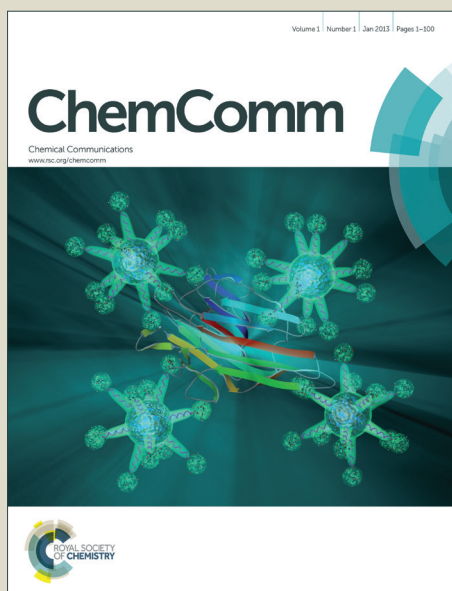


ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

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

Xiaofei Hu,^a Kai Zhang,^a Liang Cong,^a Fangyi Cheng,^a and Jun Chen^{*a,b}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Here we first demonstrate that by simple treatment of heating and ball-milling, soil is enabled with 77.2% defect degree and acts as a high-performance anode material for soil/Li half cells and 18650-type LiNi_{0.915}Co_{0.075}Al_{0.1}O₂ (NCA)/soil full batteries that displayed a high and stable capacity of 3200 mAh (corresponding to 176 Wh·kg⁻¹ and 522 Wh·L⁻¹) in the 200th cycle at a high current of 4 A.

Rechargeable lithium-ion batteries (LIBs) have extensive applications ranging from consumer electronics to electric vehicles (EVs) and energy storage for smart grids.^{1–5} There is thirsty and increasing demand of advanced LIBs with long life, high capacity, high safety, low cost, and green sustainability. Exciting, LIBs equipped with lithium nickel-cobalt-aluminum oxide (NCA) cathode and graphite anode have been recently applied in a Tesla car (e.g. Tesla Model S85) with the powering of 7104 18650-type cells.⁶ However, large-scale application of LIBs in EVs inevitably raises much concern on the capacity, safety, cost, and sustainability of both anode and cathode materials. As one of the key points, the relatively low capacity of graphite (LiC₆: 372 mAh g⁻¹)⁷ and safety hidden problem of such anode need to be greatly improved for better electrochemical performance.

As a viable anode material for LIBs, SiO₂ has recently drawn much attention due to the ability of a high reversible capacity of 749 mAh g⁻¹ and a low discharge voltage of 0.01–1V.⁸ Pure SiO₂ precursor (quartz) treated by high-energy ball milling had exhibited a reversible capacity of 800 mAh g⁻¹ for 100 cycles at 0.1 A g⁻¹ with 90% capacity retention.⁹ This means that the volume change of mechanical strain during reversible lithiation and delithiation would be inhibited to a certain extent.^{10,11} Meantime, the introduction of massive defects or Li-inactive phase (such as copper coating) to Li-active material could suppress the mechanical deformation during electrochemical lithiation and delithiation.^{12,13} As an important natural resource, soil generally consists of minerals (e.g. SiO₂, aluminosilicate), organic matters, and water.^{14,15} The main composition of soil is SiO₂, which should have the potential of storing Li. While, the second composition of soil is aluminosilicate, which should act as a buffer media to form a stable scaffolding for alleviating the volume expansion of SiO₂ during lithiation/delithiation. In addition, soil is undoubtedly cheaper and more easily obtained than sand and man-made pure SiO₂ nanomaterials. Thus, we are inspired to exploit soil with heat-treatment and ball-milling for

introducing defects as high-performance anode materials of LIBs.

We here report the first application of soil, being simply heated and ball milled to introduce defects, as a new anode material of LIBs. First, soil/Li half cells exhibited 547.1 mAh g⁻¹ at 0.2 A g⁻¹ after 250 cycles with 99.1% capacity retention (the 5th discharge capacity is 552.2 mAh g⁻¹, which are based on the mass of soil and conductive carbon). The conversion reaction of SiO₂ to form Li₂Si₂O₅ and Si followed by the alloying reaction of Li₁₂Si₇ was first detected by in-situ Raman for lithium-storage mechanism of the soil anode. Second, 18650-type batteries assembled with LiNi_{0.915}Co_{0.075}Al_{0.1}O₂ (NCA) cathode and soil anode delivered a high and stable capacity of 3200 mAh (corresponding to gravimetric and volumetric energy density of 176 Wh·kg⁻¹ and 522 Wh·L⁻¹, respectively) for 200 cycles with charge/discharge current of 4 A.

