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A Polyimide derivative containing different carbonyl groups for flexible lithium ion batteries

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A novel polyimide derivative PMAQ is prepared by a condensation polymerization of pyromellitic dianhydride and 2, 6diaminoanthraquinone and a flexible electrode film PMAQ-SWNT is further fabricated by filtration with single-wall carbon nanotube dispertions. PMAQ connets different carbonyl groups of dianhydride and quinone together, therefore combines the advantages of different units together. Electrochemical tests show that PMAQ-SWNT can transfer three electrons reversibly and theoretical calculation also prove that. PMAQ-SWNT shows high capacity of 190 mA h g⁻¹ and superior rate performance, remaining 120 mA h g⁻¹ at 20 C. PMAQ-SWNT is a promising flexible electrode because of good performance and flexibility.

Introduction

Flexible electronics is a promising technology that will be widely used in the future.¹⁻³ Many flexible electronic devices have been demonstrated such as flexible displays, batteries, sensors and etc.⁴⁻⁸ With the development of flexible electronics, there will have great chances in the areas including communication, entertainment and health care. One basic requirement is that the flexible electronic devices should still work when bent, folded or stretched. Therefore, the power sources of these flexible devices must also be flexible and operate well when deformed.⁹ Lithium ion battery (LIB) is one of the best candidates of power sources because of high energy density, high voltage and long cycle life.¹⁰ The challenge to realize flexible batteries is to prepare electrode with high capacity, good rate capability, high cycling stability and flexibility, as well as proper electrolyte and good package. ^t The active material which is intrinsically flexible will be the best candidate to prepare flexible electrode. ¹¹

Organic materials used for batteries have attracted much research interest because they are renewable, designable and intrinsically flexible.¹²⁻¹⁵ Various organic materials such as conducting polymers,¹³ organosulfur compounds,^{16, 17} organic

radical polymers,¹⁸⁻²⁰ layered compounds,^{21, 22} bipolar porous polymeric frameworks,²³ tetracyano quinodimethane (TCNQ),²⁴ trioxotriangulene (TOT)²⁵ and organic carbonyl compounds have been studied. Recently, much progress has been made in organic carbonyl compounds for Li-ion batteries. ²⁶⁻³⁰ Polyimide, as a kind of organic carbonyl compounds, has high capacity and good thermal stability. Half of the carbonyl groups on dianhydride component can be used and the capacity can be regulated by choosing different monomers.³¹ Quinone derivative is another typical carbonyl compound. The material comprising quinone sub-structures has the ability that all of the carbonyl groups can react with lithium ions. The aromaticity plays an important role to stabilize it. 32, 33 To utilize the active organic material in flexible batteries. Lee et al. has made a free-standing electrode film using single-wall carbon nanotube and lumiflavine. ³⁴ However, when the content of active material is high, the cycling performance is sacrificed. If dianhydride component and quinone sub-structure can be polymerized together, the carbonyl groups from different monomers will both contribute to the capacity. Moreover, this polymer can integrate the high capacity of quinone unit and high stability of polyimide unit together.

In this paper, a novel polyimide named as PMAQ is designed and synthesized by a condensation polymerization of pyromellitic dianhydride (PMDA) and 2, 6diaminoanthraquinone (AQ), and a binder-free flexible organic cathode film was further prepared by composition with highly conductive single-wall carbon nanotube (SWNT). The selfstanding SWNT network acts as binder and current collector, PMAQ is electroactive material in the flexible electrode. PMAQ is proved to be a kind of organic carbonyl compound with high capacity and outstanding thermal stability, which combines the advantages of dianhydride and quinone. The high conductivity of SWNT guarantees a good electrical conductivity

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and flexibility of the electrode, which is important for the flexible lithium ion batteries. The electrode delivers high capacity of 190 mA h g⁻¹ and good rate performance, remaining 120 mA h g⁻¹ at 20 C. Moreover, it has high cycling stability, and the capacity retains 91.5% after 300 cycles charging/ discharging tests.

Experimental

Synthesis

Synthesis of PMAQ: In a typical preparation of PMAQ composite, AQ (476.48mg, 2 mmol) was first dissolved in 20 mL of NMP under refluxing and stirring for 30 minutes, and then PMDA (436.24mg, 2 mmol) was added into the mixture under stirring for another 30 minutes. The above mixture was reacted for 12 h in sand bath under nitrogen atmosphere. After being cooled down to room temperature, the precursor was filtered and washed several times with methyl alcohol and acetone, and then dried at 80 °C. Afterward, PMAQ was prepared by calcination at 300 °C under argon for 6 h and following extraction with acetone for 12 h.

Preparation of PMAQ-SWNT Film: The typical preparation process of the PMAQ-SWNT composite is as follows. First, SWNT were dispersed in deionized water with sodium deoxycholate by sonication in a ultrasonic bath for 2 h. Then an appropriate amount of PMAQ was added into the asobtained SWNT dispersion. The mixture was further ultrasonicated for 1 h at an ice bath. Then the PMAQ-SWNT thin film was fabricated through vacuum filtration and then dried under vacuum oven at 80 °C overnight.

