

Preparation and electrochemical performance of hollow-spherical polypyrrole/ V_2O_5 composite

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Abstract: In order to improve the lower practical capacity and bad cyclability of crystalline V_2O_5 (c- V_2O_5), the vanadium oxide (V_2O_5) and polypyrrole (PPy) hybrid with hollow-spherical(HS) structure was studied. HS nanocomposite comprised of conductive polypyrrole and vanadium pentoxide (PPy/ V_2O_5) was synthesized by polymerization of pyrrole monomer (Py) in the hollow-microspherical V_2O_5 host. This novel hybrid was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and tested as the cathode material for lithium-ion batteries (LIB) by galvanostatic cell cycling and electrochemical impedance spectroscopy (EIS). The hollow-spherical polypyrrole/vanadium oxide (HS-PPy/ V_2O_5) composites, in which PPy molecules are intercalated between the layers of V_2O_5 , exhibit slight reduced capacity and substantially improve cyclability and electrochemical activity compared with the pure HS- V_2O_5 .

Key words: V_2O_5 ; hollow microspheres; cathode; lithium-ion batteries

1 Introduction

The transition metal oxide V_2O_5 has attracted great attention as cathode material for lithium-ion batteries (LIB) due to its high theoretical capacity and energy density [1]. However, many limitations such as poor cycling behavior and weak power performance are yet to be solved [2–3]. In general, two functionalization routes are widely used to optimize the overall properties of the V_2O_5 cathode. One route is the insertion of metallic cations or conductive polymer in the interlamellar space of the oxide, forming the so-called “bronze vanadium oxide” or the organic-inorganic hybrid, respectively. Taking the latter for instance, the composites usually have advantages of both organic and inorganic components and exhibit good synergistic effect [4–5], so the modified materials are expected to obtain higher electrical conductivity and more stable layered-structure, and thus, better electrochemical properties [6–7]. The other route is the production of V_2O_5 in nanometric scale. In this kind of material, the diffusion path is shorter than that in a macroscopic material and the kinetic of intercalation is faster due to the high area to mass

ratio [8–9].

Recent studies showed that the hollow spheres of metal oxide integrate the small size effects of ultrafine particles, such as surface effect, volume effect and quantum effect. The spherical shell material has some features, such as ability to hold large amounts of guest molecules or large-sized object, low density, large specific surface, and strong surface penetrability [10–11]. Therefore, when the hollow spheres are used as the cathode materials of lithium-ion batteries, they can present good electrochemical properties.

The objective of this work is to combine the two routes mentioned above to prepare a nanostructural polymer/ V_2O_5 hybrid with particular morphology. Recently, the synthesis of the hollow-microspherical V_2O_5 (HS- V_2O_5) crystal was reported [12]. The objective of this work is to study the influence of the PPy/ V_2O_5 hybrid and check the viability of this previous insertion step to improve the electrochemical behaviour. The PPy is selected as the conductive polymer to modify this product to obtain a novel hollow-microspherical hybrid nanocomposite. The as-prepared nanocomposite is tested as the cathode material for LIB and the effects of PPy on the electrochemical properties of the HS- V_2O_5

are discussed.

2 Experimental

HS-PPy/V₂O₅ nanocomposite was synthesized by injection and polymerization of Py in the V₂O₅ host. Briefly, 0.20 g hollow microspheres of c-V₂O₅ (preparation described elsewhere [12]), 0.728 g ferric chloride (used as oxidant) and 0.32 g C₇H₇NaO₃S (used as dopant) were added in 20 mL distilled water. After stirring the suspension in ice bath for a moment, different amount (0.01, 0.02, 0.03 and 0.04 mL) of pyrrole monomer was injected into the reaction system under the protection of Ar atmosphere. The subsequent polymerization process lasted about 4 h and the formed precipitate was collected by centrifugation, washed several times with ethanol and then heated at 80 °C under vacuum to obtain the final product.

The mass of PPy in the whole composite was quantified by the conversion rate (*n*) of PPy during the polymerization process, which was determined by the following equation:

$$n = \frac{m(\text{PPy/V}_2\text{O}_5) - m(\text{V}_2\text{O}_5)}{m(\text{Py})} \times 100\% \quad (1)$$

where the *m*(PPy/V₂O₅), *m*(V₂O₅) and *m*(Py) represent the mass of the as-synthesized composite, the host V₂O₅ and the injected pyrrole monomer, respectively. In this work, the conversion rate of PPy varied from 18.2% to 19.5% with the injection dosage of Py (0.01–0.04 mL).