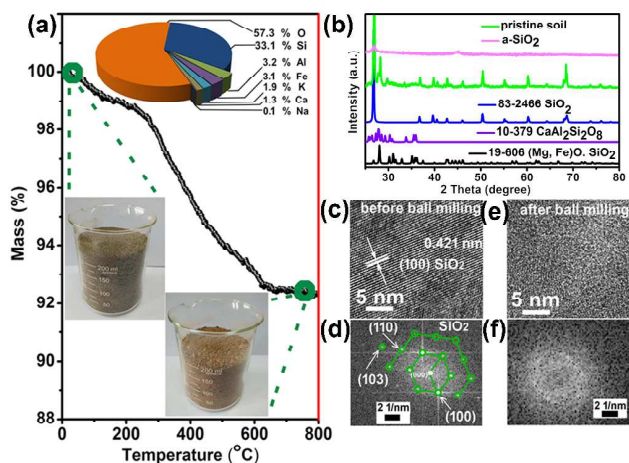


Fig. 1 (a) TGA and DSC of pristine soil below 800 °C. The inset digital photograph depicts the states of pristine soil and heated soil at 750 °C. The inset pie chart is the elementary composition of soil with mass percentage (wt%). (b) XRD analysis of pristine and a-soil. The ball milling treatment was carried out after heating. (c) HRTEM image and (d) selected area electron diffraction (SAED) patterns of soil without ball milling. (e) HRTEM image and (f), SAED patterns of a-soil.

Soil on the surface of earthcrust as an inexhaustible natural material is easily minable and extremely cheap. The soil used here belongs to North China plain, which is one of the world's top ten plains with the consisting of mineral substances, organic matters, moisture, and air. In order to remove the moisture and little organic matters from soil and obtain dried electrode

material, heating is needed. The heating temperature was settled by thermal gravity analysis (TGA) in air (Fig. 1a), which showed that 7.6% weight loss was observed at 670 °C and afterwards constant weight appeared. The weight loss from room temperature to 250 °C is attributed to water. While the weight loss between 250 °C and 670 °C stems from the oxidation of organic matters in soil. A sufficient heating was applied to soil at 750 °C for 2 h. After the heating, the color of soil turns khaki from brown (the digital photographs of Fig. 1a), indicating the transform of Fe element from low valence to high valence. Afterwards, in order to obtain uniform and small soil particles and especially to activate SiO₂ within soil by introduction of defects, mechanical ball milling was further applied to obtain various activated soil. Based on the formula of crystallinity degree,¹⁶ the formula of defect degree was defined as: $X_d = A_a / (A_c + A_a)$ (X_d : defects degree, A_a : amorphous area, A_c : crystallized area on the X-ray diffractogram). The ball milling of soil with 700 r min⁻¹ and 300 r min⁻¹ for 20 h are labeled as a-soil and b-soil, respectively. As the ball milling strength increases, soil without ball milling, b-soil, and a-soil own defect degree of 19.4%, 57.4%, and 77.2%, respectively (Table S1, ESI). The pristine soil principally matches with SiO₂ (JCPDS Card No 83-2466, Fig. 1b), confirming that the main content of soil is crystalline SiO₂. The disturbance peaks at low degree mainly originate from bits of aluminosilicates of soil. While a-soil thoroughly loses sharp characteristic peaks, indicating its abundant defects (or amorphization). The diffraction peaks of SiO₂ in a-soil are weakened by mechanical ball milling, which is consistent with previous report for pure SiO₂.⁹ Moreover, the characteristic peaks of Raman spectrum of a-soil also extremely weaken (Fig. S1a of Electronic Supplementary Information, ESI), indicating the increasement of the amorphous state of soil.

