Supporting Information

Novel Functional Material Carboxymethyl Cellulose Lithium (CMC-Li) Enhanced Performance of Lithium- Ion Batteries

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1. Experimental

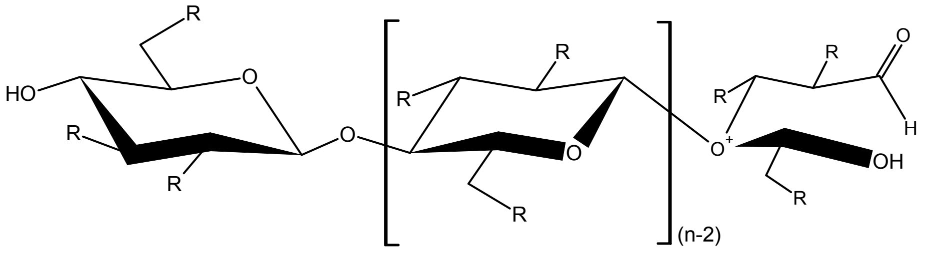
1.1 Powder preparation

The purified cotton (M100) was supplied by Xi' An North Hui Chemical Industry Co., LTD (Xi' An, China). Methylene chlorides (MC), Monochloroacetic acid, tetrahydrofuran (THF), Glacial acetic acid, hydrochloric acid (36.5% solution), ethanol (EtOH) were supplied by Beijing Chemical Fine Chemical Co., LTD (Beijing, China). LFP was kindly supplied by Shanxi power source Co. Ltd. (Taiyuan, Shanxi, China.).

The preparation process of CMC-Li can be clarified by the slurry process in a solution of isopropyl alcohol in our laboratory. CMC-Lis with different degree of substitution (DS) were prepared by selecting the DS of CMC-Na and the amount of lithium hydrate. Related product experimental details and electrospinning details are presented in our previous published articles.[1-3] In this paper, CMC-Lis with six different DS values were prepared, respectively. CMC-Li-1 (DS=0. 62, Mw = 900 g mol^{-1}), CMC-Li-2 (DS=0. 84, Mw = 2,500 g mol^{-1}), CMC-Li-3 (DS=1. 20, Mw = 4,300 g mol^{-1}), CMC-Li-4 (DS=0.65, Mw = 90,000 g mol^{-1}), CMC-Li-5 (DS=0.90, Mw = 150,000 g mol^{-1}), CMC-Li-6 (DS=1.25, Mw = 250,000 g mol^{-1}).

Synthesis of CMC-Li

The preparation process of CMC-Li can be clarified by the following schematic equation:



Cellulose (R=OH, Cell-(OH)$_3$)

$$\text{Cell-(OH)}_3 \xrightarrow[\text{ClCH}_2\text{COOH}]{\text{NaOH}} \text{Cell-(OH)}_{3-x}(\text{ONa})_{x-n}(\text{OCH}_2\text{COO}^-\text{Na}^+)_n \ (\text{Cell-CH}_2\text{COONa})$$

$$\text{Cell-CH}_2\text{COONa(CMC-Na)} \xrightarrow{\text{HCl}} \text{Cell-CH}_2\text{COOH(CMC-H)} \xrightarrow{\text{LiOH}} \text{Cell-CH}_2\text{COOLi(CMC-Li)}$$

The CMC-Na used in this experiment was obtained by preparing the slurry process in solution of isopropyl alcohol in our laboratory, through alkalization, etherification, neutralization, washing on cellulose. The DS was measured by the method of Grey alkali. DS of CMC-Li and CMC-H depends on the DS of raw materials CMC-Na. Their specific preparation processes are described as in (1) and (2).

(1) The preparation of CMC-H

The acid form of CMC-H was synthesized by treating CMC-Na with a HCl solution (c = 20%, wt %) in an ethanol/water mixture (95:5 by volume) for 2 h at 35°C. Pure CMC-H was obtained by filtering, washing with an ethanol / water mixture (85:15 by volume) and drying (T = 105°C) of the products.

(2) The preparation of CMC-Li

CMC-Li was synthesized by treating the above-mentioned CMC-H in a solution of LiOH.H_2O (c = 7%, wt %) in an ethanol/water mixture (90:10 by volume) for 2 h at 50°C. When the reaction was finished, acetic acid was added to adjust pH of the solution to pH = 7. Pure CMC-Li was obtained by filtering, washing with an ethanol / water mixture (85:15 by volume) and drying (T = 105°C) of the products.

