



An *in-situ* enabled lithium metal battery by plating lithium on a copper current collector

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ABSTRACT

An *in-situ* enabled lithium battery (or called a "Li-free" battery) is proposed by using Li-rich Li₂CuO₂ additive to pre-plate Li metal onto Cu current collector. Conventional Cu foil is unsuitable for efficient Li cycling particularly due to poor adhesion of Li deposits to the Cu substrate and the dendritic deposition nature of Li metal. As a solution to this problem, a very thin Li metal layer is *in-situ* pre-plated onto the Cu surface and served as the primer layer for next Li cycling in the battery. Results show that the addition of Li₂CuO₂ not only provides extra Li⁺ ions for forming a very thin Li primer layer on the Cu current collector but also enhances rate capability of LiNi_{0.80}Mn_{0.10}Co_{0.10}O₂ cathode, which is probably because the presence of CuO particles (one of Li₂CuO₂ decomposition products) increases liquid electrolyte uphold in the cathode.

1. Introduction

Minimizing of excessive Li is of particular significance in commercialization of rechargeable Li batteries. In batteries using a Li foil as the anode, capacity of the anode is extremely excessive compared with that of the cathode due to the lack in the technology that can make and handle very thin Li foils to match the capacity of cathode. The excessive Li not only reduces energy density but also increases safety hazard of the battery as residual Li immediately becomes a strong fuel upon exposure to air or water in an accident. In efforts to develop safe Li batteries, a Li-free battery has been proposed by *in-situ* plating Li metal onto the Cu current collector [1,2]. Without the use of air and moisture sensitive Li metal, the Li-free battery is furthermore advantageous in cost over the conventional Li metal batteries. However, the progress in this research has been very limited due to rather low cycling efficiency of Li metal on the Cu substrate in carbonate-based electrolytes [2–4]. For the Cu substrate, poor adhesion of Li deposits, which typically results in the formation of mossy "dead" Li, is particularly responsible for inefficient Li cycling. In many cases, the Li metal deposited on the Cu substrate cannot be fully stripped, instead, some "dead" Li powders remain as mossy sediments [2,5,6]. Two approaches have been reported to be effective in enhancing the adhesion of Li deposits: One is to increase the pressure between two electrodes [7,8], and the other is to modify the surface of Cu substrate with a more lithiophilic material, such as functional graphene materials [9,10], structured carbon nanotubes [11], highly conductive carbon [12], as well as Li-alloy forming

tin [4], which could be applied to the Cu surface either by slurry-coating or by chemical depositing technique.

Taking the fact that the plated Li cannot be fully stripped into account, in this work we intendedly pre-plated a very thin Li metal layer on the surface of Cu current collector and let resultant Li metal layer permanently stay on the Cu surface to serve as a primer layer for next Li cycling in the battery. We believe that next Li deposits have better adhesion to the pre-plated Li primer layer compared with the Cu substrate. In order to implement this proposal, an extra Li⁺ ion source material (LSM) is needed for *in-situ* pre-plating Li primer layer. Ideally, the LSMs are required to be capable of irreversibly providing high delithiation capacity in the operating potential range of the cathode while not affecting the battery's performance [13]. In past years, many Li-rich compounds, such as Li₆CoO₄ [14], Li₅ReO₆ [15], Li₂CuO₂ [13,16], Li₂MoO₃ [17], Li₂RuO₃ [18], Li₂O [19], Li₂S [20,21], have been studied as the LSM to compensate for initial capacity loss of the Li-ion batteries, or eliminate costly and complicated pre-lithiation of the negative electrode for Li-ion capacitors. On the other hand, fluoroethylene carbonate was verified to be a favorable solvent for efficient plating and stripping of Li metal due to its ability to participate in forming robust solid electrolyte interphase (SEI) with Li metal [22]. On the basis of the above backgrounds, in this work we selected Li₂CuO₂ as the LSM and a fluoroethylene carbonate containing solution as the electrolyte to demonstrate and validate our proposal.

