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Soil as an inexhaustible and high-performance anode material for Li-ion batteries

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Experimental Details

Synthesis. The soil comes from our campus of Nankai University, belonging to North China Plain. The soil was washed by water and heated in muffle furnace at 750 °C for 2 h. Afterwards, the soil was ball milled for 20 h at 700 r min^{-1} (labeled as a-soil) and ball milled for 20 h at 300 r min^{-1} (labeled as b-soil).

Materials characterization. The pristine soil and treated soil were characterized by powder X-ray diffraction (Rigaku MiniFlex600, Cu Kα radiation). The Brunauer-Emmett-Teller (BET) specific surface area was obtained by BELSORP-mini instrument. The morphology and element distribution of samples were observed by field-emission scanning electron microscopy (SEM, JEOL JSM7500F) and transmission electron microscopy (TEM, Tecnai G2 F20). Thermogravimetric analysis (TGA) was performed on a TG-DSC analyzer (NETZSCH, STA 449 F3) with a heating rate 5 °C min^{-1} from 20 °C to 800 °C in air atmosphere. Perkin Elmer PHI 1600 ESCA system provides XPS data. The contact angles were tested on a Dataphysics OCA20CA system. The tap density was obtained by JZ-7 powder tapping apparatus (Chengdu jingxin). The electrical conductivity was tested on electrochemical workstation versa STAT 4. Measurement of tapped density: 10 g a-soil, 10 g artificial graphite, and 10 g KS-6 were put into the glass tubes separately. Via JZ-7 tapped density analyzer, the tubes with scales rocked up and down for 5000 times.

Afterwards, we measured the tapped volume of each sample in the glass tubes. The tapping density was calculated by the following equation: tapped density = mass/tapped volume.

Preparation of electrodes. First, a mixture of 50 wt% soil (a-soil or b-soil), 40 wt% KS-6, 10 wt% polyvinylidene fluoride (PVdF), and 1-methyl-2-pyrrolidone (NMP) were vigorously grinded in a corundum mortar for 35 min in atmosphere. Afterwards, the obtained black ink was casted onto a piece of nickel foam and dried at 100 °C for 10 h in an air dry oven. Finally, the soil electrodes were obtained. Similarly, the KS-6 electrodes were fabricated by grinding 90 wt% KS-6, 10 wt% PVdF, and several drops of NMP for 35 min in atmosphere.

Electrochemical investigation in CR2032 coin-type soil/Li half cells. The electrochemical performance was evaluated at room temperature using CR2032 coin-type cells. The half cells consist of a Li anode, a glass fiber separator (16 mm in diameter, 0.3 mm in thickness, porosity 92%–98%), and an soil electrode (or KS-6 electrode). The commercial electrolyte is 1 M LiPF6 in ethylene carbonate/diethyl carbonate (EC/DEC, in 1:1 volume ratio) solution. For soil electrodes and KS-6 electrodes, the total mass loading on the current collector is ~1.0 mg cm^{-2} (the mass of each piece of Ni foam is about 22.6 mg). All the battery assembly process was carried out in a glove box (Mikrouna Universal 2440/750) with H_2O content and oxygen level lower than 1 ppm. After stayed in ambient air for 5 h, these batteries endured galvanostatic discharge/charge on a LAND battery testing system under room temperature. Cyclic voltammetry curves (CVs) were operated on Parstat 263A electrochemical workstation (Princeton Applied Research & AMETEK Company). In addition, the capacity and current density are based on the mass of anode excluding current collectors and binders.

