the dissolution of transition metal ion.

In summary, this work from Ma's group not only creatively puts forward qua-functional electrolyte additive for the improvement of LMBs, but also provides good experience for the exploration of multi-functional additive. It will inspire researchers to explore new multi-functional electrolyte additives in future.

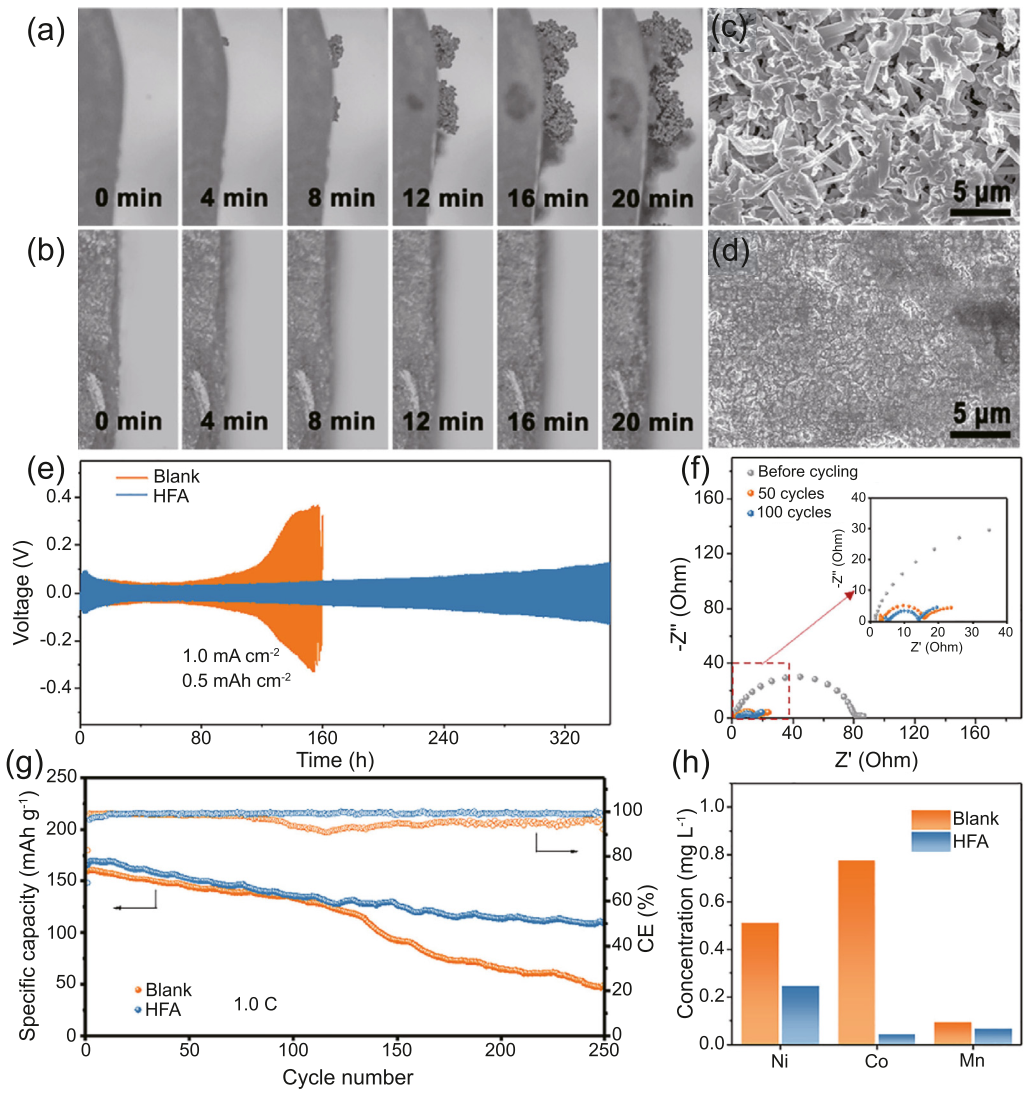

Fig. 2. (a and b) In situ optical images of Li plating with blank and HFA-contained electrolyte. (c and d) SEM images of Li anode after 50 cycles in blank and HFA-contained electrolyte. (e) electrochemical performance of Li||Li symmetric cells in different electrolytes. (f) EIS spectra of the symmetric cell in HFA-contained electrolyte. (g) Cycling performance of Li||NCM622 cells in different electrolyte. (h) ICP-MS result of the electrolyte. Reprinted with permission from Ref. [13]. Copyright (2021) Wiley.

Conflict of interest

There is no conflict of interest.

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