CMC-Lis with different DS were prepared by selecting the DS of CMC-Na and the amount of LiOH.H_2O. Selecting CMC-Na with high DS (1.00) and using high amounts of $LiOH.H_2O$, the CMC-Li with DS (1.00) was prepared, and the CMC-Li with DS (0.62) was obtained from the CMC-Na with high DS (0.62).

Electrospinning:

CMC-Lis were dissolved in a mixed solvent of water, and a small amount of PEO (c = 2 %, wt %) was added to obtain the solution. LFP was added to solvent, and then intermittent ultrasound concussion was carried out 10 min later. CMC-Li was completely dissolved and poured into the needle. The processing conditions were adjusted at a flow rate of 4 ml/h, with an applied voltage of 25 KV, at a capillary tip-to-target distance of 10 cm and a temperature of 25 ^{o}C, and nano CMC-Li fiber and LFP / CMC-Li fiber were obtained by an electrospinning device.

1.2 Structural characterization and electrochemical measurements

XRD diffraction experiments were performed with a Inel Cps 300 diffract meter using the Cu Kα radiation (λ-1.54056Å).

Characterization of structured polymer electrolytes for versatile-shaped batteries: Morphology and structure of electrospun CMC-Li fiber were observed with a scanning electron microscope (SEM, JSM-6700F) after gold coating. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) results were obtained with electrochemical workstation CHI660E from Shanghai Chen Hua Instruments Co., Ltd. The coin cells (CR2025) were assembled to test the electrochemical performance of the as-prepared LFP: acetylene black: binder is 80: 10: 10, using 1.0 M $LiPF_6$ ethylene carbonate (EC): diethyl carbonate (DEC): dimethyl carbonate (DMC) =1:1:1 by volume as the electrolyte and a Li foil as the counter electrode. The cells were charged and discharged galvanostatically in the fixed potential window from 2.0 to 4.2 V on a Shenzhen Neware battery cycle (China) at room temperature. The calculated capacity was based on the whole mass of the cathode electrodes. EIS was measured by applying an alternating potential of 5 mV over the frequency ranging from 10^{-1} to 10^{5} Hz after 5 cycles. CV was conducted in a cell at 0.1 mV s^{-1} and performed from 4.2 V to 2.0 V.