Assembling 18650-type Battery. The NCA was synthesized following previous report with modified procedures.[1] The cathodes were prepared by mixing NCA (80 wt%), carbon black, and PVdF in N-methyl-2-pyrrolidone (NMP). The slurry was pasted onto the copper foil by a blade and dried in the vacuum oven at 100 °C for 10 h. Then, the cathodes were pressed (under 15 MPa) and weighed. The anodes were prepared by mixing a-soil (70 wt%), KS6, and PVdF in NMP. The weight of NCA on cathode and soil on anode are 16 g and 10 g, respectively. While, the active materials in conventional 18650 LIB include anode graphite (8–11 g) and cathode NCA (14–17 g). Each battery was assembled by stacking two cathodes and three anodes with electrolyte of 1 M LiPF_6 in EC/DEC (1:1 volume ratio) and Celgard 2340 as separator. The 18650-type batteries (Φ18mm×H65mm, 49 g) were assembled in one humidity-control working room (⩽ 3.0%) and the electrochemical performance was tested by LAND battery testing instrument. The current density was 4 A with voltage window of 2.0−3.0 V. The result was summarized by repeated tests for reliability.

Calculating theoretical capacity of SiO_2. The the discharge mechanism of SiO_2 was expressed as follows:

$$(4/5)Li^+ + SiO_2 + (4/5)e^- \longrightarrow (2/5)Li_2Si_2O_5 + (1/5)Si \qquad (1)$$

$$xLi^+ + Si + xe^- \longrightarrow Li_xSi \qquad (2)$$

According to theoretical calculation formula (C_{th} = 26800×n/M, n = electron number, M = molar mass), the theoretical capacity (mAh g^{-1}) of SiO_2 is $\frac{26800\cdot\frac{4}{5}}{60}+\frac{26800\cdot x\cdot\frac{1}{5}}{60}$, namely, '357 +89x' mAh g^{-1}.

Table. S1 Defects degree and crystallinity degree of the samples.

samples	Defects degree (X_d, %)	Crystallinity degree (X_c, %)
a-soil	77.2	22.8
b-soil	57.4	42.6
Soil without ball milling	19.4	81.6

Extremely high ball milling peed requires more extra energy consumption. Besides, limited by the service ability of our ball grinder, thus, the strength of 700 r min^{-1} for 20 h (a-soil) is settled as the upper limit.