The XRD patterns were measured by a Philips X'pert diffractometer using a graphite monochromator and Cu K_α radiation. The scanning range was 10°–60°. The SEM and TEM images of the samples were taken with JEOL JSM-5900LV scanning electron microscope and JEOL JEM-100CX transmission electron microscopy, respectively.

For the electrochemical study, the working electrodes were prepared by mixing the active material with acetylene black (conducting additive) and PVDF (binder) in a mass ratio of 16:3:1, followed by pressing the mixture onto Al foils. Such pallets were vacuum-dried at 80 °C for 12 h before entering the argon-filled glove box in which the gas-tight coin cells were assembled. The metallic Li, membrane (Celgard 2400) and 1 mol/L LiPF₆/EC/DEC (1:1 by volume) were used as the counter and reference electrodes, separator and electrolyte, respectively. Galvanostatic charge/discharge tests were performed over the potential region of 4.0–2.0 V at a constant current density of 80 mA/g using Neware BTS-610. The EIS of each electrode was conducted on an advanced electrochemical system PARSTAT2273, with an AC voltage amplitude of 5 mV over the frequency range of 10 mHz–100 kHz.

3 Results and discussion

3.1 X-ray diffraction study

The XRD patterns of the hollow-spherical vanadium oxide (HS-V₂O₅) before and after modification with PPy (*V*(Py)=0.03 mL) are presented in Fig. 1. The pristine V₂O₅ crystallizes in an orthorhombic structure (PDF 41–1426) with its most intense peak located at 20.369°, which corresponds to the (001) diffraction and is related to the typical layered-structure. The PPy/V₂O₅ composite displays a set of diffraction peaks which approximate to those of the unmodified V₂O₅, indicating that the layered-structure is preserved in the composite material. The crystallite sizes estimated from the Scherrer equation for pure and modified V₂O₅ are 100 and 110 nm, respectively.

Figure 1 also confirms the intercalation of organic polymer into layers of V₂O₅. The (001) reflection shifts to lower angle of 20.369° and the corresponding interlayer expands from 4.3573 to 4.3792 Å calculated by Jade 5.0 software, which are in accordance with the previous reports for the organic polymer insertion [13–14] and suggest that a parallel polymer chain lies between the V₂O₅ slabs. Thus, a more stable structure

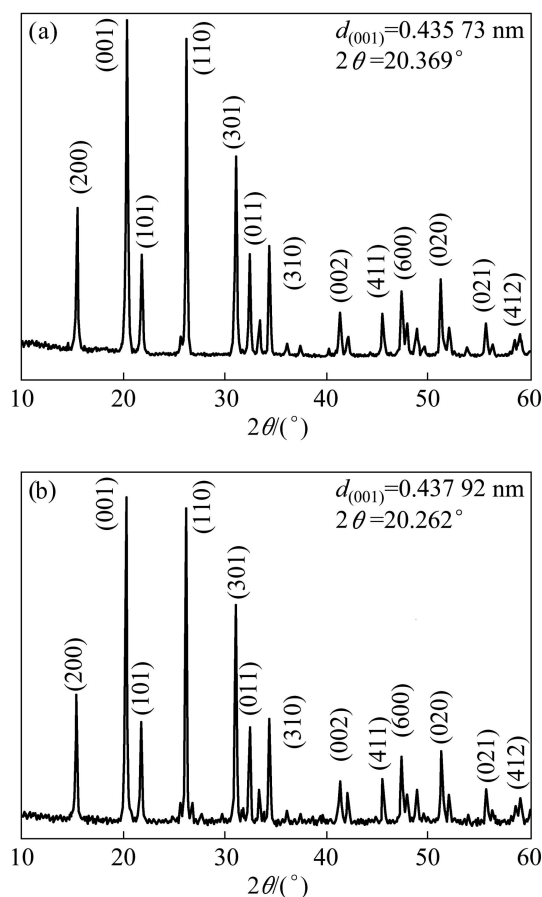


Fig. 1 XRD patterns of hollow microspheres of V₂O₅ (a) and PPy/V₂O₅ (b)

