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A Novel Lithium-Doping Approach for an Advanced Lithium Ion Capacitor

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Although electrochemical double-layer capacitors (EDLC) have the advantages of high rate capability, good durability, and superior cycle life over presently available secondary batteries, they have drawbacks in terms of energy density and cost. Especially, their relatively low energy storage capacity is mainly responsible for their limited usage.[1] To overcome this limitation, various types of hybrid capacitors have been developed and successfully commercialized. The lithium ion capacitor (LIC), one of the hybrid capacitors under development, has a specific energy and energy density of around 30 Whkg^{-1} and 20 WhL^{-1}, respectively. These values are more than three times higher than the values of a conventional EDLC.[2]

LICs consist of an activated carbon cathode (positive electrode) and a carbonaceous lithium-intercalating anode (negative electrode). The flat discharge profile of the negative electrode enables improvement of LICs by allowing higher utilization of the cathode within an expanded voltage window. In fabrication, lithium doping of the anode is necessary process prior to charge the capacitor. During the doping process, metallic lithium is oxidized to release lithium ion, while the reduction of the lithium ion occurs at the surface of the anode. Throughout the process, the voltage of the anode decreases until it is close to 0 V (vs. Li/Li$^+$). The lithium doping is a necessary process for LICs and metallic lithium is currently used as the lithium source. The metallic lithium has to be handled with caution to minimize risks since lithium metal reacts violently with moisture, causing fire and explosion.[3] We therefore propose a new lithium-doping method that uses a stable lithium metal oxide, Li_2MoO_3 as an alternative lithium source, thanks to its huge charge capacity and the irreversibility of the first cycle.[4] The innovative use of Li_2MoO_3 simplifies the lithium-doping process and meets the stringent safety requirements for use of LICs. Herein, the advantages of our novel concept will be discussed in detail.

Schematic diagrams comparing different lithium-doping methods are given in **Figure 1**. According to the cell configuration of a conventional LIC, metallic lithium is incorporated in the cell, as illustrated in Figure 1a. By means of electrical short-circuiting, lithium ions can be inserted into anode materials. In this way, it would be difficult to load the amount of desired lithium precisely during cell fabrication because the loaded metallic lithium cannot be fully inserted into the anode materials. Moreover, any remaining metallic lithium in the LIC would cause safety issues. In contrast, our proposed concept for LICs is that Li_2MoO_3 is integrated into the cathode, as presented in Figure 1b. Lithium ion can be electrochemically extracted from the Li_2MoO_3 and then effectively inserted into the anode. The inserted lithium ions are only partially recovered to the Li_2MoO_3 within the operating-voltage range of LICs. After lithium ion extraction, the delithiated phase $Li_{2-x}MoO_3$ in the cathode contributes in a limited way to the electrochemical reaction of the LIC. The lithium-doping level is quite controllable in this approach because the inserted amount of lithium is proportional to the amount of Li_2MoO_3 included in the cathode materials.

Li_2MoO_3 has rhombohedral symmetry that is close to that of the α-NaFeO$_2$ structure.[5] It can be predicted that Li_2MoO_3 can release lithium better than another phase such as one with monoclinic symmetry. The Li_2MoO_3 was prepared by carbothermal reduction of Li_2MoO_4 and its final composition and particle size were optimized in advance. Close observations with field-emission scanning electron microscopy (FESEM) (Figure 1c and 1d) clearly show the morphology of Li_2MoO_3, which has a particle size of a few micrometers. The irregularly shaped particles are partially covered with amorphous carbon after the carbothermal reduction. The high-resolution transmission electron microscopy (HRTEM) image combined with selected-area diffraction pattern analysis (SADP) also confirms that the Li_2MoO_3 has a typical rhombohedral symmetry with d spacing of approximately 0.25 nm, as shown in Figure 1e.

The irreversibility of the Li intercalation from Li_2MoO_3 was apparent at the first cycle, as shown in **Figure 2**a. During the first charge, two distinctive plateaus are observed around 3.6 and 4.4 V (vs. Li/Li$^+$), which correspond to lithium ion extraction from lithium layers and transition metal layers in the Li_2MoO_3 structure, respectively. The initial charge capacity was delivered to over 250 mAhg^{-1} when Li_2MoO_3 was charged up to 4.7 V (vs. Li/Li$^+$). For subsequent discharges, less than 30% of lithium ions can be recovered to the host structure under a 2.5 V (vs. Li/Li$^+$) cut-off condition. Figure 2b shows in situ X-ray diffraction (XRD) patterns of single-phase Li_2MoO_3 powder during the first cycle. All reflections are indexed to the hexagonal structure, which belongs to the $R\text{-}3m$ space group. According to the fine refinement of the Li_2MoO_3 structure, it has a cubic close-packed oxide ion lattice with basal planes of octahedral interstices filled

