

Optimization of Localized High Concentration Electrolytes (LHCE) for Li LiCoO₂ Batteries used in Consumer Electronics Applications

Final Report for I3T Project 75934

September 2021

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Final Report for the I3T Project 75934**Optimization of Localized High Concentration Electrolytes (LHCE) for Li||LiCoO₂ and Si|| LiCoO₂ Batteries used in Consumer Electronics Applications**

Ji-Guang Zhang

Oct. 1, 2019 - Sep. 30, 2020

1. Introduction

PNNL's previous work on novel electrolytes has been designed for Li/NMC or Li-S batteries because these two battery systems are the best options for large scale electrical vehicle applications which focus more on high specific energy (500 Wh/kg) instead of high volumetric energy (Wh/L) which is more important for consumer electronics. In practice, the performance of electrolytes is very sensitive to the selection of cathode materials because different cathodes have different catalytic effect and surface stability in a given electrolyte. For consumer electronics applications, the best cathode material to date is still LiCoO₂ (LCO) which has the highest volumetric energy density and the most stable electrochemical stability.

This project will optimize localized high concentration electrolyte (LHCE) for Li/LCO and Si/LCO batteries for consumer electronics applications, including select the best solvent and diluent, optimize the ratios of the solvents and the salt concentration. Results will be demonstrated not only in both coin cells, but also in pouch cells, which is required for large-scale commercial applications. This work can provide better understanding that would also benefit other LMB projects, including Li/NMC and Li/S batteries for electric vehicle applications. In the history of rechargeable batteries, all batteries have been first used in small scale consumer electronics, then eventually penetrate to large scale applications such as electrical vehicle or grid. We believe this development route will also be true for LMBs. By developing the best electrolyte for Li/LCO and Si/LCO chemistry, we will not only get the early market entry in consumer electronics, but we can also accumulate experience on the practical application of LMBs which can be used to further develop other types of LMBs for EV and other large-scale applications pursued by DOE.

2. Experiments and Results

PNNL has demonstrated in Li-NMC systems that LHCE can enable dendrite-free cycling of Li-metal anodes with high Coulombic efficiency and excellent capacity retention in LMBs. At the same time, LHCE exhibits low concentration, low cost, improved conductivity, and good wettability. The objective of this project is to tailor and improve the electrolytes for Li metal and Li ion batteries used for consumer applications where LCO cathode is still the best candidate for high energy density (Wh/L) batteries.

Recently, we have investigated the electrochemical performances of Li||LCO batteries using galvanostatic cycling within the voltage range of 3.0-4.5 V under different temperatures. A medium-high cathode loading of $\sim 13.5 \text{ mg cm}^{-2}$ (or $\sim 2.6 \text{ mAh cm}^{-2}$ under 4.5 V) was used to ensure that an appreciable amount of Li metal was deposited and stripped each cycle. The charge and discharge rates were 0.63 and 1.9 mA cm^{-2} , respectively. In the conventional carbonate electrolyte (1 M LiPF₆ in ethylene carbonate (EC)-ethyl methyl carbonate (EMC) (3:7 by vol.) with 2 wt.% vinylene carbonate (VC), referred as BL-carbonate electrolyte hereafter), the Li||LCO cell, with 450 μm thick Li and 75 μL electrolyte, shows a continuous capacity fading along with obvious overpotential increases in voltage profiles at room temperature (Figures 1a). Figure 1b shows the cycling performances of Li||LCO cells dramatically improved when a newly formulated ether-based LHCE (named AD-ether electrolyte or M57 as shown in the Table 1) is employed. The electrolyte consists of lithium bis(fluorosulfonyl)imide (LiFSI), 1,2-dimethoxyethane (DME) and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE), with a molar ratio of 1: 1: 3. TTE has a negligible ability to dissolve LiFSI compared to DME, thus it is rarely involved in the solvation of the salt ions. Previously, a ratio of 1: 1.2 between LiFSI and DME was found to be useful for the Ni-rich LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathode under 4.4 V. Here, the higher salt/solvent ratio selected is to minimize the amount of “free” solvent DME while maintaining a good miscibility with the diluent TTE. The cycling stability of Li||LCO cells is dramatically improved in the AD-ether electrolyte.