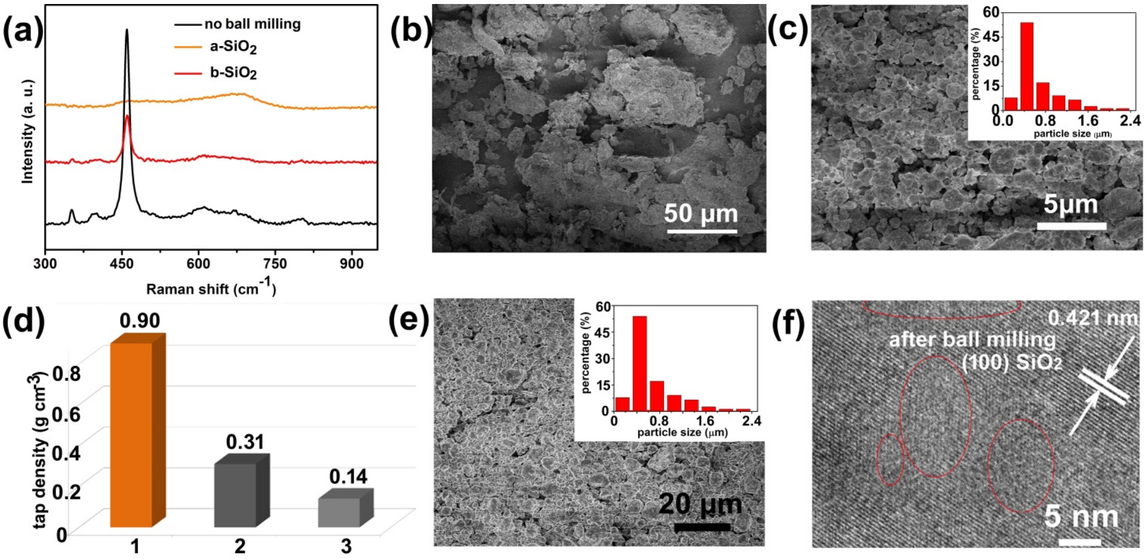

Fig. S1 (a) Raman spectrum of the ball milled soil at 700 r min for 20 h (a-soil) and at 300 r min for 20 h (b-soil). Before ball milling, soil was heated at 750 °C for 2 h. (b) SEM image of heated soil without ball milling. (c) SEM image of a-soil. 100 random particles were selected to count particle sizes. The inset graph is particle size distribution of a-soil. (d) Tap densities. Sample 1, 2, and 3 are a-soil, artificial graphite, and graphite KS-6, respectively. (e) SEM image of b-soil with its size distribution. (f) HTEM of b-soil. The b-soil shows discontinuous lattice fringes.

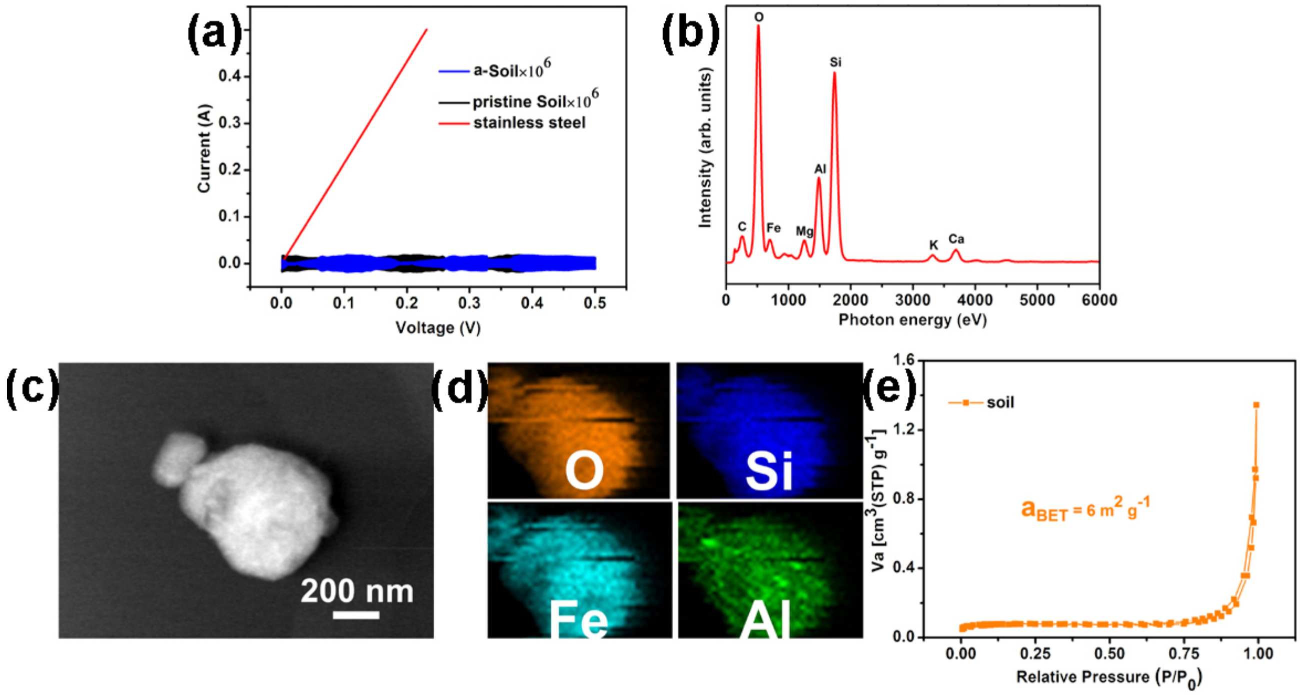

Fig. S2 (a) Electrical conductivity test. The current of pristine soil is similar to the negligible current of plastic film, far smaller than stainless steel, indicating poor conductivity of pristine soil. The conductivity of treated soil (a-soil) is different from pristine soil. (b) EDX analysis of treated soil. The two highest peaks are O and Si elements, which is consistent with the ICP result (pie chart) in Fig. 1. (c, d) Element maps of the main elements (O, Si, and Al) within treated soil. (e) N_2 adsorption-desorption isotherms of a-soil. Each curve in (a) has been fitted to one formula.

