A 4.8 V Li||LiCoO$_2$ battery

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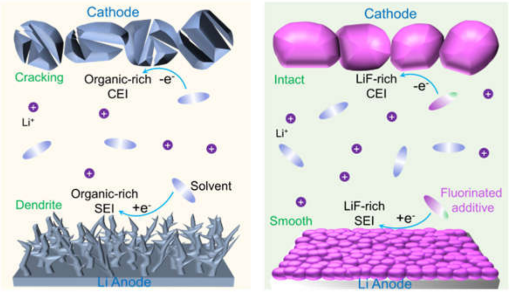
Introduction

Elevating the charging voltage of the LCO cathode is the short-circuit to release its theoretical discharge capacity (274 mAh g^{-1}), whereas severe phase transition and parasitic reactions of highly delithiated LCO cathode above 4.55 V will lead to fast decay of the cathode. Besides, the uncontrolled lithium dendrite growth and low coulombic efficiency in traditional electrolytes hinder the application of Li anode.

Optimizing electrolytes to establish LiF-rich solid-electrolyte interphase (SEI) and LiF-rich cathode electrolyte interphase (CEI) is efficient in stabilizing the Li anode and LCO cathode, despite some progress achieved in creating LiF-rich SEI or CEI, developing LiF-dominated interphases for both Li anode and ultrahigh-voltage LCO cathode is tricky.



Methodology

The simple fluorination of organic molecules will decrease the electron density of the whole molecule, which simultaneously lowers both HOMO and LUMO energy levels, thus making it easy to be reduced and difficult to be oxidized. With a long-chain alkane (octane, C_8H_{18}) as the precursor, the sole fluorination of octane into electron-deficiency C_8F_{18} only grants it with reduction active site, whereas the carboxylation of octane into electron-rich octanoate ($C_7H_{15}COO^-$) can only render it an oxidation active site. To address this paradox, incorporating an electron-rich carboxyl group ($-COO^-$) into this electron-deficient perfluorinated molecule is a good choice, and we choose lithium pentadecafluorooctanoate (LiPFOA, $C_7F_{15}COO^-Li^+$) as the representative additive because it simultaneously possesses electron-deficiency and electron-rich fragments.

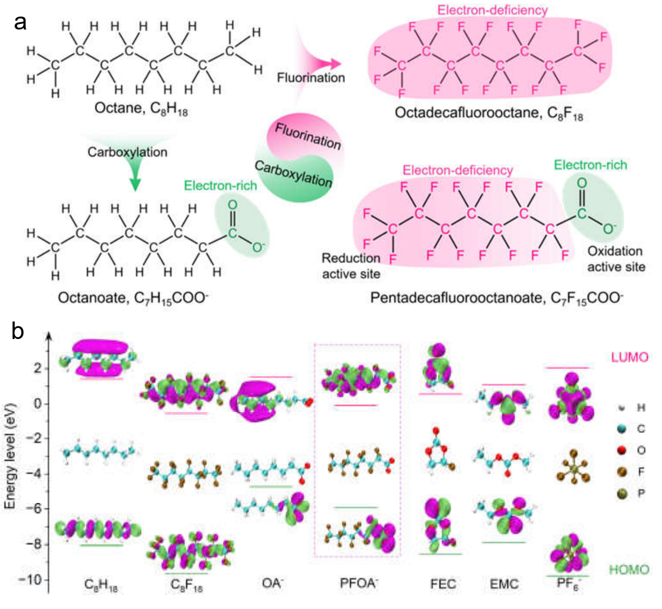


***Figure 1**. (a) Design principle of fluorine-rich additive with dual active sites for reduction and oxidation. (b) Frontier molecular orbital energy levels of different molecules.*

Objectives

The discharge capacities of the LCO cathode increase with the charging cut-off voltage. LCO cathode delivers only 135 mAh g^{-1} at 4.2 V and 0.2C, which is approximately half of the theoretical specific capacity. When the cut-off voltages are elevated to 4.5, 4.7 and 4.8 V, the discharge capacities increase to 185, 230 and 244 mAh g^{-1}, respectively. Meanwhile, the energy densities surge 40.7%, 78.8% and 91.6%, respectively.

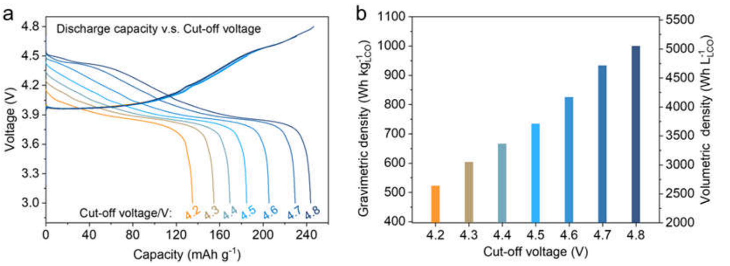


***Figure 2**. (a) 0.2C charge-discharge profiles of the LCO batteries with LiPFOA at the different cut-off voltages and (b) the corresponding gravimetric/volumetric energy density.*

Research accomplishments

LiPFOA-derived LiF-rich SEI and SEI empower the Li||LCO batteries to show excellent cycling stabilities at 4.7 and 4.8 V. Furthermore, we also present a 2.7 Ah Li||LCO pouch cell at 4.8 V, which delivers a specific energy of 544 Wh kg^{-1}.

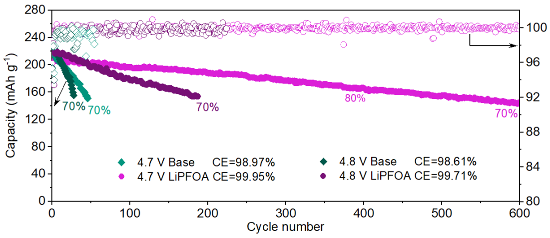


***Figure 3**. Cycling stabilities of the 4.7&4.8 V Li||LCO batteries with different electrolytes.*

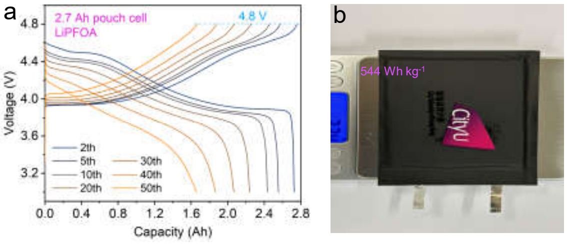


***Figure 4**. Charge-discharge voltage profiles (a) and photograph (b) of the 4.8 V Li||LCO pouch cell.*

Conclusions and Outlooks

- We have designed and introduced LiPFOA as a fluorine-rich additive to the battery electrolyte, which is gifted with both low LUMO and high HOMO energy levels, thereby enabling the formation of robust LiF-rich SEI and CEI on both the Li anode and LCO cathode, respectively.
- The Li||LCO batteries exhibit high capacity retention of 70% after 600 cycles and 188 cycles at 4.7 and 4.8 V, respectively. The practicality of the LiPFOA-enabled 4.8 V Li||LCO battery has been unprecedentedly verified by a 2.7 Ah Li||LCO pouch cell, which delivers an ultrahigh energy density of 544 Wh kg^{-1} and can cycle more than 50 times.
- We trust our exploration and demonstration of a 4.8 V Li||LCO pouch cell can behave as a forerunner to energize more research on ultrahigh-voltage LCO to harvest as much energy as possible.