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2. Experimental

$\text{LiNi}_{0.80}\text{Mn}_{0.10}\text{Co}_{0.10}\text{O}_2$ (NMC811, hereafter referred to NMC) was received from Argonne National Laboratory, and Li_2CuO_2 (LCO) was synthesized by the solid-state reaction of Li_2CO_3 and CuO at 800°C in air for 24 h as described in our previous paper [13]. Their morphology and crystallographic structure were verified by scanning electron microscopy and X-ray diffraction. Electrodes consisting of 80% active material, 10% Super-P carbon black and 10% poly(acrylonitrile-methyl methacrylate) binder were slurry-coated onto an aluminum foil by using *N*-methyl pyrrolidinone solvent. Composition of the hybrid active material was expressed as (80-*x*)NMC-*x*LCO, and all electrodes had a $5.0\text{--}5.5\text{ mg cm}^{-2}$ of NMC loading. The electrolyte used was a solution of 1.0 m (molality) LiPF_6 dissolved in a 3:6:1 (wt.) mixture of ethylene carbonate, ethylmethyl carbonate, and fluoroethylene carbonate.

BR2335-sized coin cells were assembled and filled with $40\ \mu\text{L}$ electrolyte by using a Celgard 2400 separator, and cycled on a Maccor Series 4000 tester under conditions noted in figure caption or figure. Rate capability was tested by charging galvanostatically at 0.5 C to 4.2 V, followed by charging potentiostatically at 4.2 V until the current declined to 0.1 C, and the C rate was referred to a specific capacity of 150 mAh g^{-1} NMC. Ac-impedance of the cells was measured using a SI 1260 Impedance/Gain-Phase Analyzer in combination with a Solartron SI 1287 Electrochemical Interface in the frequency from 1.0×10^5 Hz to 0.01 Hz and an ac oscillation of 10 mV amplitude.

3. Results and discussion

High Li cycling efficiency is particularly important for the *in-situ* enabled Li batteries due to the limited amount of Li^+ ions available from the cathode. Bare Cu foil is shown to be unsuitable for efficient Li cycling [4,23]. Firstly, Li cannot homogeneously deposit (nucleate) on the Cu surface [23]. Secondly, adhesion of Li deposits to the Cu substrate is rather poor, as indicated by the peeling-off of Li deposits and a large gap between Li deposits and the Cu substrate [4]. The poor adhesion of Li deposits is an important cause leading to the formation of mossy “dead” Li. Due to the poor adhesion of Li deposits as well as the extreme reactivity of Li metal, the mossy Li deposits may be quickly reacted with electrolyte solvents and isolated from the Cu substrate by resultant electron-insulating reaction products, forming “dead” Li. It is further found that even in the first cycle, the Li deposits cannot be fully stripped out of the Cu substrate, instead, some grey mossy residues remain on the Cu surface. These grey residues produce hydrogen bubbles when coming into contact with water, confirming the presence of “dead” Li along with the electrolyte reaction products. In other words, the low cycling efficiency of Li metal on the Cu substrate is not only due to the high reactivity of Li metal with electrolyte solvents but also due to the formation of “dead” Li as a result of the poor adhesion of Li deposits to the Cu substrate.

In order to avoid the poor adhesion problem, we propose pre-plating a very thin Li metal layer on the Cu surface so that next Li can be plated and striped on the Li primer layer. Fig. 1a schematically explains our proposal. In the case that Li deposits are completely stripped, in each cycle the SEI on the Li surface is broken and “dead” Li is formed. The broken SEI fragments and “dead” Li are loosely accumulated as mossy sediments on the Cu surface, and the similar process repeats cycle-by-cycle. Because each cycle irreversibly consumes Li^+ ions from the cathode, such a battery cannot last long. On contrast, in the case that Li deposits are partially stripped (namely equivalent to the presence of a very thin Li primer layer), next Li cycling occurs on the surface of Li metal, and the SEI remains intact on the surface of Li metal, which effectively prevents the formation of “dead” Li.