Stainless steel: $y = -0.0013 + 2.2x$;

Pristine soil: $8.8\times10^{-5} + 3.8\times10^{-4}\ x$;

a-soil: $-2.86\times10^{-4} + 3.0\times10^{-3}\ x$.

The larger slope relates to higher conductivity. a-soil improved one order of magnitudes in terms of slope in composition with pristine soil.

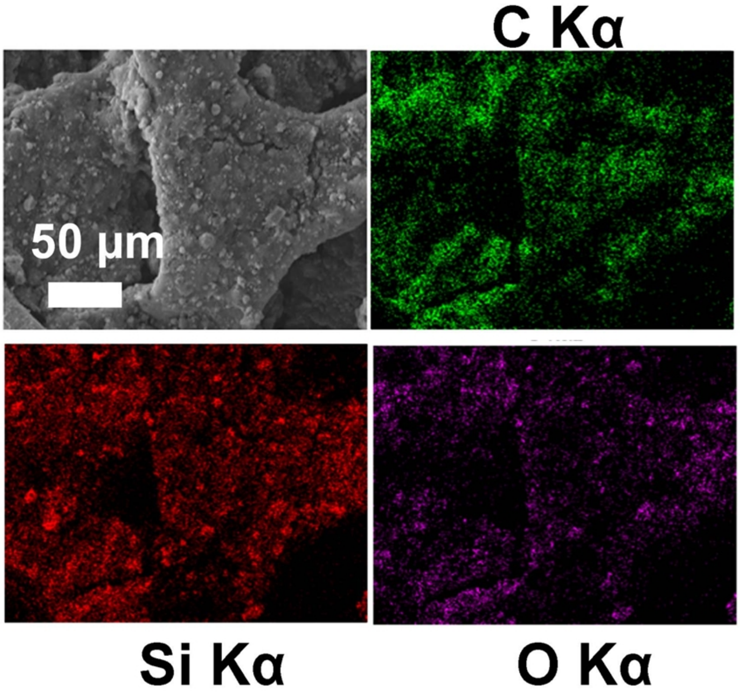

Fig. S3 The electrode consists of a-soil, KS-6 as conductive carbon, PVdF as binder, and Ni foam as current collector. The ratio of soil to KS-6 is 5:4 (details can be seen in Methods). Obviously, the porous structure of Ni foam was not blocked but evenly coated by loading materials, which is beneficial for accommodation of soil volume expansion during lithiation.[2]

The a-soil was employed as anode materials for LIBs. For instance, the morphology and element mapping of electrode are shown in Fig. S3. The uniform distribution of C, Si, O, and Ni elements reveals that soil was mixed evenly with KS-6. The high porosity of Ni foam is maintained for accommodating the volume expansion of discharge products.[3] The contact angle of a-soil to ethylene carbonate/diethyl carbonate (EC/DEC, in 1:1 volume ratio) is much small (22º, Fig. S4), suggesting the superior wettability of organic electrolyte to soil.

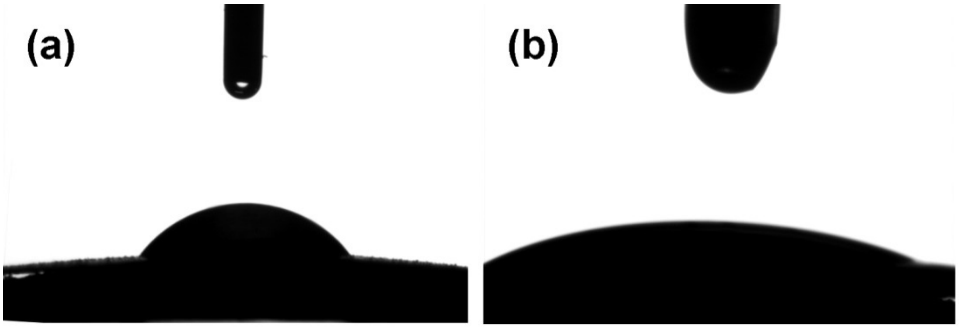

Fig. S4 The contact angle of a-soil to (a) water and (b) ethylene carbonate/diethyl carbonate (EC/DEC).