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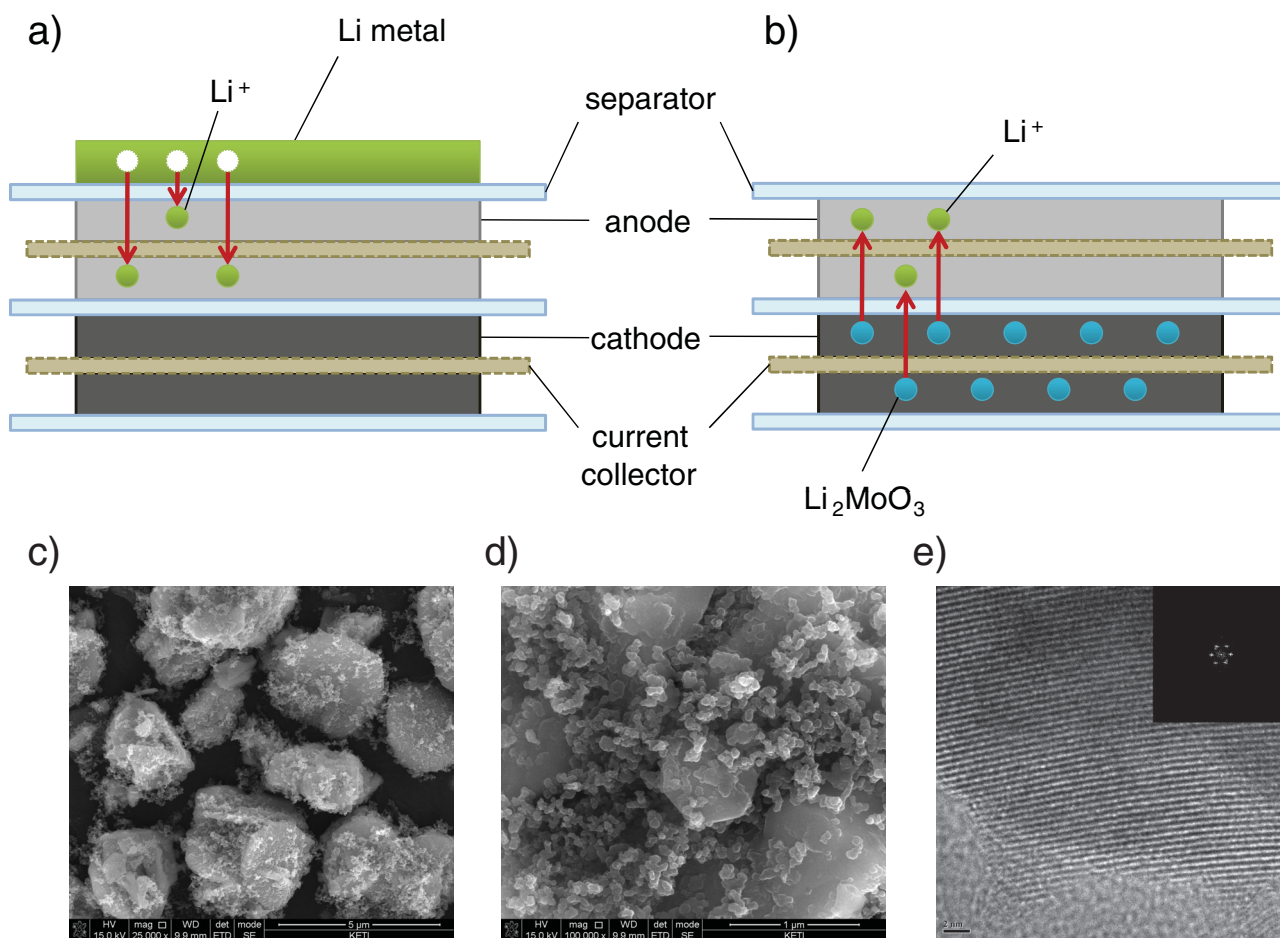www.MaterialsViews.com