At RT, the cell can maintain 92.9% of the initial capacity after 300 cycles (Figure 1b). Meanwhile, the cell shows very consistent voltage profiles over the entire cycling, with minimum middle voltage drop, which implies the excellent cathode stability under high voltage in the AD-ether electrolyte. The greatly increased cell CE of about 99.9% suggests that the undesired side reactions between the electrolyte and the LCO cathode under high voltage are largely suppressed. Furthermore, the AD-ether electrolyte could enable superior cell cycling performances under elevated temperatures. Under 45 °C and 55 °C, the cell capacity retentions are 83.6% (300 cycles) and 81.3% (200 cycles), respectively. The lower cell CEs observed during earlier cycles under elevated temperatures (Figure 1b) are due to the accelerated electrolyte side reaction kinetics compared to that under RT. Nevertheless, the CEI gradually stabilizes to inhibit parasite reactions and improves the cell CEs to a high level. Overall, the AD-ether electrolyte significantly improves the Li||LCO battery cycling performance under 4.5 V. In a separated long-term cycling test, the cell delivers a high specific capacity of 136.7 mAh g^{-1} (corresponding to $\sim 80\%$ capacity retention) after cycling for 800 times under RT (charge and discharge at 0.63 and 1.9 mA cm^{-2} , respectively) without dendrite-induced cell short-circuiting (Figure 1c, where lower discharge capacities in first few cycles are likely due to the initial passivation film formation on that batch of Li metal chips).