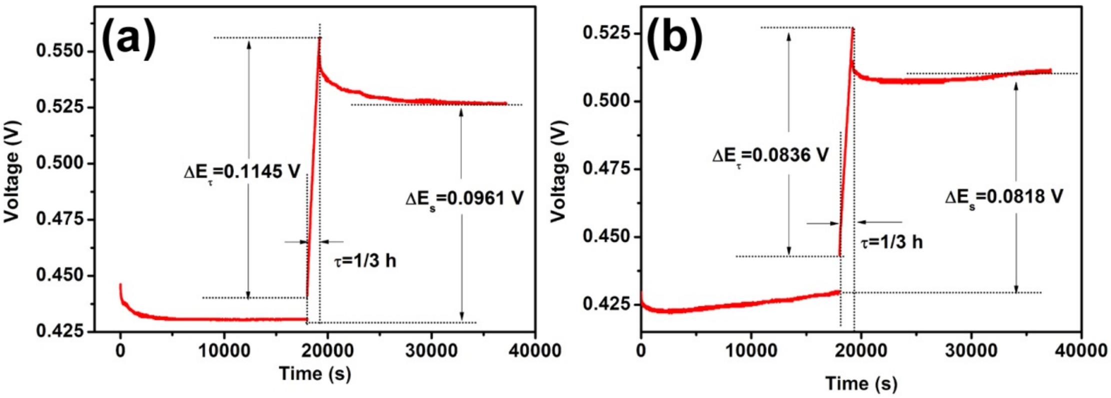

Fig. S5 Galvanostatic intermittent titration technique (GITT) charge voltage curves during fourth cycle for soil/Li cells. (a) b-soil electrode. (b) a-soil electrode.

The equation for ionic diffusion coefficient (D_{Li}) can be written as[3]:

$$D_{Li} = \frac{4}{\pi\tau}\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2\left(\frac{V_m\times m_b}{A\times M_b}\right)^2$$

where V_m is the molar volume of the active materials, M_b and m_b are its molecular weight and mass, respectively. Assuming that soils have the same V_m, M_b, m_b, and the total contact area (A), then

$$\frac{D_{Li}b}{D_{Li}a} = \left(\frac{0.0961\times0.0836}{0.0818\times0.1145}\right)^2 = 0.736$$

The results indicate that ball milled soil with faster ball milling peed owns higher ionic diffusion coefficient of Li$^+$ during de-lithiation.