Characterization

The functional groups and chemical bond of the synthetic material were measured using a Fourier transform infrared (FTIR) spectrometer (Spectrum One, Perkin-Elmer). Elemental analysis was obtained by Flash EA 1112. TGA was tested on Perkin-Elmer Diamond TG/DTA at 10 °C min⁻¹ to 800 °C under a nitrogen atmosphere. The surface morphologies of the samples were observed by field-emission scanning electron microscope (Hitachi S4800). Mechanical tests were performed in a TA Instruments Dynamic Mechanical Analyzer Q800. The preload force is 0.004 N and speed is 50 μ m min⁻¹.

Electrochemical Tests

PMAQ-SWNT film was cut into discs with a diameter of 11 mm, and directly be used as the working electrodes without any binder and conductive carbon. The cathode was separated from the lithium anode by a separator (Celgard 2325). The electrolyte was 1 M LiN (CF₃SO₂)₂ (LiTFSI) solution dissolved in a mixed solvent of 1, 3-dioxolane and dimethoxyethane (1:1, in weight). A pure lithium foil was used as a counter electrode. The half-cells were assembled in an argon-filled glove box. The rate performance and galvanostatic charge–discharge performance were carried out by the Arbin instruments testing system (Arbin-SCTS). The electrochemical impedance spectroscopy (EIS) and the cyclic voltammogram (CV) were measured by a VMP3 Potentiostat /Galvanostat (Biologic).

Results and discussion

Material synthesis and structural analysis

As shown in Fig. 1a, the PMAQ was prepared by the copolymerization of PMDA and AQ. The structure of PMAQ is characterized by FTIR spectroscopy. As showed in Fig. 1. The absorption peaks at 1858 and 1773 cm⁻¹ of PMDA are the asymmetric stretching vibration and symmetric stretching vibration of C—O bonds, respectively. These two peaks shift to 1776 and 1721 cm⁻¹ in polymer PMAQ. The strong peaks at 1238 and 925 cm^{-1} of PMDA are attributed to C–O–C, which disappear in PMAQ. The new peak at 1359 cm⁻¹ in PMAQ is stretching vibration of C-N bond, indicating the PMDA and AQ unit is connected by C-N bond successfully. There are two peaks at 3426 and 3337 cm^{-1} , which can be attributed to asymmetric and symmetric stretching vibration of -NH₂ in AQ. In the spectrum of PMAQ these two peaks disappear. Two peaks locate at 1658 and 1629 cm⁻¹ in AQ are signals of C—O bonds, which shift to 1676 cm^{-1} in PMAQ. The band at 1573 cm⁻¹ in AQ assigns to the anthraquinone ring, which shift to 1595 cm⁻¹ in PMAQ. This means that PMDA and AQ unit are well retained in polymer chains. PMAQ has a formula of C₂₄H₈N₂O₆. The content of C, H and N is 68.58%, 1.92% and 6.67% respectively. The elemental analysis shows that the content of C, H and N is 66.7%, 2.09% and 6.93%, very close to the theoretical value. It further confirmed the successful synthesis of PMAQ. Thermal gravimetric analysis shows that the decomposition temperature of PMAQ is higher than 500 $^\circ$ C in nitrogen atmosphere. This suggests that PMDA and AQ are completely polymerized, and PMAQ has a thermal stability as good as other polyimides. ^{35, 36} The thermal stability is better than the polyimide which reacted with aliphatic amines.³⁷ PMAQ is synthesized by PMDA and aromatic amine AQ. Aromatic amine is more rigid than aliphatic amine in polyimide backbone, therefore it has higher thermal stability. The high thermal stability is beneficial to the safety of organic electrode material.





As shown in Fig. 2, SWNT aqueous dispersion was prepared with 0.1% weight concentration using sodium deoxycholate as surfactant. Then the PMAQ active material was added into the SWNT aqueous dispersion and sonicated. And then fabricated through vacuum filtration. The PMAQ particles were well entangled within the SWNTs network, forming free-standing electrodes without the introduction of any binder. PMAQ-SWNT film with different content of carbon nanotube (named PMAQ-10% SWNT, PMAQ-20% SWNT, and PMAQ-30% SWNT) can be prepared. These films are all flexible and exhibit good mechanical properties.



Fig. 2 Schematic of the preparation process of PMAQ-SWNT film.

The surface morphology of PMAQ-SWNT nanohybrids have been investigated using scanning electron microscopes. It varies a lot with the change of content of SWNT. When the composite has 10 % SWNT, a lot of PMAQ particles can be observed (Fig. 3a) with little carbon nanotube bundles. When the content of SWNT is 20 %(Fig. 3b), the PMAQ particles become less and the SWNT network can be clearly observed.



Fig. 3 SEM images of PMAQ-SWNT with different content of SWNT (a)10% SWNT, (b)20% SWNT, (c) and (d)30% SWNT.