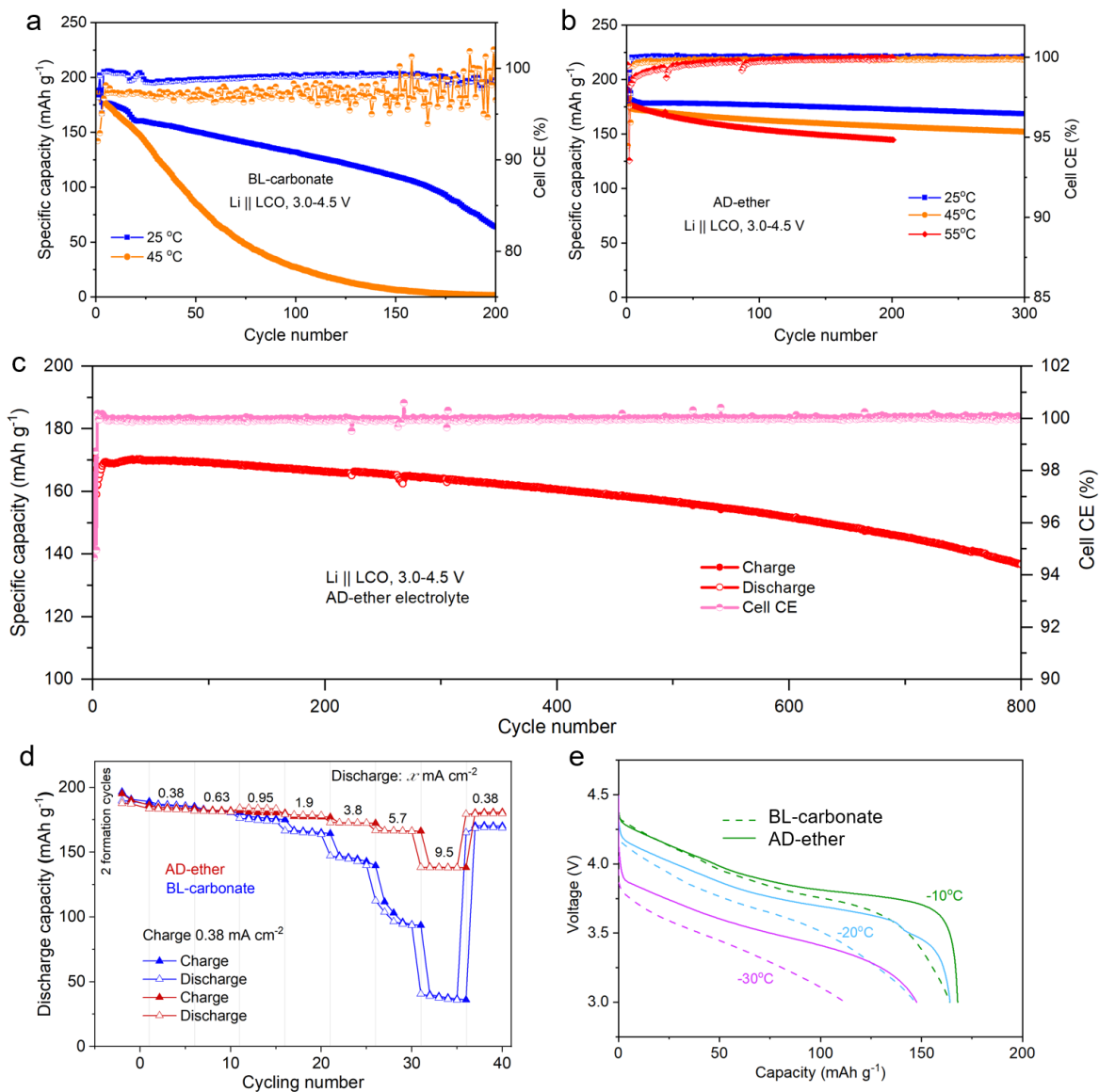


Figure 1. Electrochemical performances of Li||LCO batteries. (a) Cycling performances in the BL-carbonate electrolyte at 4.5 V under RT and 45 °C. (b) Cycling performances in the AD-ether electrolyte at 4.5 V under RT, 45 °C and 55 °C. (c) Long-term cycling stability test in the AD-ether electrolyte under RT. (d) Cell discharge rate capability tests at RT in different electrolytes. (e) Discharge tests under low temperatures in different electrolytes.

A specific capacity of nearly 140 mAh g⁻¹ can be achieved at 9.5 mA cm⁻² discharge rate for the AD-ether electrolyte, far better than that measured in the BL-carbonate electrolyte (Figure 1d). In addition, when tested at sub-zero temperatures (-10, -20 and -30 °C), the cells with the AD-ether electrolyte exhibit apparently higher discharge capacities and average voltage outputs (Figure 1e). It is indicated that the AD-

ether electrolyte not only shows excellent electrochemical stabilities with the Li metal anode and the reactive LCO cathode at high voltage and under elevated temperatures, but also improves the battery rate capability and low-temperature discharge behaviors. Therefore, the use of the AD-ether electrolyte, instead of the conventional BL-carbonate electrolyte, addresses many critical challenges confronted with high energy density Li||LCO batteries and significantly promotes their practical applications.

2.1 Optimization of LHCE for Li||LCO batteries under practical condition

In addition to the previous test with flooded electrolyte and thick Li foil (450 μm), we investigated our LHCE electrolytes under practical condition, where commercial LCO cathode (3.5 mAh/cm²) were used as cathode, thin lithium (50 μm) was used as anode and lean electrolyte (4 g/Ah) was sealed in the coin cell. Table 1 shows the list of LHCE electrolytes have been investigated under this practical condition.

Table 1. The list of electrolytes for Li||LCO evaluation at practical condition

Code Name	Electrolyte	Anode	Cathode
LHCE-1	1LiFSI-1.2DME-3TTE	Li metal	LCO
LHCE-2	1LiFSI-1DME-3TTE (mole ratio)	Li metal	LCO

As shown in Figure 2, stable cycling were obtained in Li||LCO cells with LHCE-1 and LHCE-2 under practical condition at high voltage. The initial capacity of the Li||LCO cells were 180 mAh/g when charged to 4.5 V. Meanwhile, high CE of 96.5% were obtained in the initial cycle for both electrolyte. In addition, CE quickly increase to 99.7% after the formation cycles and is stable during the cycling.