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Figure 1. Schematic diagrams showing different lithium-doping methods; a) conventional lithium doping using metallic lithium in the cell and b) proposed method using Li_2MoO_3 as an alternative lithium source. c) and d) FESEM images at different magnifications showing the morphology and microstructure of single-phase Li_2MoO_3 after the carbothermal reduction, and e) HRTEM image of the Li_2MoO_3 combined with SADP.

alternately with lithium and lithium/molybdenum (1:2 molar ratio).[6] Interestingly, the peaks at 18.0° and 36.5°, which correspond to (003) and (006) planes of Li_2MoO_3, respectively, gradually decreased when lithium ions were extracted until 4.7 V (vs. Li/Li$^+$) and then were not fully recovered during the subsequent discharge. In addition, we observed a peak at 18.5° which might be attributed to a $Li_{2-x}MoO_3$ phase during discharge.[4] Ex situ X-ray photoelectron spectroscopy (XPS) was also conducted to identify the chemical state of Li_2MoO_3 during the first charge, and the spectra are shown in Figure 2c. The samples were charged to three different states, corresponding to 4.3, 4.5, and 4.7 V (vs. Li/Li$^+$). As regards the Mo 3d binding energy, the peak gradually shifted from 232.4 to 233.1 eV when the cut-off voltage was increased from 4.3 to 4.7 V (vs. Li/Li$^+$).[7] The change of peak position originates from the oxidation of Mo^{4+} to Mo^{6+}, due to the gradual extraction of lithium ion from the host material. Moreover, there is no visible shift of the O 2p peak (532.5 eV), which is indirect proof that the oxygen stays intact even in a fully charged state (4.7 V vs. Li/Li$^+$). It is interesting to note that the Mo^{4+}/Mo^{6+} redox reaction allows lithium ion extraction without oxidation in the oxygen 2p orbital. These results reveal that the use of Li_2MoO_3 is not accompanied by

significant oxygen evolution even at high voltage, unlike other transition metal oxides with high capacities such as Li_2MnO_3 and Li_2NiO_2.[8] From the structural characterization, we speculate that the Li_2MoO_3 is able to effectively provide lithium ions for its intended purpose without unexpected effects.