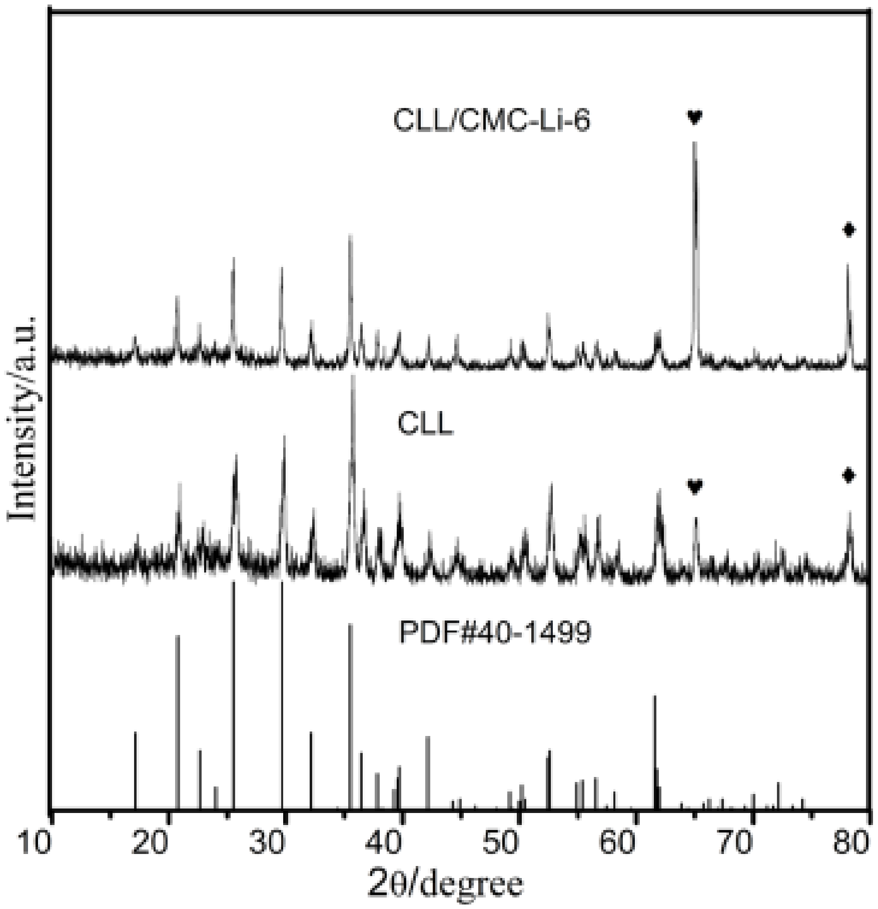


Fig. S1 XRD patterns for the electrode slices with CLL as cathode material, PVDF and CMC-Li as a binder. (PDF#40-1499 is standard XRD of $LiFePO_4$, "♥" is standard XRD of Li_3P (114) and "♦" is standard XRD of Li_2O_2 (114))