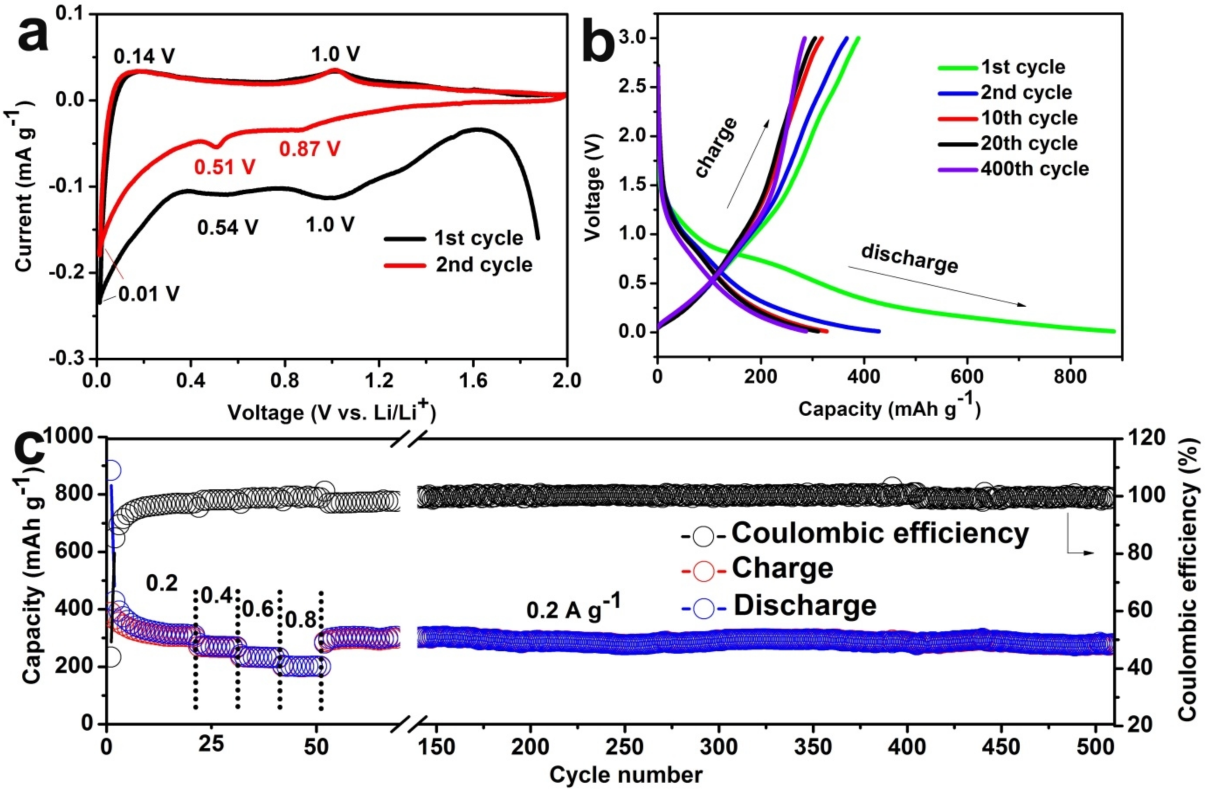

Fig. S6 Electrochemical performance of b-soil/Li half cells. (a) Cyclic voltammetry curves of b-soil/Li half cells with sweep speed of 0.1 mV s^{-1}. (b) Galvanostatic discharge–charge curves of b-soil/Li half cells at 0.2 A g^{-1}. (c) Cycling rates of b-soil/Li half cells.

For b-soil/Li half cells, cyclic voltammetry (CV) was applied in the 0.01–2.0 V voltage window (Fig. S6a). There are broad reduction peaks (1.0 V in the first cycle and 0.87 V in second cycle). It leads to the large irreversible discharge capacity and low coulombic efficiency in the first cycle. Two obvious couples of oxidation/reduction peaks (0.51 V vs. 1.0 V and 0.01 V vs. 0.14 V) are observed in the second cycle. Cathodic peaks at 0.51 V and 0.01 V indicate the lithiation reactions of SiO_2 occurring in soil anode at low voltage. These two anodic peaks are indexed to de-lithiation processes of soil.

Fig. S6b presents the discharge/charge profiles of different cycles. For b-soil/Li half cells, the discharge and charge capacities in the first cycle are 980 and 430 mAh g^{-1} (43.9% as initial coulomb efficiency), respectively. In the following ~400 cycles at 0.2 A g^{-1}, the voltage profiles show a similar shape. The cycling rate performance of b-soil is shown in Fig. S6c. After initial cycles activation, the coulombic efficiency maintained ~100% until 510 cycles without fading trend. The first 55 cycles are rate test at different current densities. The b-soil displays capacities of 303.1, 266.5, 231.0, and 201.3 mAh g^{-1} at 0.2, 0.4, 0.6, and 0.8 A g^{-1}, respectively.