In order to demonstrate an *in-situ* enabled Li battery, NMC is selected as the cathode material and LCO as the LSM. Fig. 1b shows voltage profile of the first cycle for a Li/NMC cell and a Li/LCO cell, respectively. The first charging of LCO consists of two voltage plateaus

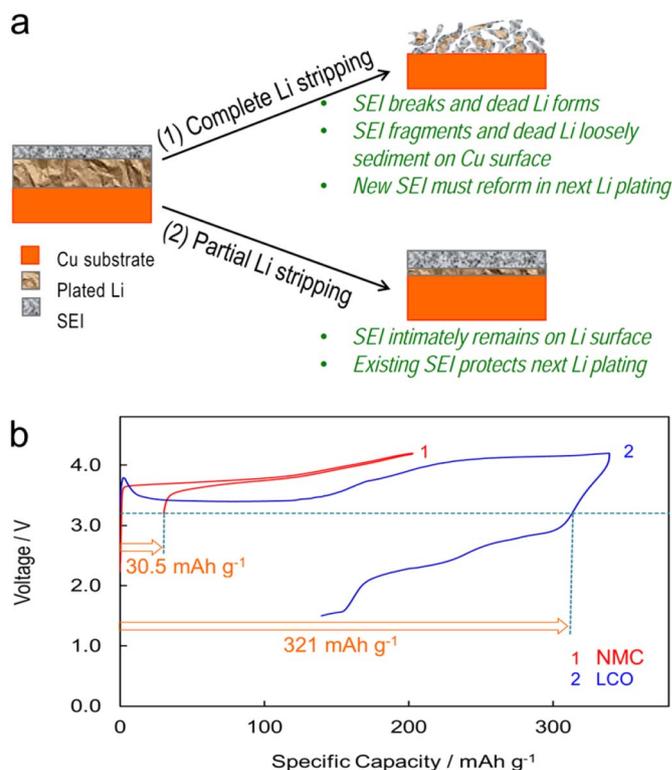


Fig. 1. (a) Schematic comparison of Li plating with complete and partial Li stripping, and (b) voltage profile of the first cycle of Li/NMC and Li/LCO cells at 0.1 mA cm^{-2} between 3.2 V and 4.2 V, where the hollow arrows indicate the Li^+ ion capacity available for *in-situ* plating Li metal on the Cu current collector.

at 3.4 V and 4.0 V, respectively, which corresponds to two reactions below [16].



Since in the second reaction LiCuO_2 is irreversibly converted (decomposed) to CuO and O_2 , the LCO can be well qualified for a LSM although it is not a good cathode material. As indicated in Fig. 1b, NMC and LCO produce a 30.5 mAh g^{-1} and a 321 mAh g^{-1} , respectively, of irreversible capacity in the potential range between 3.2 V and 4.2 V vs. Li/Li^+ . In an *in-situ* enabled Li battery, most of these irreversible capacities can be utilized to *in-situ* pre-plate the Li primer layer on the Cu current collector except for small amount of Li^+ ions consumed for forming SEI on the cathode.

Four (80-*x*)NMC-*x*LCO hybrid cathodes having a $5.0\text{--}5.5\text{ mg cm}^{-2}$ of NMC loading were prepared and first evaluated in Li metal cells. Fig. 2a indicates voltage profiles of the first cycle for four resultant Li cells. As predicted, the irreversible capacity that can be used to *in-situ* pre-plate Li primer layer onto the Cu current collector is dramatically increased with an increase in the *x* value. Next, the fresh hybrid cathodes were used to assemble *in-situ* enabled Li cells by using a bare Cu foil as the current collector. Resultant Cu/(NMC-LCO) cells were first formed at 0.1 mA cm^{-2} for two cycles to plate a Li primer layer, and then cycled at 0.5 mA cm^{-2} . Their cycling performances are presented in Fig. 2b. It can be seen that for the cell with $x = 0$ (i.e., the pristine Cu/NMC cell without LCO), its capacity fades very fast, linearly declining to zero at the 39th cycle. With the addition of LCO, the cell's performance is dramatically improved, and the capacity retention increases with the *x* value, in which the latter is likely associated with the integrity of the Li primer layer. As *x* equals to 10 and 20, the amount of Li deposits may not be sufficient to fully cover the surface of Cu current collector. As *x* increases to 40, a complete Li primer layer can be formed on the surface of the Cu current collector so that the cell can operate as