Before ball milling, the morphology of soil is irregular particles with large range of sizes from about one to hundreds of micrometers (Fig. S1b, ESI). While after ball milling, soil particles were fragmented to be a narrow size at ~0.5 μm (Fig. S1c, ESI). Notably, the tap density of a-soil is about twice larger than artificial graphite and 5 times larger than graphite KS-6 (Fig. S1d, ESI). The heated soil before ball milling shows distinct (100) (103) (110) lattice planes of SiO₂ (Fig. 1c and d), suggesting its monocrystal characterization. While, there is not obvious lattice fringes in a-soil (77.2% defects degree) (Fig. 1e and f). The above difference of soil indicates that the decrease of crystalline degree and increasement of defects are enhanced from ball milling. In addition, ball milling treatment obviously increases electrical conductivity of soil (Fig. S2a, ESI). Furthermore, energy dispersive spectroscopy (EDS, Fig. S2b, ESI) combined with inductively coupled plasma emission (ICP) analysis shows that Si content is determined to be 33.13 wt% in soil and the corresponding SiO₂ content is ~64.2wt% (Fig. 1a, inset pie chart). O, Si, Al, and Fe elements (the four most abundant elements of soil) are uniformly distributed (Fig. S2c and d, ESI). The specific surface area of a-soil is 6 m² g⁻¹ (Fig. S2e, ESI).

We fabricated soil electrode with even distribution of active materials and good infiltration to the electrolyte (Fig. S3 and S4, ESI). To investigate the electrochemical performance of soil anode, 2032 coin-type soil/Li half cells were assembled with Li

metal as counter and reference electrode and 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 by volume) as electrolyte. Li⁺ diffusion coefficients of a-soil were 26.4% larger than that of b-soil (Fig. S5, ESI), suggesting that the activation degree of soil depends on the defects from the ball milling strength. The b-Soil/Li half cells were electrochemically tested first (Fig. S6, ESI). They showed 43.9% initial coulomb efficiency (430 mAh g⁻¹/980 mAh g⁻¹) and average discharge voltage of ~0.5 V. Even after 510 cycles, they still kept 92.4% capacity retention (280.2 mAh g⁻¹).

For a-soil/Li half cells, cyclic voltammetry (CV) was applied in 0.01–3.0 V voltage window (Fig. 2a). The closed area in the first cycle is quite larger than that in the second cycle during the cathodic process. This is owing to the irreversible reactions between the electrode material and the electrolyte, which involves the formation of solid electrolyte interface (SEI) layer.¹³ This leads to the large irreversible discharge capacity and low coulombic efficiency in the first cycle. Two couples of oxidation/reduction peaks (0.33 V vs. 0.92 V and 0.01 V vs. 0.17 V) are observed in the second cycle. Cathodic peaks at 0.33 V and 0.01 V show the lithiation reactions of SiO₂ occurring in soil anode at low voltage, which corresponds to the main capacity during discharge (voltage range of 0.01–0.50 V)¹⁰. Two anodic peaks are indexed to de-lithiation processes of soil. The inset graph of Fig. 2a presents the discharge/charge profiles of different cycles, showing that the plateau voltages are consistent with those of CV peaks. In comparison with b-soil, a-soil/Li half cells exhibit higher initial coulomb efficiency (649.9/1368 = 47.5%) and lower discharge voltage of ~0.1 V (Fig. 2b). The 5th discharge capacity is 552.2 mAh g⁻¹ after initial activation cycles. The irreversible capacity stems from electrolyte decomposition and SEI layer formation.¹¹ In the following 50 cycles at 0.2 A g⁻¹, the voltage profiles show a similar shape.