The lithium-doping process is necessary to fulfil the criteria of a conventional LIC system. Control of the level of lithium doping is a critical factor that governs the electrochemical properties of LICs. To emphasize the advantages of our approach to the lithium-doping process, the electrochemical properties of the LIC, employing different amounts of Li_2MoO_3 as a lithium source, were carefully evaluated using coin-type half cells results are given in **Figure 3**a. The cells were galvanostatically charged up to 4.7 V (vs. Li/Li$^+$) with a constant current of 0.1 C to supply lithium ions to the anode material. Different contents of Li_2MoO_3 were included in the cathodes; 0 wt%, 5 wt%, and 10 wt%, and the delivered charge capacities after lithium doping were estimated to be 137.2, 156.1, and 184.5 mAhg^{-1}, respectively. The discharged capacity of an LIC is proportional to the amount of Li_2MoO_3 incorporated into the cathode. This result gives an important indication that the lithium-doping level could be controlled by the amount of Li_2MoO_3 included in
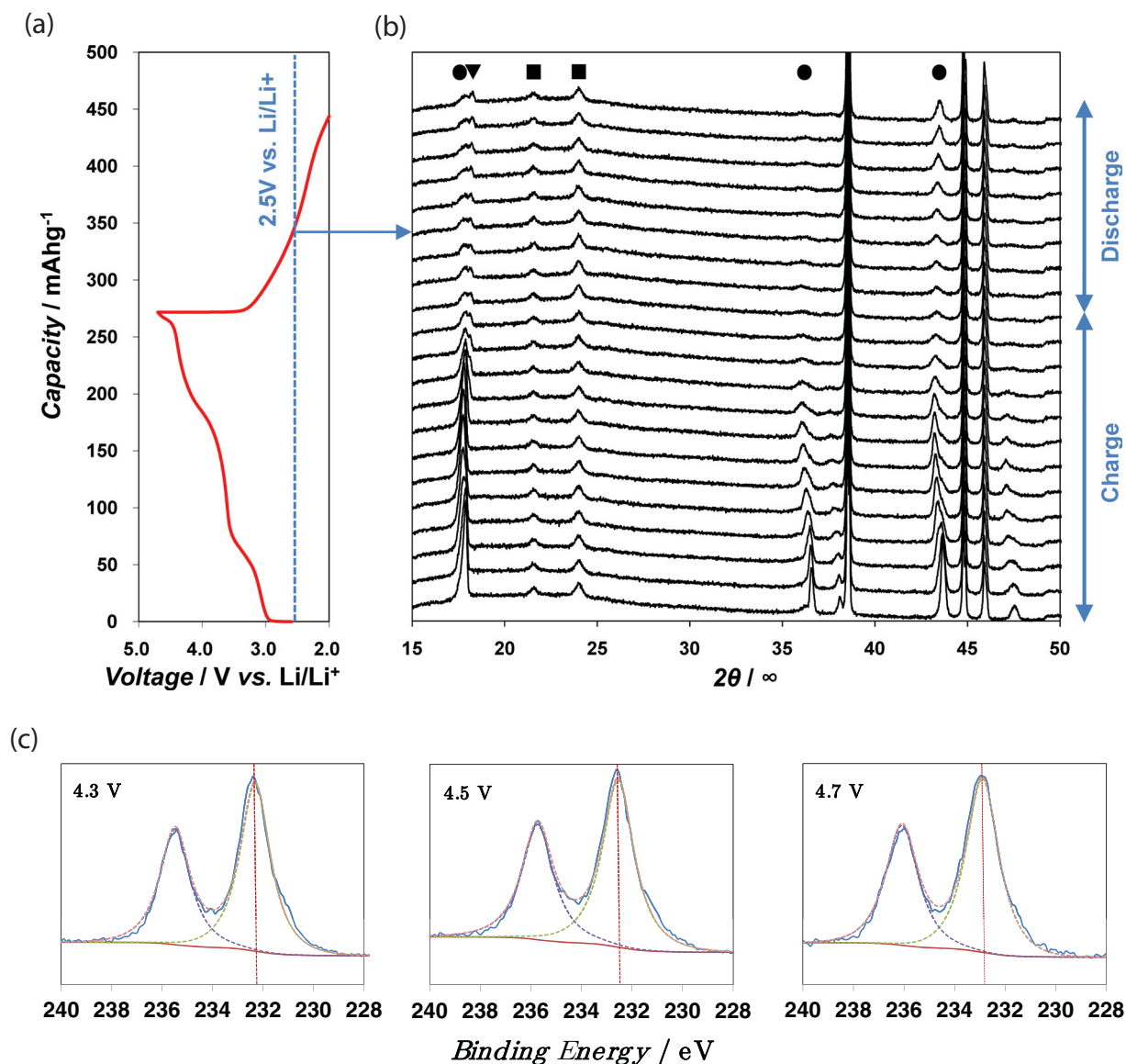
Figure 2. a) A galvanostatic voltage profile and b) in situ XRD patterns of optimized Li_2MoO_3 powder during the first cycle in a voltage range of 2.0 – 4.7 V (vs. Li/Li^+); reflections are indexed to Li_2MoO_3 (●), $Li_{2-x}MoO_3$ (▼), and Be window (■). c) Ex situ XPS spectra for Mo 3d binding energy of Li_2MoO_3 obtained at different cut-off voltages.

the cathode. This controllable lithium-doping level is one of the most promising features of our new concept described above.

For comparative purposes, we assembled two full cells under the optimized conditions. Both cells were prepared with the necessary level of lithium doping to achieve 60% anodic capacity; one by the conventional method using metallic lithium and one by our proposed method using Li_2MoO_3. To ensure the required lithium-doping level, 25.6 wt% Li_2MoO_3 was incorporated into the cathode (for calculations see Supporting Information). After the doping, each cell was galvanostatically charged and discharged with a constant current of 0.1 C in a voltage range from 1.5 to 3.9 V. The cell prepared by doping with Li_2MoO_3 exhibited a discharge capacity of 0.50 F, which was higher than for the conventional LIC (0.39 F) at the subsequent cycle. The partial reversibility of Li_2MoO_3 might be responsible partially