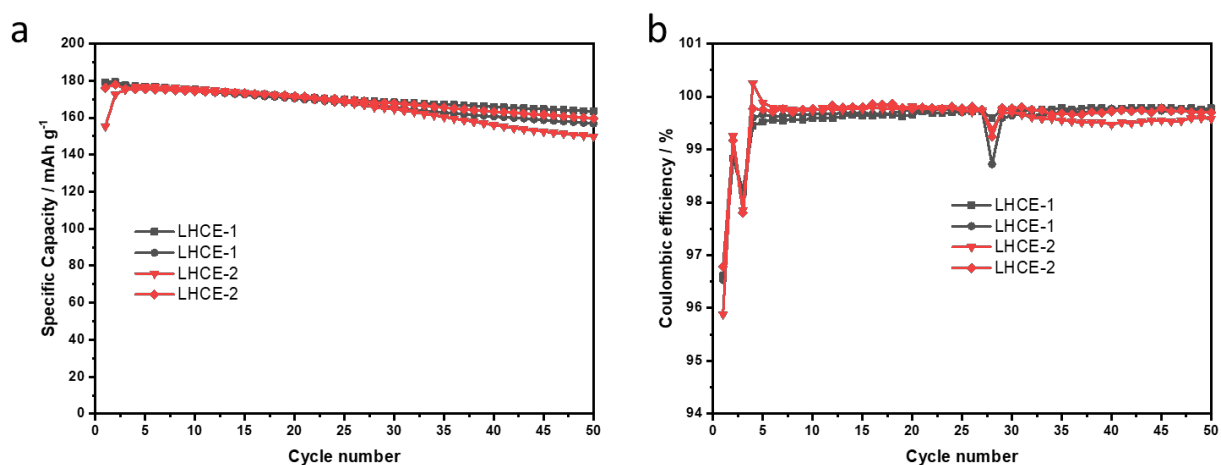


Figure 2. Electrochemical performances of Li||LCO batteries under practical condition (3.5 mAh/cm² LCO cathode, 50 μm and lean electrolyte). (a) Specific capacity and (b) Coulombic efficiency of Li||LCO cells under RT at high voltage of 4.5 V.

2.2 Optimization of LHCE for anode free Cu||LCO batteries

In order to further improve the energy density and safety of the Li||LCO cells, Li anode was replaced with Cu current collector, forming anode-free Cu||LCO cells. 5 LHCE electrolytes with different amounts of DME solvent and different type and amount diluents (TTE and TFEO) as shown in Table 2 have been investigated in this work.

Table 2. The list of electrolytes for Li||LCO evaluation

Code Name	Electrolyte	Anode	Cathode
LHCE-1	1LiFSI-1.2DME-3TTE	Cu	LCO
LHCE-2	1LiFSI-1DME-3TTE (mole ratio)	Cu	LCO
LHCE-3	1LiFSI-1.1DME-3TTE (mole ratio)	Cu	LCO
LHCE-4	1LiFSI-1.2DME-2TFEO (mole ratio)	Cu	LCO
LHCE-5	LiFSI-1.2DME-2.25TTE-0.75TFEO (mole ratio)	Cu	LCO

Two types of LCO electrodes (named LCO-1 and LCO-2 for the vendor 1 and 2) were first evaluated with the same electrolyte (LHCE-5). Cu||LCO cell using LCO-2 show better cell performance than those using LCO-1 cathode as shown in Fig. 3. To eliminate the cathode influence, LCO-1 was selected to evaluate all the electrolytes in Cu||LCO cells.

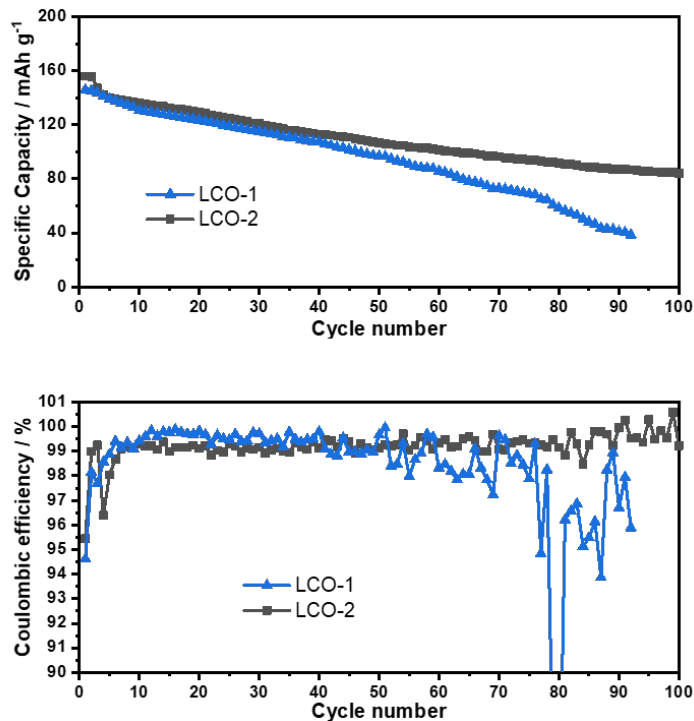


Figure 3. Electrochemical performances of Cu||LCO batteries with different type of LCO. (a) Specific capacity and (b) Coulombic efficiency of Cu||LCO cells under RT. Cells were tested between 2.8-4.3 V at

0.1 C charge and 1 C discharge after two formation cycles at 0.1 C. Cu anode disks (diameter of 1.43 cm) were slightly larger than the LCO cathode (diameter of 1.27 cm).

Figure 4 compared the Cu||LCO cells with electrolytes LiFSI-xDME-3TTE (x=1.2, 1.1 and 1 respectively). As show in Figure 4a-4c, these three electrolytes with different amount of DME show very similar cell performance with 200 cycle. Capacity retention of ~58% were achieved in the Cu||LCO cells after 100 cycles and 40% capacity retention after 200 cycles.