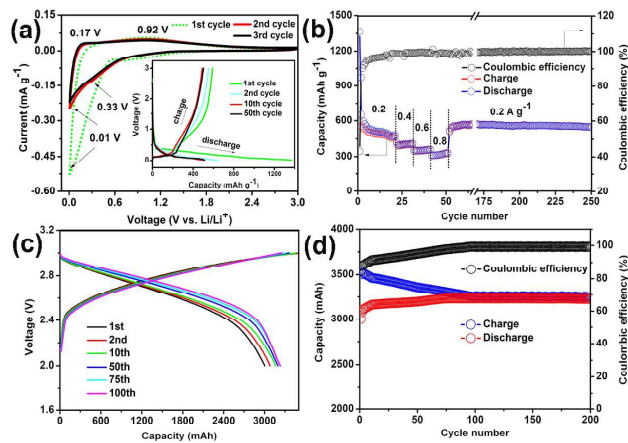


Fig. 2 (a) Cyclic voltammetry curves of a-soil/Li half cells with sweep speed of 0.1 mV s⁻¹. The inset graph is galvanostatic discharge-charge curves of a-soil/Li half cells at 0.2 A g⁻¹. (b) Cycling rates of a-soil/Li half cells. The capacity and current density are based on the mass of soil and conductive carbon. Electrochemical behavior of 18650-type batteries based on NCA/a-soil system: (c) Galvanostatic discharge/charge voltage profiles. (d) Cycling and coulombic efficiency at a current density of 4 A g⁻¹ in the voltage range from 2–3 V.

The cycling rate performance of a-soil is shown in Fig. 2b. The coulombic efficiency quickly climbs to above 90% in the initial

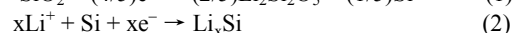
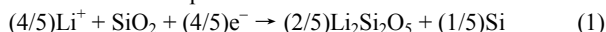
three cycles and maintained ~100% until 250 cycles without fading trend. The first 50 cycles are rate test at different current densities. The a-soil displays capacities of 570.2 (4th cycle), 400.5 (28th cycle), 352.7 (38th cycle), and 311.7 (48th cycle) mAh g⁻¹ at 0.2, 0.4, 0.6, and 0.8 A g⁻¹, respectively. It is worth noting that even at 0.8 A g⁻¹, the capacity still maintains 54.7% of that at 0.2 A g⁻¹. Encouragingly, the capacity returns to 565.5 mAh g⁻¹ when the current density goes back to 0.2 A g⁻¹ (68th cycle), corresponding to 99.2% capacity retention. Even after 250 cycles, the cell with a-soil still keeps ~100% capacity retention (547.1 mAh g⁻¹). Thus, the capacity and capacity retention of a-soil electrode is superior to b-soil electrode, indicating that the defect formation from the ball milling with higher speed is beneficial for the improvement of electrochemical performance.

The heated soil without ball milling exhibits a capacity of ~60 mAh g⁻¹ at 0.2 A g⁻¹ (Fig. S7, ESI), which is much inferior to ball milled soil, conforming that the high energy ball milling is able to activate soil and improve the ability of lithiation. In details, high-energy ball milling could repeatedly impact each Si 2p and O 1s binding energy of Si-O-Si network and lead to atomic rearrangement from the crystalline state to amorphous state.^{17,18} The structural transformation results in the change in the valence charge, which is related to the Li-reactivity of milled amorphous soil. Fig. S8 (ESI) shows no big difference of electrode morphology between pristine state and 200th fully charged state, indicating the superior stability of a-soil electrode.

To confirm the possibility of NCA/a-soil for commercial application, 18650-type full batteries were further assembled. Fig. 2c and 2d present the charge/discharge profiles and cycling performance of the assembled batteries. Low coulomb efficiency would lead to extra lithium-consumption for the formation of SEI film. For NCA/soil LIB, low coulomb efficiency (3000.7/3545.4 = 84.6%) results in only partial utilization of lithium within NCA and the reduction of the capacity. However, a robust discharge capacity of >3100 mAh with an average voltage of 2.55 V is obtained. Excitingly, initial test shows that such batteries run 200 cycles with slightly growing capacity (activated process until 70th cycle) and finally stable capacity of 3200 mAh (an average voltage of 2.65 V, 176 Wh·kg⁻¹ and 522 Wh·L⁻¹). The capacity increment is consistent with the initial activated process in the soil/Li half cells. Notably, the weight specific energy of the proposed NCA/soil system is larger than the commercial LIBs (100–150 Wh·kg⁻¹).³ In addition, the capacity per unit battery of NCA/soil system is compared to the commercial 18650 batteries used in Tesla (3100 mAh per unit battery).⁷ This means that soil is favorable for large-scale application as the anode of LIBs.