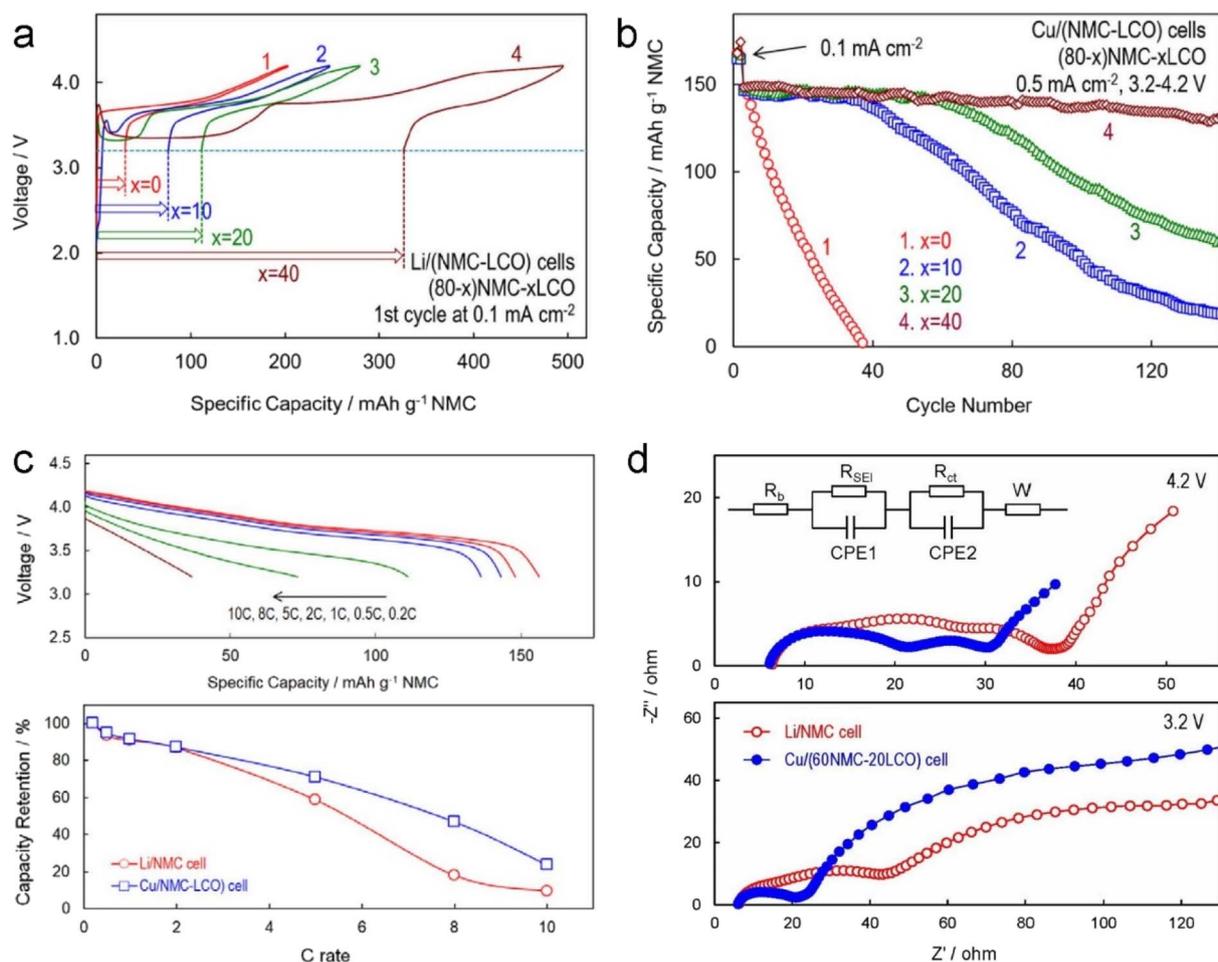


Fig. 2. (a) Voltage profile of the first cycle for Li/(NMC-LCO) cells recorded at 0.1 mA cm^{-2} , (b) capacity retention of Li-free Cu/(NMC-LCO) cells cycling at 0.5 mA cm^{-2} except for the first 2 cycles at 0.1 mA cm^{-2} , (c) rate capability of Cu/(60NMC-20LCO) cell compared with Li/NMC cell by discharging to 3.2 V, and (d) impedance spectra of Li/NMC and Cu/(60NMC-20LCO) coin cells at 4.2 V and 3.2 V, respectively.

a conventional Li battery. It should be noted that the function of the Li primer layer is to enhance the adhesion between Li deposits and the anode current collector. For this purpose, the requirement for the thickness of the Li primer layer is same for various cathodes. In other words, the amount of LCO required for forming the Li primer layer is constant for different cathodes. Therefore, the loss in the battery's energy density caused by the added weight of LCO can be minimized by reducing the weight percentage of LCO in the hybrid cathode while increasing the total loading of the hybrid cathode, namely through a high energy density battery design.

As indicated in Eq. (2), full delithiation of LCO generates oxygen, while oxygen is hard to be removed from the coin cell (note that for large cells, the oxygen can be easily released simply by performing the first charging before the cell is sealed). In order to examine the effect of oxygen on the cell's performance, rate capability of a Li-free Cu/(60NMC-20LCO) cell was representatively evaluated and the results are shown in Fig. 2c, where the top part shows discharging voltage profile at various C-rates and the bottom part compares its capacity retention with a conventional Li/NMC cell. It is surprised to observe that the presence of reactive oxygen does not hurt the cell's performance visibly. Instead, the cell's rate capability is