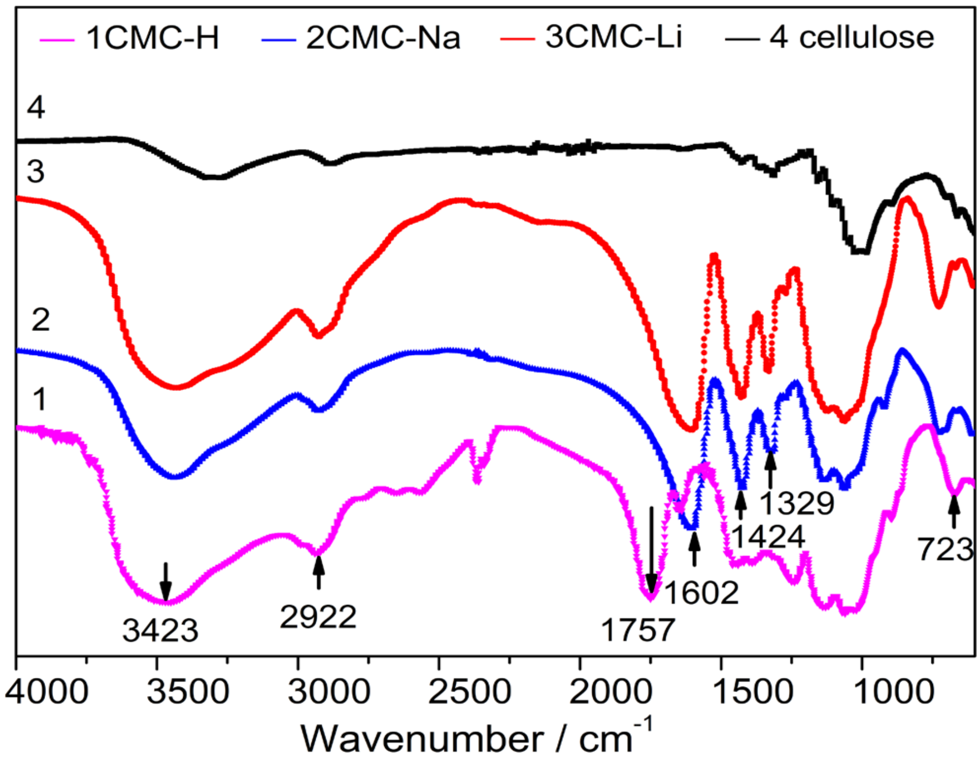


Fig. S2 FTIR spectra of cellulose, CMC-Li, CMC-Na and CMC-H

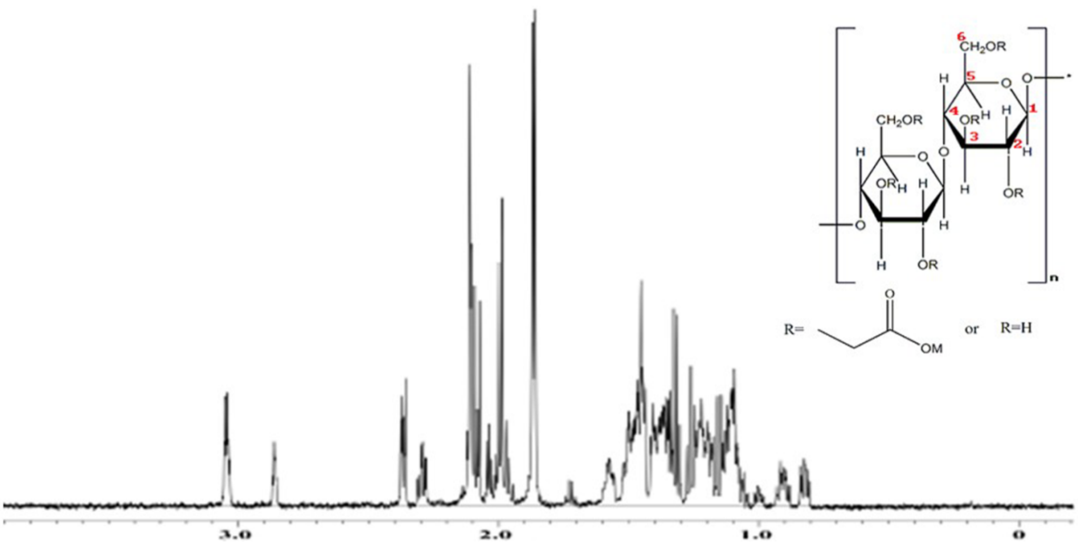


Fig. S3 The ^{1}H-NMR spectrums of CMC-Li

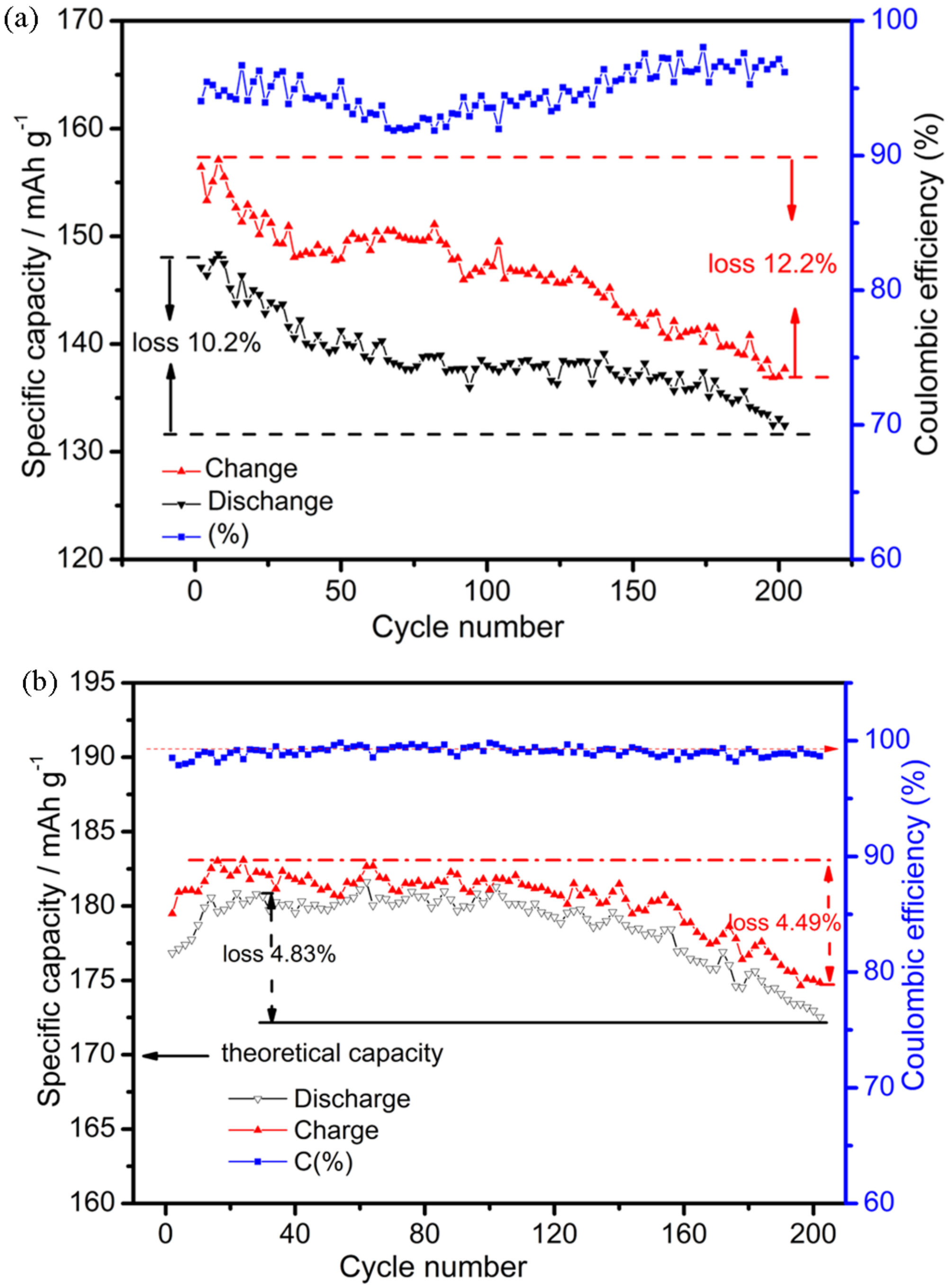


Fig. S4 The curve analysis of different materials and binders. (a) The charge and discharge specific capacity of battery with LFP as cathode material and PVDF as a binder; (b) The charge and discharge specific capacity of battery