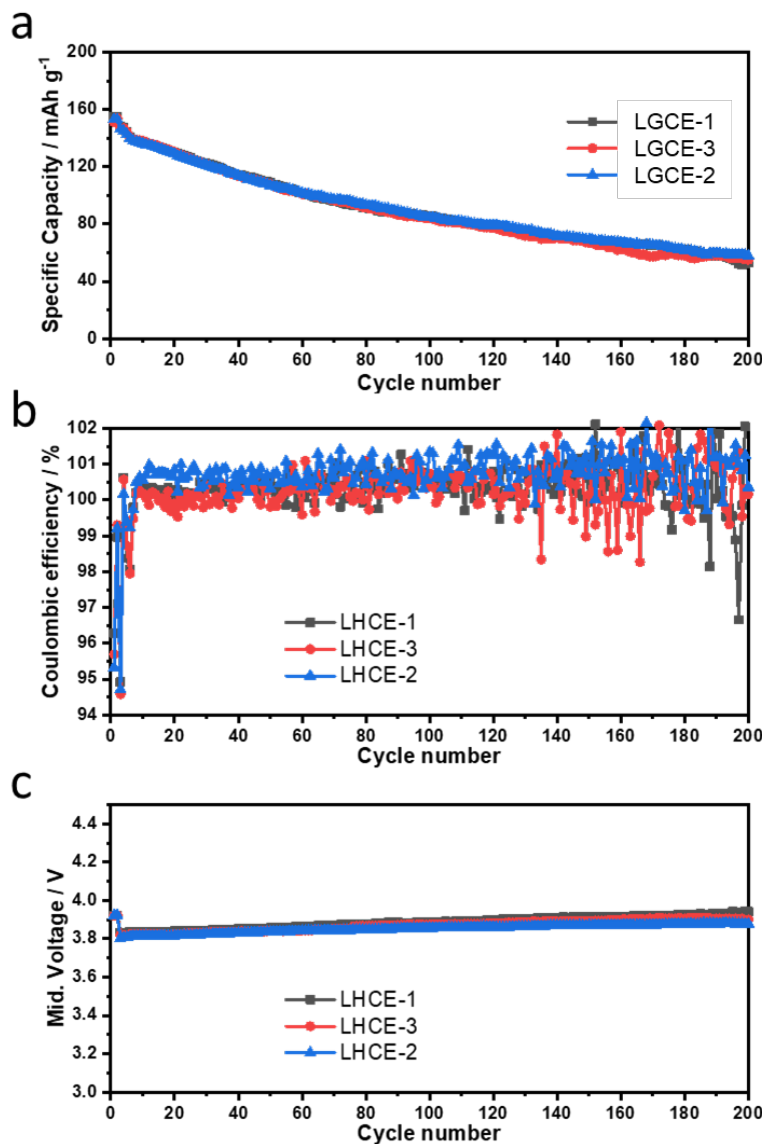


Figure 4. Electrochemical performances of Cu||LCO batteries as a function of cycle number with different electrolytes. (a) Specific capacity; (b) Coulombic efficiency, and (c) Middle voltage of Cu||LCO cells under RT. Cells were tested between 2.8-4.3 V at 0.1 C charge and 1 C discharge after 2 formation cycles at 0.1 C. LCO cathode and Cu anode disks have the same size (diameter of 1.27 cm).

In addition to the solvent amount variation, we also evaluated the electrolyte performance with different diluents. As shown in Figure 5, the specific capacity of the Cu||LCO cells with three different electrolytes were similar (Figure 5a). However, differences are shown in the CE and Mid. V. As shown in Figure 5b, by LHCE-4 with TFEO as diluent, the Cu||LCO cell has higher average CE, close to 100% than that of 99.4% in LHCE-1 and LHCE-5, which may be related to higher oxidation stability of the LHCE-4. However, as shown in Figure 5c, cell using LHCE-4 has slightly lower (0.05 V) Mid. Voltage than those using LHCE-1 and LHCE-5, which is possibly caused by the higher viscosity of TFEO than TTE. TFEO has much larger molecular weight of 310 than 232 of TTE. Mixture of TTE and TFEO lead to the electrolyte behave more like TTE diluent.