improved. In order to understand this unusual improvement, the cells' impedances at charged state (4.2 V) and discharged state (3.2 V) were representatively analyzed (Fig. 2d). According to the equivalent circuit shown in the inset of Fig. 2d, it is found that at both states, two cells have very similar R_b and R_{ct} . However, the Cu/(60NMC-20LCO) cell has much lower R_{SEI} compared with the Li/NMC cell. These results suggest that the enhanced

rate capacity is not due to an increase in the cell reaction kinetics, instead, to an increase in the ionic conductivity of SEI or in other words of the grain boundary between the particles of cathode components. This merit is because the CuO particles, being another decomposition product of LCO, increase uphold of the liquid electrolyte in the cathode.

4. Conclusions

In summary, we proposed and demonstrated an *in-situ* enabled Li battery by using a Li-rich Li_2CuO_2 additive to *in-situ* pre-plate a very thin Li primer layer onto the Cu current collector. Bare Cu substrate cannot support efficient cycling of Li metal particularly because of the poor adhesion between Li deposits and the Cu substrate. By *in-situ* pre-plate a very thin Li layer on the Cu surface, next Li can be plated and stripped on the Li primer layer, which greatly increases the cycleability of Li metal. Results of a proof-of-concept Cu/(NMC-LCO) cell validate that the *in-situ* enabled Li battery is practically viable. Because the *in-situ* enabled Li batteries are assembled without use of Li metal and the amount of Li metal plated in the activation process (*i.e.*, the first charge) is low, they are very competitive with the conventional Li metal batteries in reducing the cost and increasing the safety.

Conflicts of interest

There are no conflicts of interest to declare.

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