To investigate the reaction mechanism of soil electrode, we combined XPS, ex situ XRD, in situ Raman, and HRTEM analysis. We choose b-soil (57.4 % defects degree) rather than a-soil (77.2% defects degree) owing to that b-soil is more easily obtained and has stronger characteristic signals in various characterization methods. XPS measurement was carried out to detect the Si 2p and O 1s of the pristine b-soil electrode and the discharged anode to 0.01 V (Fig. S9a and b, ESI). The peak position of Si 2p and O 1s shifts toward low energy after discharging to 0.01 V, indicating lithiation behavior of SiO₂.¹⁹ XRD confirms the rise up and down of Si at discharged to 0.2 V and 0.01 V, respectively (Fig. S9c, ESI). Combining XPS and

XRD results as well as previous reports,^{20,21} the discharge mechanism was expressed as follows:



The above electrochemical reaction mechanism of SiO₂ with lithium ions is reported for the first time by Fu's group,⁸ while the x value is to be decided. According to theoretical calculation formula ($C_{\text{th}} = 26800 \times n/M$, n = electron number, M = molar mass), the theoretical capacity of SiO₂ is '357 + 89x' mAh g⁻¹ (calculation process can be seen in *Experimental Details*, ESI). We need spectroscopy method to verify the x value.

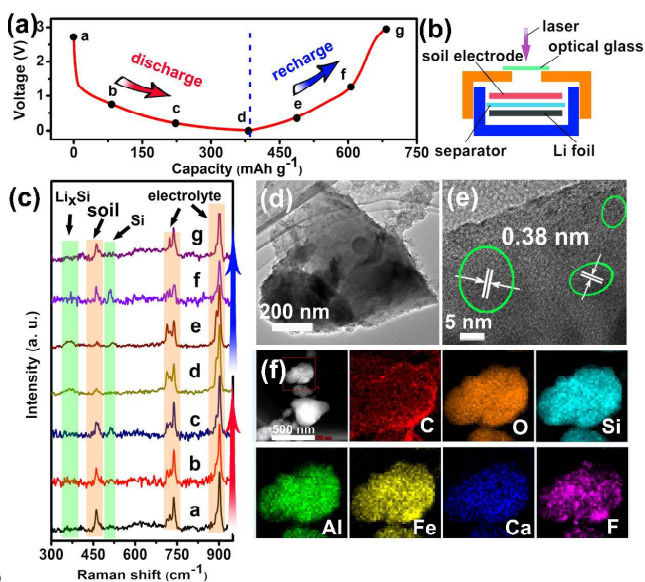


Fig. 3 (a) Discharge and charge curves at 0.2 A g⁻¹. (b) Design of in situ Raman LIBs. (c) In situ Raman spectra of 7 points marked in (a). The red arrow stands for discharge direction and blue arrow means charge direction. (d), TEM images after the 1st discharge. (e), The HRTEM image after the 1st discharge with lattice distance of 0.38 nm, corresponding to Li₁₂Si₇ (221) plane. (f), Element mapping of soil electrode after the first discharge. Before sample preparation of EDS test, the discharged soil electrode was thoroughly washed with EC/DEC solution and then vacuum-dried to remove residual EC/DEC solution.

We further performed in-situ Raman analysis of soil-based LIBs to monitor the discharge and charge reactions on a current collector of Cu mesh. Representative 7 points were selected on the second discharge/charge profiles of b-soil electrode (Fig. 3a). We assembled a simple device for in situ Raman test (Fig. 3b). Soil side of the cell case is cut through a hole and sealed with ultra-thin optical glass in a glove box filled with pure Ar.²² The laser vertically crosses the glass and Raman signals are collected on soil anode. Raman spectrum signals with wavelength of 532 nm were collected at 7 different discharge/charge states (Fig. 3c). Raman peaks at 512 cm⁻¹ and 362 cm⁻¹ are indexed to Si (450–520 cm⁻¹) and Li_{12/7}Si, respectively.^{21,23} Thus, the value of x in formula (2) is 12/7. For Raman peak of Si, we observed the initial appearance and later disappearance on discharge as well as opposite phenomenon on charge. Moreover, Raman peaks of Li_{12/7}Si rise up and subsequently fall down in discharge and charge process, respectively. The changes of the above peaks confirm formula (1) and (2). The characteristic peaks (at ~500 cm⁻¹) of soil are detected before discharge (black line-a). As LIBs discharged, these peaks weakened but never disappeared, even at