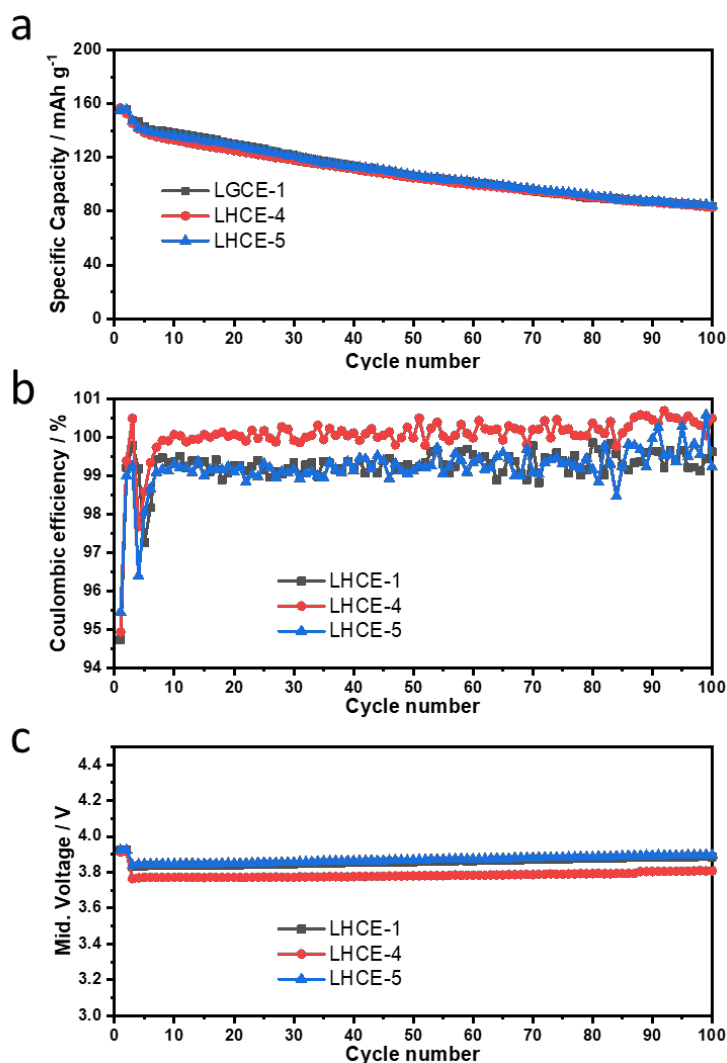


Figure 5. Electrochemical performances of Cu||LCO batteries with different electrolytes. (a) Specific capacity, (b) Coulombic efficiency, and (c) Middle voltage of Cu||LCO cells under RT. Cells were tested between 2.8-4.3 V at 0.1 C charge and 1 C discharge after two formation cycles at 0.1 C. Cu anode disks (diameter of 1.43 cm) were slightly larger than the LCO cathode (diameter of 1.27 cm).

2.3 Stabilize Porous Si Structure to Enable Highly Stable Si Anode for Li-Ion Batteries

In addition to Li||LCO and Cu||LCO batteries that are the long term potential candidates for consumer electronics, Si||LCO batteries are the near term solution for high energy density Li ion batteries. Therefore, we further investigated the LHCE electrolytes for Si||LCO cells compared to the baseline electrolyte. Table 3 shows the electrolyte formulation and cell chemistry.

Table 3. The list of electrolytes for Si||LCO evaluation

Code Name	Electrolyte	Anode	Cathode
Conventional electrolyte	1.2 M LiPF ₆ in EC-PC-EMC (1:3:6 by wt) + 1 wt% VC + 7 wt% FEC	Si	LCO
LHCE-6	LiFSI-2DMC-TTE+addtives-1	Si	LCO
LHCE-7	LiFSI-2DMC-TTE+addtives-2	Si	LCO

In house prepared C/SiC/p-Si composite anode was used in this study. Figure 6 shows the cycling stability of the C/SiC/p-Si composite in half cell. Excellent stability was observed in this cell with a 100% capacity retention after 200 cycles. When paired with LCO cathode, stable cycling was obtained with both types of commercial LCO electrodes in the cell using LHCE-6 electrolyte as shown in Figure 7. For the cell using LCO-2, 71% capacity retention was achieved after 400 cycles.