during the reversible insertion/extraction of Li^+ can be expected because the PPy molecules can serve as supports to prevent the layers from collapsing. The increment in the $d_{(001)}$ in our experiment is much lower than that reported by BOYANO et al [14]. However, the different V_2O_5 matrixes used in each research should be taken into account. Comparing with the amorphous V_2O_5 xerogel used by BOYANO et al [14], the highly crystallized V_2O_5 has more strong bonding energy and better thermodynamics stability, therefore, the relatively lower change in the structure upon modifying is reasonable.

3.2 SEM and TEM study

Representative SEM and TEM images for pure V_2O_5 and PPy/ V_2O_5 hybrid are displayed in Fig. 2 and Fig. 3, respectively. Figs. 2(a) and (b) clearly show the microspherical morphologies of V_2O_5 . The modification with PPy seems not to affect this morphology strongly as can be seen in Figs. 2(c) and (d). The microspheres of both samples are accumulated by many crystal grains with an average size of about 100 nm, which coincides with the XRD conclusion. These fine grains may provide highly developed surface area for charge-transfer reaction and short paths for Li^+ diffusion during the electrochemical reaction. The inner cavities are noticeable in Fig. 3, which may produce a buffer effect on the volume change and relieve the pulverization during the electrochemical cycling. After intercalating the PPy, the wall of the microspheres becomes thicker,

corresponding to the interlayer expansion analyzed in XRD as well.

3.3 Electrochemical tests

Galvanostatic cycling tests were carried out at a current density of 80 mA·h/g, which corresponds to the $C/7$ rate, assuming that the full capacity of V_2O_5 is 560 mA·h/g. The charge/discharge curves for HS- V_2O_5 and HS-PPy/ V_2O_5 hybrid electrodes ($V(\text{Pr})=0.03$ mL) are compared in Fig. 4. At the beginning of the cycle, both samples exhibit three typical plateaus, corresponding to the coexistence of $\alpha+\epsilon$, $\epsilon+\delta$ and $\delta+\gamma$ phases, respectively [4], which means that the modification with PPy causes negligible impact on the phase compositions of V_2O_5 during the charging/discharging process. A slight decrease in potential is observed for HS-PPy/ V_2O_5 whose plateaus appear at ~ 3.4 , 3.3 and 2.4 V analogous to other V_2O_5 -based hybrids [15–16]. The decreased voltage seems to be independent of cathodic polarization but associated with a partial reduction of vanadium during the polymerization of the organic molecules [17]. The presence of lower valence state of vanadium may lead to a decrease in the amount of inserted Li^+ and a farther decrease in the discharge capacity. The initial capacity of pure oxide achieves 324.3 mA·h/g but declines steeply as the retention after the 50th cycle is only 32.7%. On the other hand, despite of lower maximum capacity 236.4 mA·h/g, the PPy/oxide claims significantly improved cyclability with 89.1% capacity retention at the same cycling condition (in Fig. 5).