for this increased capacity within the operating voltage range. There is a huge difference between the two doping methods in the efficiency of lithium ion extraction after lithium doping. The cell that was predoped using metallic lithium shows an efficiency of only 64.6% at the first cycle while 86.7% efficiency was obtained in the cell predoped with Li_2MoO_3. This greater efficiency could be attributed to the kinetically favorable characteristics of Li_2MoO_3 that arise from its stable structure during cycling (see Supporting Information). The influence of incorporation of Li_2MoO_3 on cyclic performance was also investigated, as shown in Figure 3b. Cyclic performance was achieved at a high rate current of 10 C. The LIC cell including Li_2MoO_3 exhibits much higher capacitance than that of the conventional LIC, without significant capacity degradation. The achieved capacity retention values after 200 cycles were estimated to
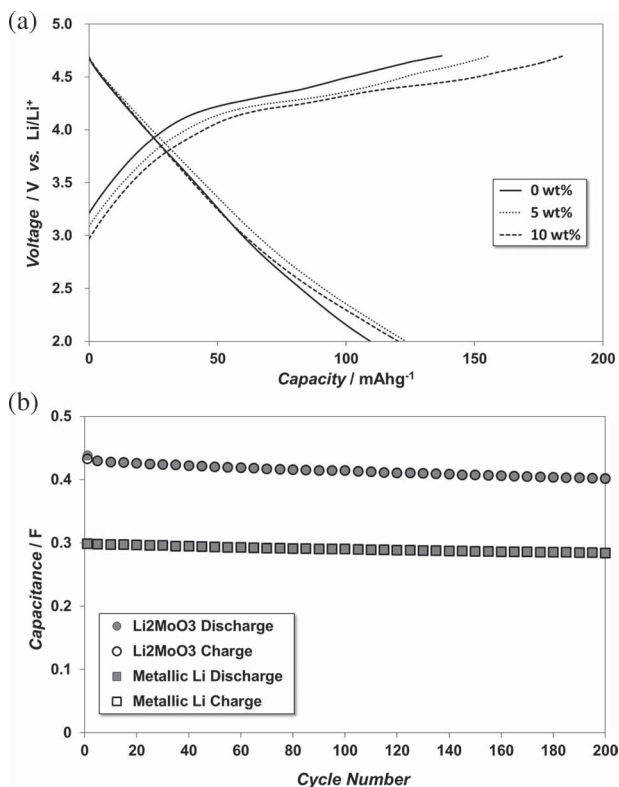
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Figure 3. a) The galvanostatic voltage profiles of cells, containing various amounts of Li_2MoO_3, during the lithium-doping process (0.1 C, ca. 2.5 – 4.7 V vs. Li/Li$^+$) and b) a comparison of cycle performance (10 C, ca. 1.5 – 3.9 V) for the LIC including Li_2MoO_3 (●) and a conventional LIC (■).

Figure 4. A comparison of rate capabilities (0.2 to 40 C) for the full cells prepared by different lithium-doping methods: a) conventional method using metallic lithium, b) proposed method using Li_2MoO_3. The lithium-doping level was controlled at 60% of anodic capacity in both full cells.

be 92.0% and 94.5% for the cells made using Li_2MoO_3 and metallic Li, respectively. A small loss of cyclic retention at the initial cycle might be caused by the relatively large particle size of Li_2MoO_3.

The rate capabilities of LICs prepared by different lithium-doping methods are compared in **Figure 4**. After the lithium-doping process, both cells were galvanostatically charged with a current of 0.1 C and discharged at different currents up to 40 C. The cell prepared by means of lithium doping with Li_2MoO_3 exhibited higher capacity without a significant increase in voltage drop, even at high current. According to previous reports,[9] lithium ions could be electrochemically extracted from the Li_2MoO_3. The delithiated phase, $Li_{2-x}MoO_3$ (0 < x < 1.7), is expected to be a metallic conductor due to the strong Mo–Mo overlap in its local electronic structure while the product when the lithium ions are fully extracted, MoO_3, is regarded as an insulator. Therefore, it is very important to control the operating potential of LICs containing Li_2MoO_3 during the lithium-doping process to maintain good electronic conduction and high lithium ion mobility after lithium ion extraction from the cathode. Another important factor that affects the rate capability and cyclic performance is the particle size of the materials in general. In its current form, with a particle size of a few microns, the proposed LIC could generate higher impedance at high current density than conventional LICs, which would lead to poor rate capability
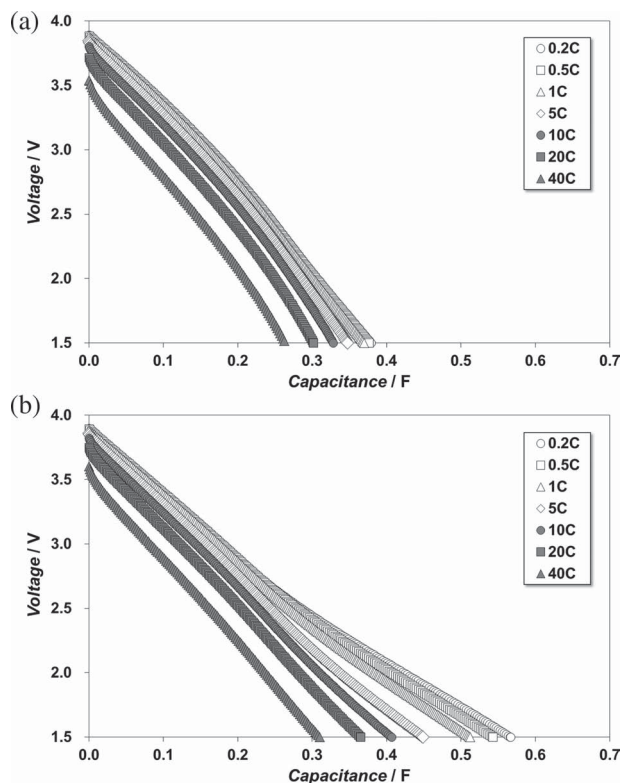
and cyclic retention. In this respect, there is a strong need to optimize particle size. It is expected that better rate capability could be achieved when the particle size is modified on the nanoscale.