with CLL as cathode material with CMC-Li as the binder, after 200 cycles, the cycle efficiency was nearly close to 100%, the charge and discharge specific capacity beyond the theoretical capacity of LFP.

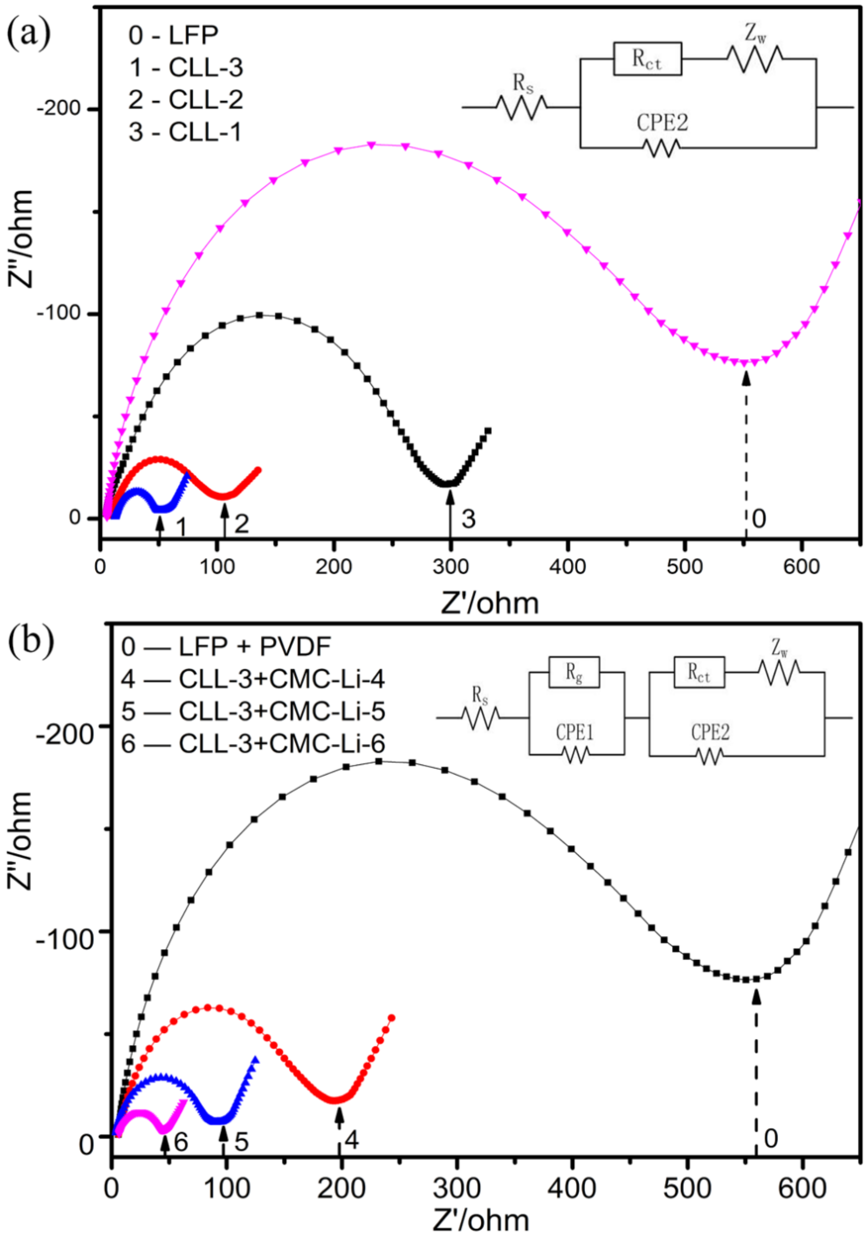


Fig. S5 The curve analysis of EIS with different materials and binders. (a) Different CLL as cathode material is used in batteries. (b) Different CMC-Lis as a binder and CLL-3 as cathode material are used in battery.