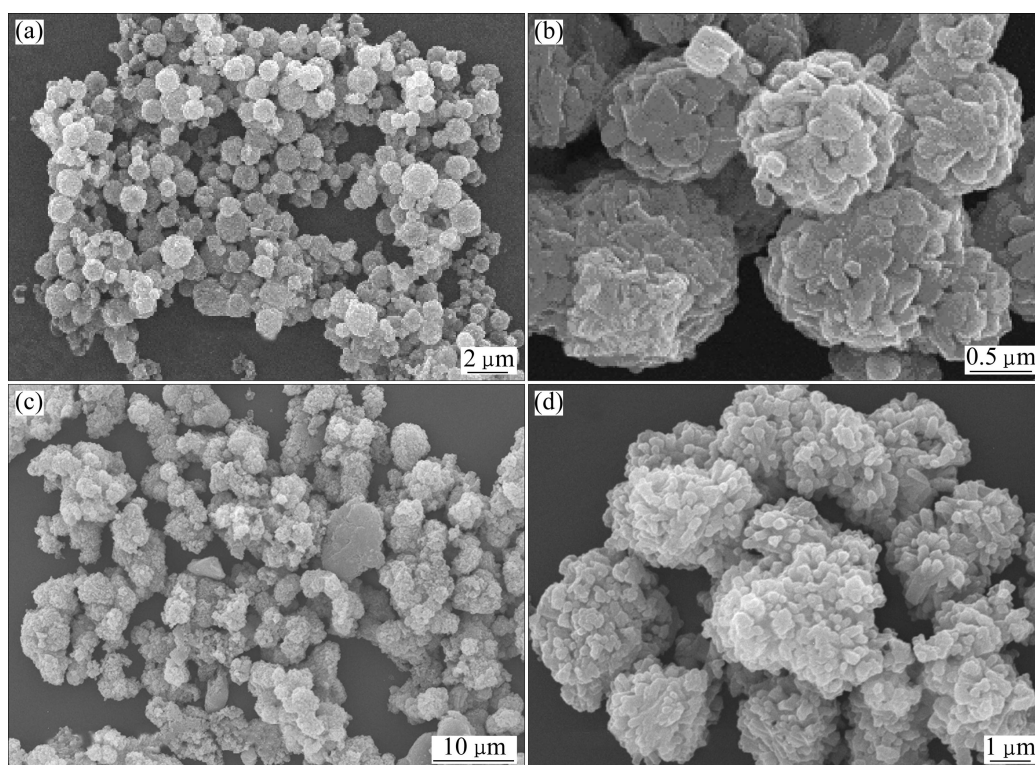


Fig. 2 SEM images of hollow microspheres of V_2O_5 (a, b) and PPy/ V_2O_5 (c, d)

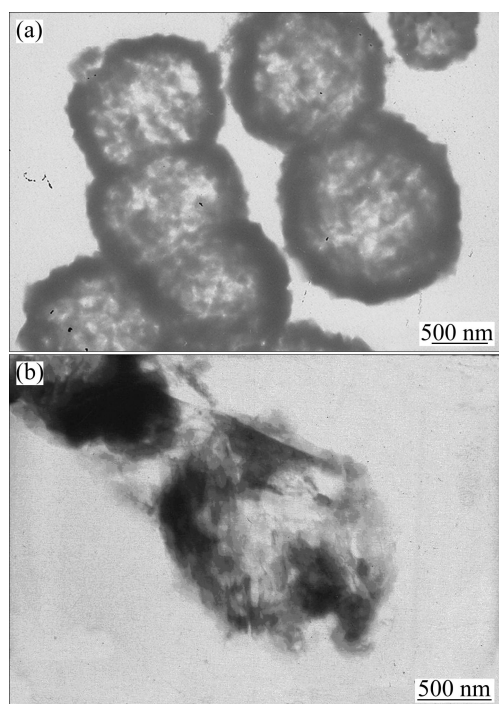


Fig. 3 TEM images of hollow microspheres of V_2O_5 (a) and PPy/V_2O_5 (b)

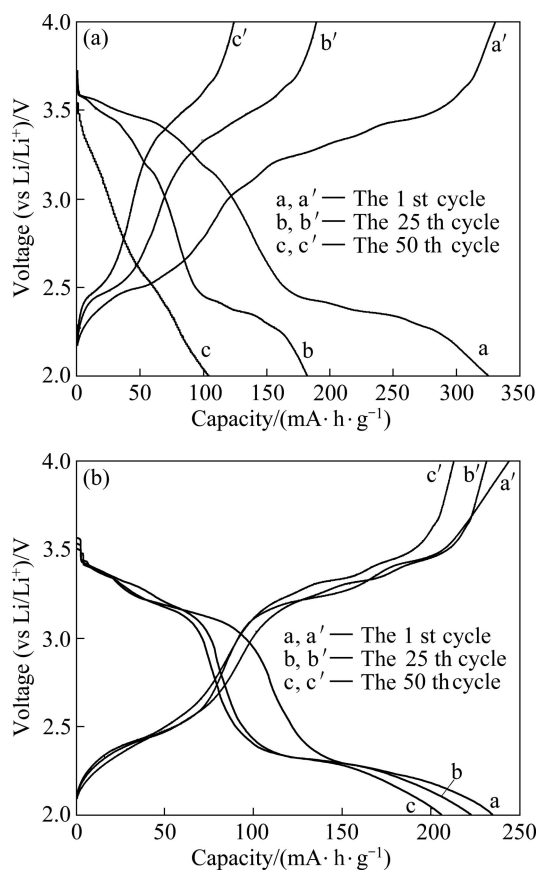


Fig. 4 Voltage — specific capacity curves of hollow microspheres of V_2O_5 (a) and PPy/V_2O_5 composite (b) at the 1st, 25th and 50th cycle charge/discharge at discharge rate of $C/7$