the end of discharge (yellow line-d). This confirms the insufficient lithiation of soil with a measured discharge capacity (382 mAh g^{-1}), which is lower than the theoretical capacity of SiO_2 ($357 + 89 \times 12/7 = 509.6 \text{ mAh g}^{-1}$). In addition, Raman peaks at 730 and 900 cm^{-1} belong to the electrolyte of EC/DEC (Fig. S10, ESI). For these peaks, no distinct variation is observed, suggesting the stability and adequate supply of electrolyte to battery reactions. We know that as lithiation-degree of Si increases, the discharge voltage plateau decreases.^{23,24} Therefore, the fact that the discharge voltage of a- SiO_2 ($\sim 0.1 \text{ V}$) is lower than b- SiO_2 ($\sim 0.5 \text{ V}$) arises from larger lithiation-degree of Si.

Fig. 3d and Fig. S11a (ESI) show TEM images of discharged b-soil particles without obvious lattice fringes. On the contrary, the distinct lattices of soil particles before the initial discharge (Fig. S11b, ESI) are seen. The above difference indicates that lithiation process during discharge improves the amorphization degree of SiO_2 . The HRTEM image of fully discharged soil shows the lattice fringe with d-space of 0.38 nm , which agrees with $\text{Li}_{12}\text{Si}_7$ (221) (Fig. 3e). Fig. 3f displays the TEM elemental mapping images of soil particles after initial discharge. It could be clearly observed that C (red color) and F (pink color) components are uniformly distributed around the discharged soil particle. F element comes from LiF, suggesting the existence of SEI layer.^{25–27} Notably, the evenly distributed disturbance elements, i.e. Al, Fe, Ca, have a positive effect of accommodating the volume expansion (from SiO_2 to the discharge products of $\text{Li}_2\text{Si}_2\text{O}_5$, Si, or $\text{Li}_{12}\text{Si}_7$). This correspondingly improves the charge-discharge cycleability.

In conclusion, we have found for the first time the lithiation ability of inexhaustible soil and tested its feasibility as high-performance anode in both Li-ion half batteries and full batteries. After heating and ball milling, the soil with 77.2% defect degree can be reversibly discharged/charged in soil/Li half cells under 0.2 A g^{-1} , delivering stable capacities of 547.1 mAh g^{-1} even after 250 cycles with 99.1% capacity retention (compared with 5th discharge capacity). The SiO_2 and aluminosilicate within soil are respectively able to store Li and alleviate volume change of SiO_2 during lithiation/de-lithiation. Moreover, the assembled 18650-type NCA/soil full batteries with ball-milled soil exhibit a high capacity of 3200 mAh and an average voltage of 2.65 V (176 Wh kg^{-1} and 522 Wh L^{-1}) in the 200th cycle at 4 A . We also revealed a novel lithiation route in soil, i.e. the first conversion reaction of SiO_2 to form $\text{Li}_2\text{Si}_2\text{O}_5$ and Si, and then the alloying reaction of $\text{Li}_{12}\text{Si}_7$. Moreover, this study shows that electrochemical energy materials can be made from our living environment with green sustainability.

This work was supported by National Programs of (2011CB935900), NSFC (21231005 and 21322101), and MOE (B12015 and IRT13R30).

Notes and references

^aKey Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin, 300071, People's Republic of China.

^bCollaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin, 300071, People's Republic of China.

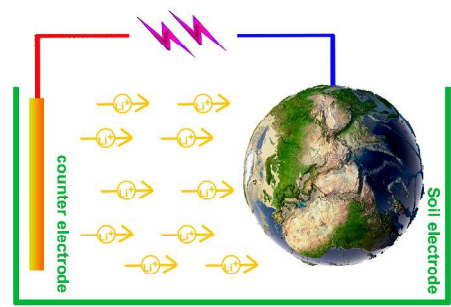
Tel/Fax: +86-22-23506808. E-mail: chenabc@nankai.edu.cn

[†]Electronic Supplementary Information (ESI) available: Experimental details and characterizations of electrodes, batteries and additional electrochemical characterization. DOI:10.1039/b000000x/