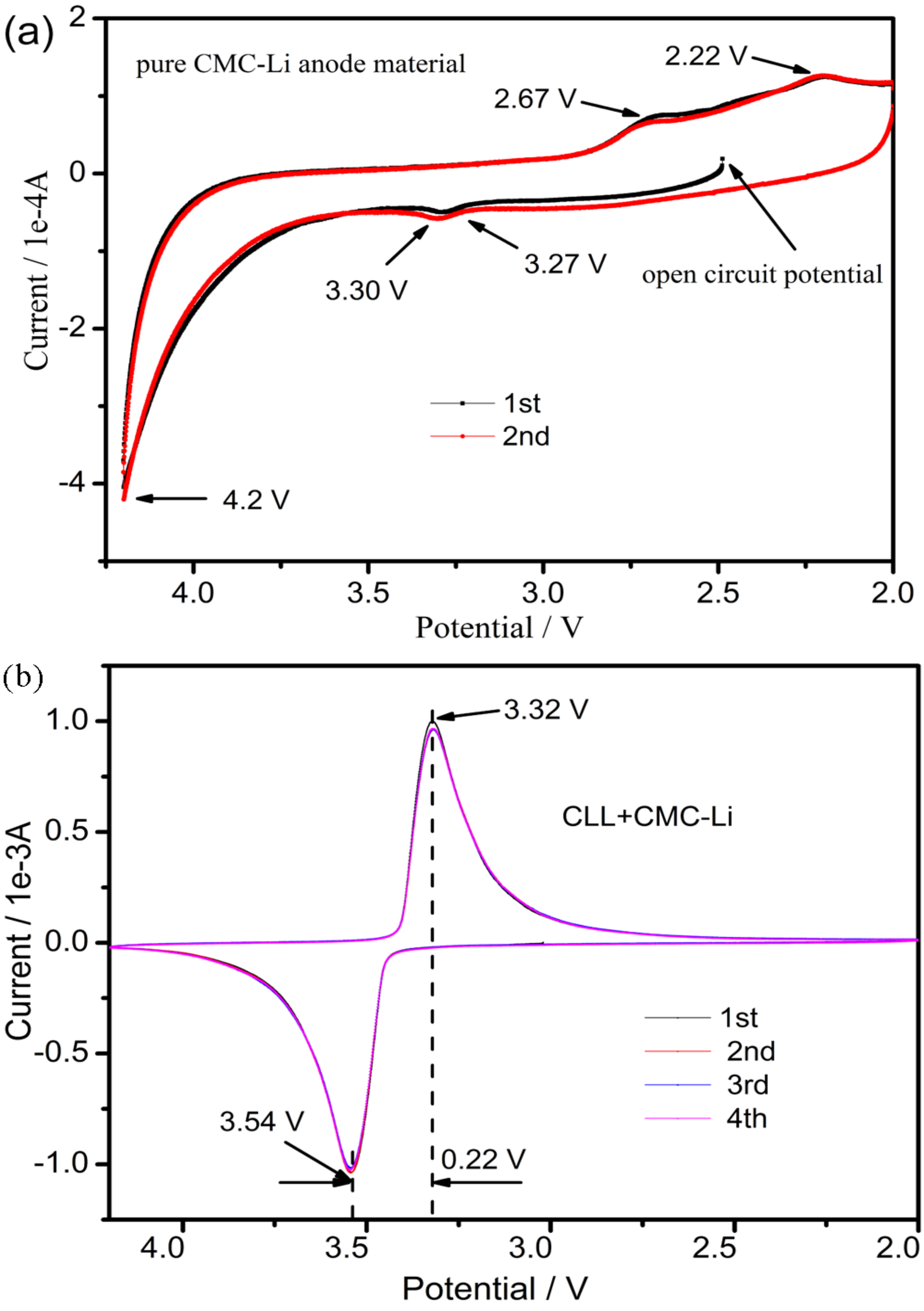


Fig. S6 The curve analysis of CV with different materials. (a) Pure CMC-Li as cathode material and binder. (b) The CV analysis of battery with CLL as cathode material and with CMC-Li as binder, and the difference of oxidation reduction peak is 0. 22 V, the polarization is very weak.