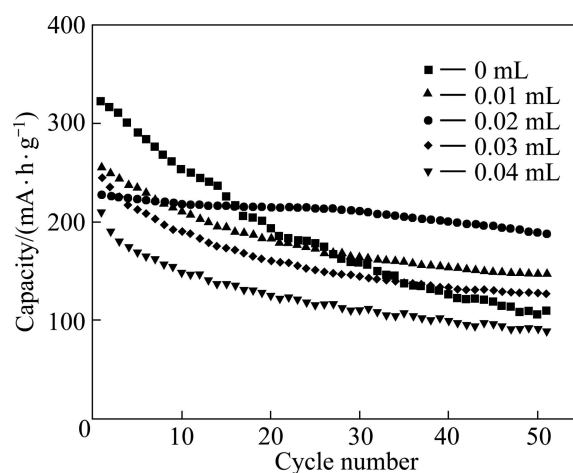


Fig. 5 Cycle behaviour of hollow microspheres of V_2O_5 and PPy/V_2O_5 produced by different dosages of pyrrole

It is important to note that there is so much difference in the character of discharge curves of two samples. The 50th discharge curve of pristine $HS-V_2O_5$ is sloping without any plateau, suggesting the inexistence of multiphase region in terms of thermodynamics. As for $HS-PPy/V_2O_5$ hybrid electrode, three distinct plateaus on the last discharge curve imply the maintenance of reversible phase transitions which depend on the amount of Li^+ inserted into the host and on the relevant change in the crystal structure. Therefore, the enhanced cycling behavior can be partly attributed to the better reversibility of insertion/extraction of Li^+ , which probably results from the more stable structure supported by the PPy molecules as analyzed by XRD.

In addition, Fig. 5 shows that the capacity retention of $PPy/c-V_2O_5$ does not increase monotonously with the content of PPy but attains maximum when the injected amount of Py is 0.02 mL. Further research is needed to offer a convincing explanation for this phenomenon.

The Nyquist plots obtained for $HS-PPy/V_2O_5$ composite electrode compared with $HS-V_2O_5$ electrode in the full-charged state are shown in Fig. 6. As can be seen, two distinct regions are observed for both samples [18]: 1) a semicircle at high frequencies related to a charge-transfer process; 2) a Warburg linear region at intermediate frequency values, associated with a mass transfer process. It is obvious that the charge-transfer resistance (R_{CT}) of $PPy/c-V_2O_5$ composite electrode is much smaller compared with that of V_2O_5 electrode, implying the larger exchange current density (J_0) of surface electrochemical reaction in PPy/V_2O_5 composite electrode. This enhanced electrochemical activity can be ascribed to the presence of high conductive PPy, and also be beneficial for the overall electrochemical properties, especial the cyclability.

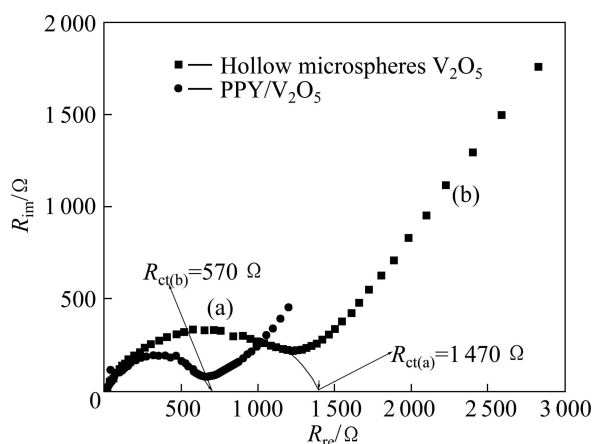


Fig. 6 Electrochemical impedance spectroscopic traces of hollow microspheres of V_2O_5 (a) and PPy/V_2O_5 (b)