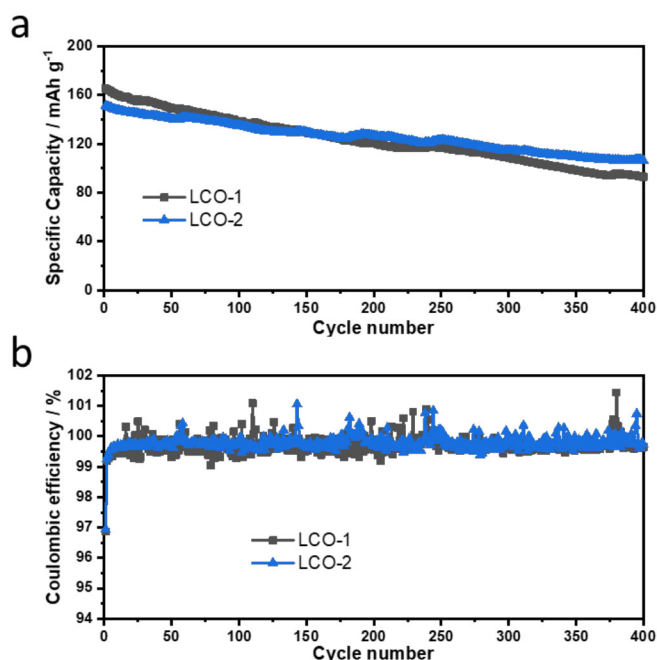


Figure 7. Electrochemical performances of Si||LCO batteries with different LCO electrode. (a) Specific capacity and (b) Coulombic efficiency of Si||LCO cells under RT. Cells were tested between 2-4.45 V at 0.7 C charge and 0.5 C discharge after 3 formation cells at 0.1 C for the first cycle and 0.2 for the second and third cycles.

2.4 Validation of LHCE for using pouch cells

The advantages of LHCE for Si||LCO batteries were validated in single layer pouch cells with a capacity of ~64 mAh. Si source used in this work is micron sized porous Si particle developed in PNNL. The cells are charged/discharged within a voltage window from 2.75 to 4.35V with 0.1C at the 1st cycle, 0.2C at the 2nd cycle and 0.5C (discharge)/0.7C (charge) thereafter. A capacity check cycle is done at every 50 cycles at 0.2C. Fig. 8 compares the cycle life of a Si||LiCoO₂ single layer pouch cell (SLP) using different electrolytes. The cells cycled in PNNL's LHCE-7 electrolyte can retain 92% capacity in 1350 cycles. This is much better than those cycled in the conventional electrolyte (1.2 M LiPF₆ in EC-PC-EMC (1:3:6 by wt) + 1 wt% VC + 7 wt% FEC) (80% capacity retention in 1000 cycles).

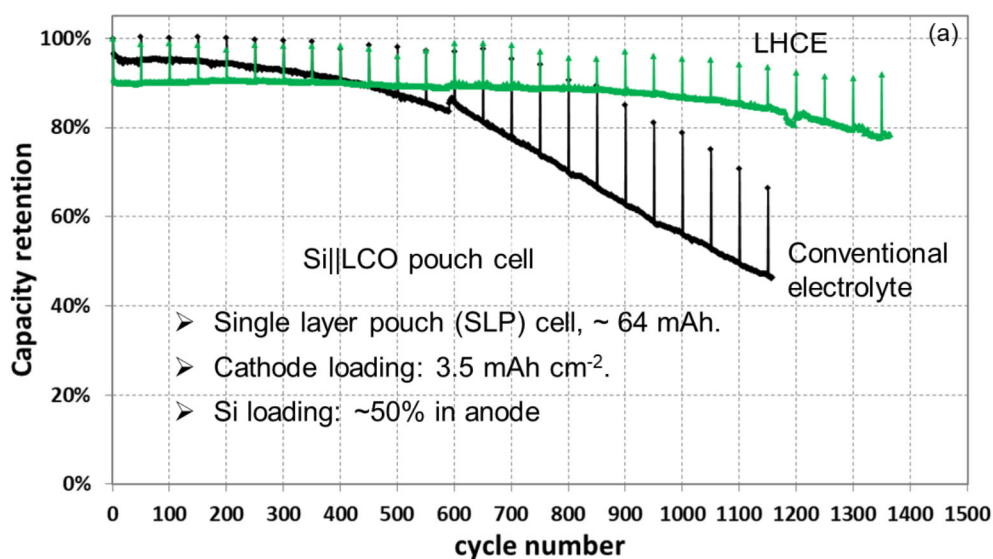


Figure 8. Comparison of the capacity retention of Si/LCO cells in the conventional electrolyte and LHCE electrolytes. The cells are charged/discharged within a voltage window from 2.75 to 4.35V with 0.1C at the 1st cycle, 0.2C at the 2nd cycle and 0.5C (discharge)/0.7C (charge) thereafter. A capacity check cycle is done at every 50 cycles at 0.2C.