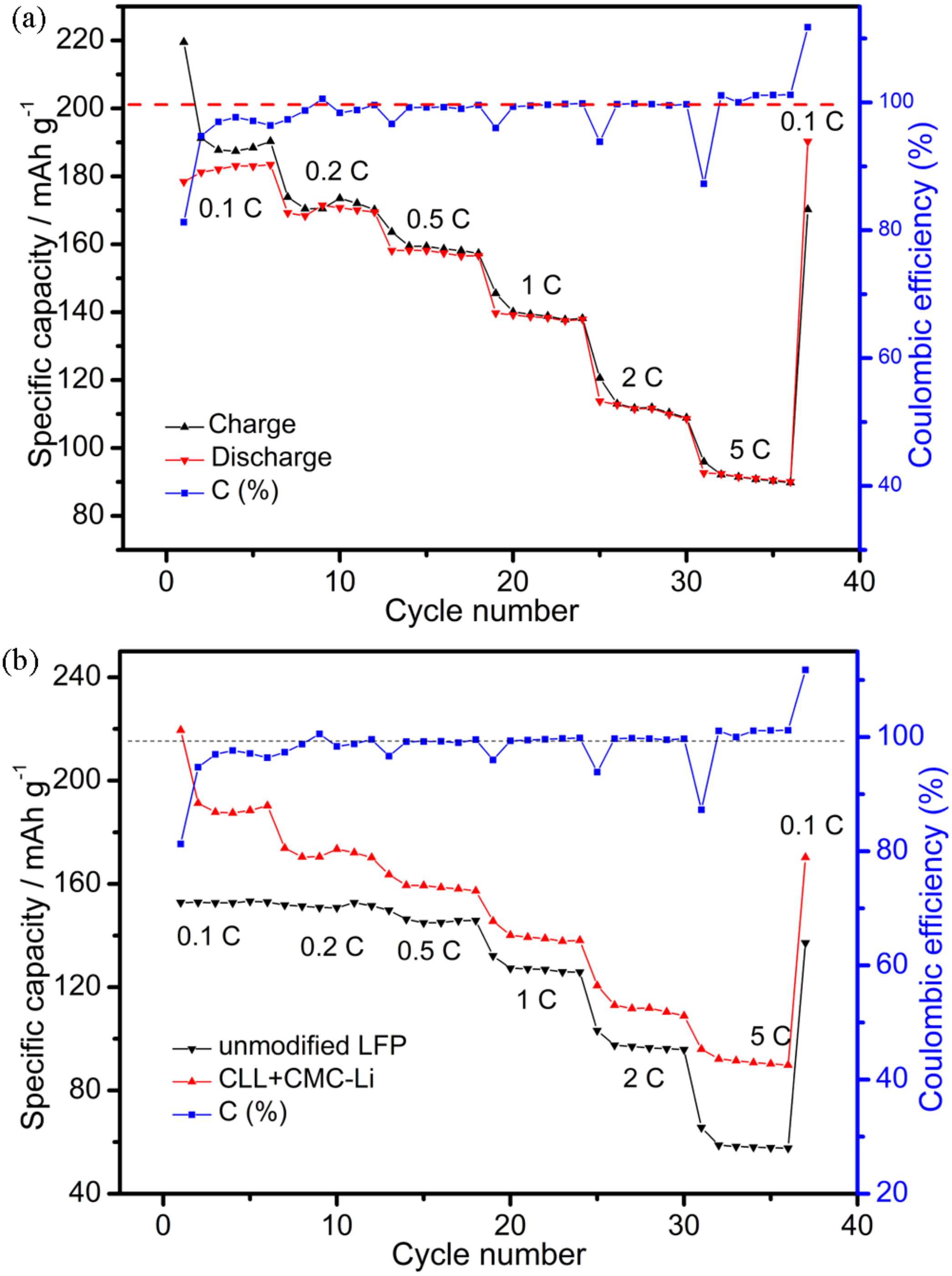


Fig. S7 The comparison of curve analysis under different charging and discharging rate with different materials. (a) The charge and discharge specific capacity of battery with CLL-3 as cathode material and CMC-Li as the binder. (b) The comparison of charge specific capacity of batteries with CLL as cathode material, CMC-Li as binder and LFP as cathode material, PVDF as a binder.

References

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