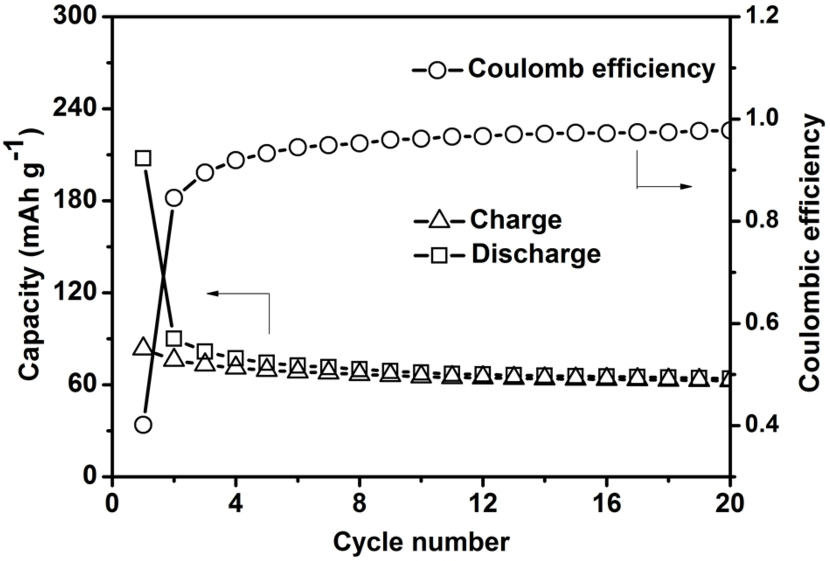

Fig. S7 Cycling performance of soil without ball milling in half cells. The current density is 0.2 A g^{-1}.

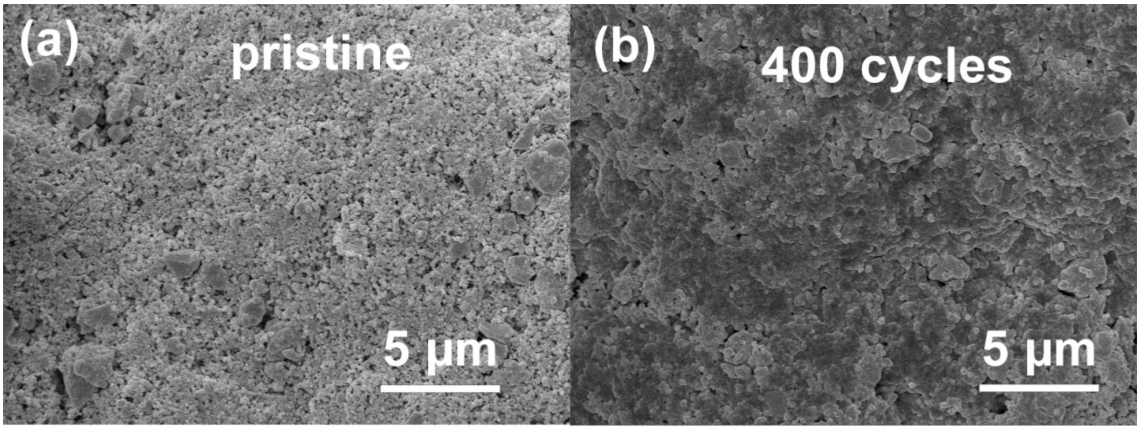

Fig. S8 SEM images of soil electrode in a-soil/Li half cells. (a) Pristine anode before discharge. (b) Anode after 400 discharge/charge cycles.