The performances of Si||LCO pouch cells with different anode loading (1500 mAh/g, 1200 mAh/g, and 1000 mAh/g) were further investigated using conventional electrolyte (1.2 M LiPF₆ in EC-PC-EMC (1:3:6 by wt) + 1 wt% VC + 7 wt% FEC). The testing results shown in Fig. 9 indicate that reduced anode loading capacity can lead to more stable cycling of the cells. This will be one of the important parameters need to be considered in practical applications.

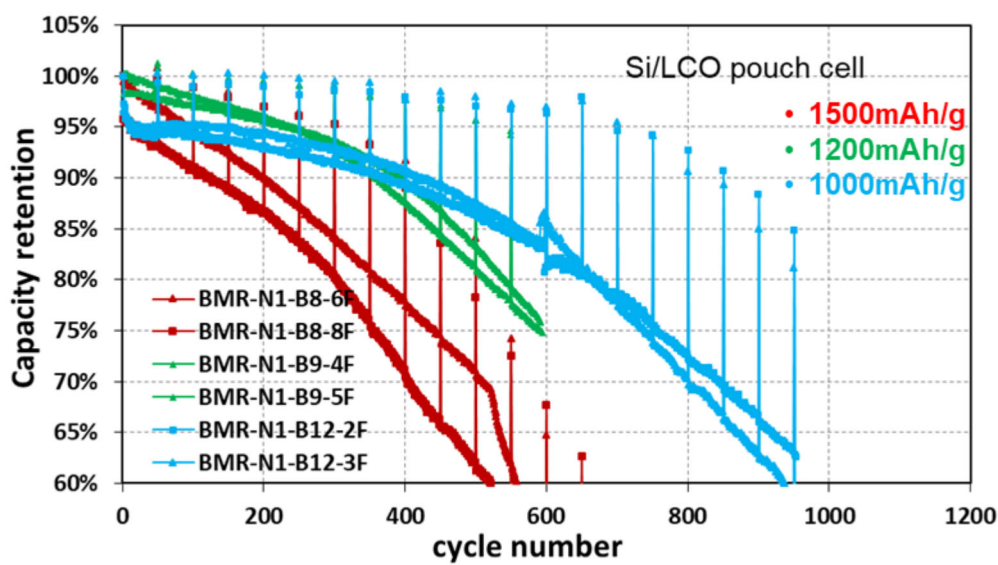


Figure 9. Comparison of the cycling performance of Si||LCO pouch cells using different cathode loadings. The cells are charged/discharged within a voltage window from 2.75 to 4.35V with 0.1C at the 1st cycle, 0.2C at the 2nd cycle and 0.5C (discharge)/0.7C (charge) thereafter. A capacity check cycle is done at every 50 cycles at 0.2C.

3. Conclusion

In summary, localized high concentration electrolytes (LHCE) with DME solvent and TTE diluent (LHCE-2: 1 LiFSI-a1 DME-b1TTE (mole ratio)) is a very promising electrolytes for Li||LCO batteries. LHCEs LiFSI-xDME-3TTE, LiFSI-1.2DME-2TFEO and LiFSI-a4DME-b4TTE/TFEO show good capacity retention in Cu||LCO cells. On the other hand, LHCE-6 and LHCE-7 electrolytes with LiFSI salt, DMC solvent, TTE diluent and proper additives are very promising electrolytes for Si||LCO batteries. These LHCE electrolytes are the good candidates to enable long cycle life of LCO based high energy density batteries for consumer electronics applications.

Publications/patent applications:

1. Ji-Guang Zhang, Ran Yi, et al., Stabilized Porous Silicon Structure for Highly Stable Silicon Anode and Methods of Making, U.S. provisional patent application filed on 5/2020.
2. Wu Xu et al., Electrolytes For Lithium Ion Batteries With Graphite and/or Silicon Anodes, U.S. provisional patent application filed on 9/2020.
3. Xiaodi Ren, Xianhui Zhang, Zulipiya Shadike, Lianfeng Zou, Hao Jia, Xia Cao, Mark H. Engelhard, Chongmin Wang, Bruce W. Arey, Xiao-Qing Yang, Jun Liu, Ji-Guang Zhang,* Wu Xu*, Designing Advanced In Situ Electrode/Electrolyte Interphases for Wide Temperature Operation of 4.5 V Li||LiCoO₂ Batteries, *Advanced Materials*, First published: November 4, 2020; <https://doi.org/10.1002/adma.202004898>.

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