As mentioned earlier, Nyquist diagrams show a semicircle and a region at low frequencies characterized by a straight line with a phase angle of 45° . Starting from the equation below [19]:

$$|Z| = \left| \left(\frac{V_M}{\sqrt{2} z F D^{1/2} S} \right) \left(\frac{dE}{dx} \right) \omega^{-1/2} \right| \quad (2)$$

and using the slope of the impedance modulus $|Z|$ as a function of the inverse of square root of angular frequency ($\omega^{-1/2}$), the apparent coefficient diffusion was determined for the three electrodes. Figure 7 shows the linear variation of the modulus of impedance versus the inverse of the $\omega^{-1/2}$. The values of diffusion coefficients were calculated from the slope. It can be seen from Fig. 7 that the slope of PPy/V_2O_5 electrode is smaller than that of $HS-V_2O_5$. It means that the diffusion coefficient of PPy/V_2O_5 electrode is greater than that of $HS-V_2O_5$. Thus, the insertion of PPy helps to open lamellar spacing

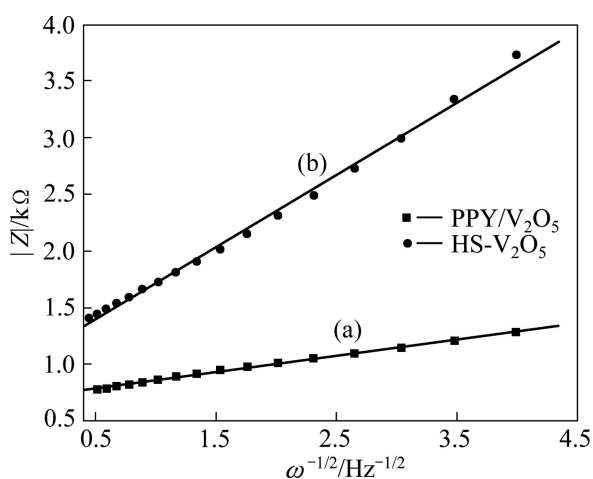


Fig. 7 Impedance modulus $|Z|$ as function of square root of angular frequency ($\omega^{-1/2}$) for PPy/V_2O_5 (a) and $HS-V_2O_5$ (b) at different applied potentials

of V_2O_5 and increases the dispersion speed of ions in lamella, which plays an important role in improving electrochemical properties of composite material, corresponding to the interlayer expansion analyzed in XRD as well.

4 Conclusions

1) PPy/V_2O_5 hollow microspherical hybrid is prepared by injection and polymerization method. The conductive polymer lies between the V_2O_5 lamellas and does not strongly affect the morphology of V_2O_5 host.

2) Comparing with the bare $HS-V_2O_5$ electrode, this novel hybrid cathode exhibits slightly reduced capacity and substantially improved cyclability. The lower discharge capacity can be ascribed to the partial reduction of vanadium during the polymerization of polymer, and the greatly enhanced cycling performance is due to the better reversibility of insertion/extraction of Li^+ and the better electrochemical activity, which presumably result from the more stable structure and the higher conductivity of $HS-PPy/V_2O_5$ composite, respectively.

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空心聚吡咯/ V_2O_5 复合材料的制备及其电化学性能

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摘要: 为改善晶态 V_2O_5 (c- V_2O_5) 正极材料实际容量较低、循环性能较差等问题, 制备了空心球聚吡咯/ V_2O_5 复合材料。利用导电吡咯单体 (Py) 在中空型 V_2O_5 层间发生原位氧化聚合反应制备聚吡咯 (PPy) /中空型 V_2O_5 复合材料 (HS-PPy/ V_2O_5)。采用 X 射线衍射仪 (XRD)、扫描电镜 (SEM)、透射电镜 (TEM) 对样品进行表征, 采用恒流充放电测试和电化学阻抗 (EIS) 测试样品的电化学性能。结果表明, Py 单体已插入中空型 V_2O_5 层间, 与纯中空型 V_2O_5 相比, 制备的 HS-PPY/ V_2O_5 复合材料比容量虽然有所减小, 但是循环稳定性有较大的提高。

关键词: V_2O_5 ; 空心微球; 正极; 锂离子电池

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