- V. Etacheri, R. Marom, R. Elazari, G. Salitra and D. Aurbach, *Energy Environ. Sci.*, 2011, **4**, 3243–3262.
- K. Kang, Y. S. Meng, J. Br  ger, C. P. Grey and G. Ceder, *Science*, 2015, **311**, 977–980.
- B. Dunn, H. Kamath and J. M. Tarascon, *Science*, 2011, **334**, 928–935.
- Z. L. Wang, D. Xu, H. X. Zhong, J. Wang, F. L. Meng and X. B. Zhang, *Sci. Adv.*, 2015, DOI: 10.1126/sciadv.1400035.
- K. Zhang, X. P. Han, Z. Hu, X. L. Zhang, Z. L. Tao and J. Chen, *Chem. Soc. Rev.*, 2015, **44**, 699–728.
- <http://www.teslamotors.com/models>. EVs of Tesla use 18650-type batteries with NCA as the cathode. For example, the MODEL S85 possesses a total capacity of 85kWh, which is supplied by 18650-type batteries. Each battery owns the energy of about 11.2 Wh (3100 mAh).
- F. Bonaccorso, L. Colombo, G. H. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff and V. Pellegrini, *Science*, 2015, **347**, DOI: 10.1126/science.1246501.
- Q. Sun, B. Zhang and Z. W. Fu, *Appl. Surf. Sci.*, 2008, **254**, 3774–3779.
- W. S. Chang, C. M. Park, J. H. Kim, Y. U. Kim, G. Jeong and H. J. Sohn, *Energy Environ. Sci.*, 2012, **5**, 6895–6899.
- M. Sasidharan, D. Liu, N. Gunawardhana, M. Yoshio and K. Nakashima, *J. Mater. Chem.*, 2011, **21**, 13881–13888.
- Z. Favors, W. Wang, H. H. Bay, A. George, M. Ozkan and C. S. Ozkan, *Sci. Rep.*, 2014, **4**, 4605–4612.
- J. Wang, X. C. Meng, X. L. Fan, W. B. Zhang, H. Y. Zhang and C. S. Wang, *ACS Nano*, 2015, **9**, 6576–6586.
- M. T. McDowell, S. W. Lee, C. M. Wang and Y. Cui, *Nano Energy*, 2012, **1**, 401–410.
- W. Chesworth, Springer, New York, U.S.A. 2008.
- A. S. E. Ackermann, *Nature*, 1923, **111**, 202–203.
- D. Choi, J. Xiao, Y. J. Choi, J. S. Hardy, M. Vijayakumar, M. S. Bhuvaneshwari, J. Liu, W. Xu, W. Wang, Z. G. Yang, G. L. Graff and J. G. Zhang, *Energy Environ. Sci.*, 2011, **4**, 4560–4566.
- S. Hofmann and J. H. Thomas, III, *J. Vac. Sci. Technol. B*, 1983, **1**, 43–47.
- C. M. Park, W. Choi, Y. Hwa, J. H. Kim, G. Jeong and H. J. Sohn, *J. Mater. Chem.*, 2010, **20**, 4854–4860.
- L. Khriachtchev and M. R  s  nen, *J. Appl. Phys.*, 1999, **86**, 5601–5608.
- N. Yan, F. Wang, H. Zhong, Y. Li, Y. Wang, L. Hu and Q. W. Chen, *Sci. Rep.*, 2013, **3**, 1568–1574.
- T. Gruber, D. Thomas, C. R  der, F. Mertens and J. Kortus, *J. Raman Spectrosc.*, 2013, **44**, 934–938.
- Q. Zhao, X. F. Hu, K. Zhang, N. Zhang, Y. X. Hu and J. Chen, *Nano Lett.*, 2015, **15**, 721–726.
- S. Huang and T. Zhu, *J. Power Sources*, 2011, **196**, 3664–3668.
- H. Ma, F. Y. Cheng, J. Chen, J. Z. Zhao, C. S. Li, Z. L. Tao and J. Liang, *Adv. Mater.*, 2007, **19**, 4067–4070.
- V. A. Agubra and J. W. Fergus, *J. Power Sources*, 2014, **268**, 153–162.
- P. Verma, P. Maire and P. Nov  k, *Electrochim. Acta*, 2010, **55**, 6332–6341.
- X. L. Zhang, F. Y. Cheng, J. G. Yang and J. Chen, *Nano Lett.*, 2013, **13**, 2822–2825.

TOC

Soil as an inexhaustible nature material is for the first time used as high-performance anode for 18650-type full batteries.



ChemComm Accepted Manuscript