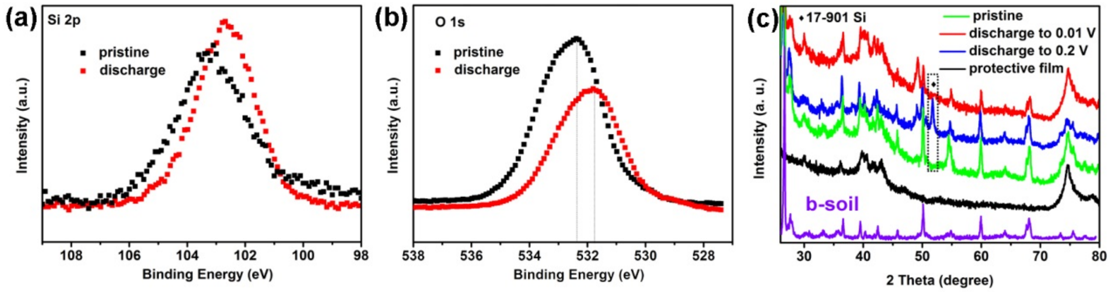

Fig. S9 XPS survey and XRD of b-soil electrode: (a) Si 2p; (b) O 1s. (c) XRD of b-soil electrode at different discharge states.

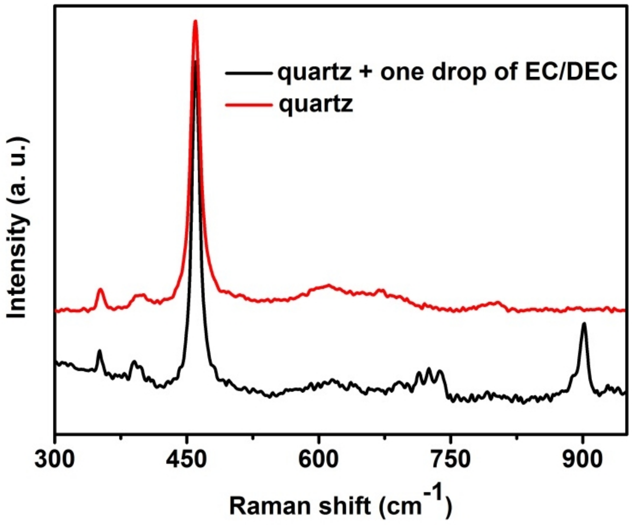

Fig. S10 Raman spectrum of commercial quartz (SiO_2) before and after adding one drop of EC/DEC. It is hard to test Raman signals just for one drop of solution, so we use quartz powders as substrate for the test.

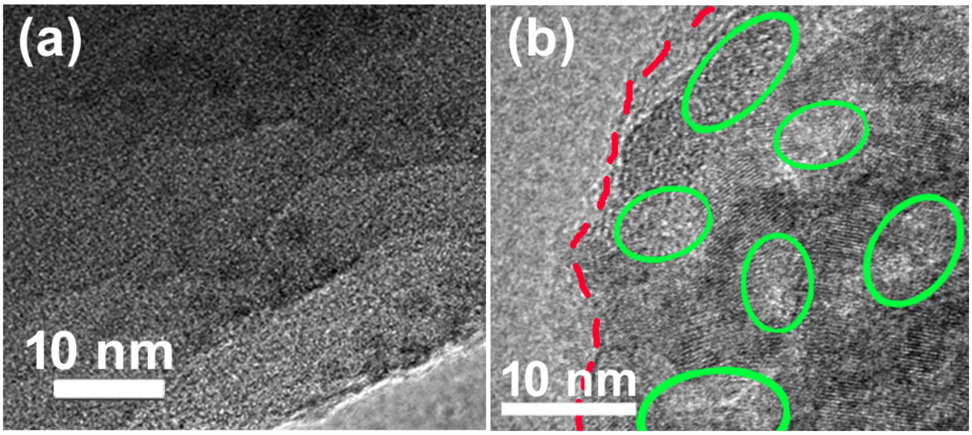

Fig. S11 HRTEM images of soil particle edges. (a), after discharge. This image is from partially enlarged particle edges in Fig. 3d. It depicts amorphous characterization without obvious lattice fringes. (b), before discharge. This image presents distinct lattices outside green circles.

Supplementary Reference

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