The concept of lithium doping with Li_2MoO_3 has been realized in an LIC to emphasize its potential use in practical applications. By incorporating Li_2MoO_3 as an alternative lithium source, the complicated lithium-doping method using metallic lithium is no longer necessary. Li_2MoO_3 can effectively provide lithium ions to an anode during the first charging process. The control of lithium-doping level, which has been regarded as one of the major difficulties with LICs, also can be managed easily because the lithium-doping level is proportional to the amounts of Li_2MoO_3 included in the cathode. Our method also addresses safety issues associated with the production of conventional LICs. The proposed lithium-doping concept does not include either metallic lithium or oxygen evolution in the process and therefore meets the safety requirements of industry.

Experimental Section

Materials Preparation: The single-phase Li_2MoO_3 powder was synthesized using a two-step reduction method. To prepare the Li_2MoO_4 precursor, stoichiometric amounts of Li_2CO_3 (>99.7%, SQM) and MoO_3 (>99.5%, Aldrich) were homogeneously mixed in a molar ratio of 1:1 and sintered at 600 °C for 5 hours under air. For further reduction of

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the obtained Li_2MoO_4 (white), carbothermal reduction was conducted; an appropriate amount of Li_2MoO_4 powder was mixed with 7 wt% of super-P (TIMCAL) and then sintered at 700 °C for 10 hours under N_2 atmosphere.

Structural Analyses: In situ XRD patterns of the final product were obtained using an X-ray diffractometer (EMPYREAN, PAN analytical) equipped with a 3D pixel semiconductor detector and a Cu-Kα radiation (λ = 1.54056 Å). To collect in situ diffraction data, the cell was charged and discharged with a constant current of 0.05 C in a voltage range of 2.5 to 4.7 V (vs. Li/Li$^+$). The morphology and microstructure of the final product were observed by FESEM (JEOL JSM-7000F) and HRTEM (JEOL JEM3010). The chemical state of the final product was identified using XPS (Thermo scientific sigma probe).

Electrochemical Measurements: The cathodes were prepared by coating slurries containing active materials (activated carbon + Li_2MoO_3, 92 wt%) and binder (PVDF; polyvinylidene fluoride, 8 wt%) dissolved in N-methyl-2-pyrolidinone (NMP) on Al mesh. The anodes were prepared in the same way on Cu mesh with active material (hard carbon, 80 wt%), conducting agent (super-P, 10 wt%), and binder (PVDF, 10 wt%). Both electrodes were dried under vacuum for 12 hours at 120 °C. The CR2032 coin-type half cells and full cells were carefully assembled in a dry room to evaluate electrochemical performance. The loading of Li_2MoO_3 (25.6 wt%) was calculated based on the corresponding anode capacity (0.404 mAh; 60% doping level) and specific capacity of Li_2MoO_3 (250 mAhg^{-1}) when charged up to 4.7 V vs. Li/Li$^+$. The fraction of active (activated carbon) and additive (Li_2MoO_3) mass were determined to be to 64.4 wt% and 25.6 wt%. The loading level and density of cathode were fixed at 7.34 mg cm^{-1} and 0.5 cm^{-1}. To assemble LIC full cells, the cathode and anode were punched into Φ12 and Φ14 size, respectively, and 100 μL of electrolyte was added into each cell. A porous polyethylene membrane was used as a separator and 1.3 M LiPF$_6$ dissolved in ethylene carbonate/dimethyl carbonate (3:7 vol., PANAX ETEC Co. Ltd) was used as an electrolyte. All electrochemical data were obtained at room temperature to within an error range of 5%.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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