SWNT network interpenetrate together and PMAQ particles are embedded in the network. The surface is not very uniform and there are aggregated PMAQ particles in some parts. When the content of SWNT is increased to 30 %(Fig. 3c), more SWNT network interpenetrate and the PMAQ particles are much less. With the increasing content of SWNTs, the dispersion of PMAQ in the SWNTs is more and more uniform, especially the PMAQ-30% SWNT. According to the SEM images in Fig. 3d, PMAQ-SWNT is composed of a highly interpenetrated network of carbon nanotubes and PMAQ particles. The size of PMAQ particles is *ca.* 800 nm. PMAQ particles are embedded in the SWNT network and connected by SWNT bundles. The highly interpenetrating network of carbon nanotubes supply electrons transport pathway and good flexibility.

Electrochemical characterization

The electrochemical performance of PMAQ-SWNT was tested using Swagelok cells. Many polymerization conditions, such as solvent, temperature and concentration affect the electrochemical performance. In this situation, PMAQ-SWNT contains 10% SWNT was chosen to study these influences. The solvent greatly affects the capacity of PMAQ-SWNT. When using m-cresol and DMF as solvent for polymerization, the capacity of PMAQ are both very low. The capacity of PMAQ-SWNT is increased to 171 mA h g $^{-1}$ at 0.1 C when NMP is solvent (Fig. S1). The formation of polyimide consists of two steps. First is the formation of poly(amic acid) and second step is the imidisation as shown in the scheme S2. The actual rate of polymerisation is strongly dependent on the solvent. The rate generally increases as the solvent becomes more polar.³⁸ The dipole moment of m-cresol, DMF and NMP is 5.15, 12.88 and 13.64×10⁻³⁰ C m, respectively. The NMP has largest polar, therefore the rate is larger in NMP system, which is beneficial to the formation of poly(amic acid) and polyimide. The temperature also influences the electrochemical performance of the composite. When reaction temperature is 160 °C, the capacity is less than 30 mA h g⁻¹. This is because temperature affects the reaction rate. When temperature is low, the degree of polymerization is not high, therefore the polymer has poor performance. In the preparation of polyimide, the monomer first reacted in solvent at temperature between 160~220 °C, then the polyimide formed by thermal imidisation at 300 °C. In the first period of reaction, the temperature is very high. It's very similar to the one step synthesis of polyimide, thus Imidisation imidisation also occurs. occurs either simultaneously with propagation, or very quickly thereafter.³⁸ Previous study found that above a certain temperature ca. 125 $^{\circ}$ C, increasing temperature will enhance molecular weight. 39 When the temperature is increased to 180 °C, the capacity of composite is enhanced. And the capacity continues to improve when reaction temperature is 200 °C. At 200 °C, PMAQ-SWNT shows best performance (Fig. S2). The capacity varies with the monomer concentration. When concentration is 0.1 mmol ml ¹, PMAQ-SWNT has both high capacity and rate capability (Fig. S3). For the formation of polyimide, the propagation reaction is reversible. The forward reaction is bimolecular and the reverse is unimolecular. Thus increases in the monomers' concentrations should shift the equilibrium to the right. ³⁸ Therefore increasing concentration can contribute to the formation of polyimide and there is an optimized concentration.

PMAQ-SWNT film can be directly used as electrode without binder and conductive carbon. As for comparison, the conventional PMAQ electrode was made from pure PMAQ, conductive carbon and PTFE with a ratio of 65:30:5 in weight. The conventional PMAQ film shows a capacity of 180 mA h g⁻¹ at 0.1 C (Fig. S4), but the rate performance is really bad. At 0.5C the capacity of PMAQ drops to zero. By contrast, PMAQ-SWNT film delivers a capacity of 183 mA h g⁻¹ at 0.1 C, and the

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pure SWNT film shows a very low capacity of 20 mA h g⁻¹ (Fig. S5), almost can be ignored. Besides the increase in specific capacity, the rate performance is also improved significantly. PMAQ-SWNT has high capacity at 5C but pure PMAQ shows no electrochemical activity at the same current density. This illustrates that the PMAQ-SWNT film delivers an excellent rate performance. A capacity of 180 mA h g⁻¹ is recovered when the current density is reduced to 0.1 C, suggesting that PMAQ-SWNT has good reversibility.

As shown in Fig. 4a, PMAQ-SWNT with different content of SWNT all show high capacity and good rate performance. The rate performance increases with increasing content of SWNT varies from 10% to 30%. When the SWNT content is 30%, PMAQ-SWNT shows best rate performance. It delivers a capacity of 120 mA h g $^{-1}$ at 20 C, remaining 63% of that at 0.1C. The capacity is ca. four times the capacity of PMAQ-10%SWNT. This is a very high rate performance for organic electrode materials. There are rarely reports on organic cathode that can deliver high capacity under both fast charging and discharging.⁴⁰ The experiment result shows that the highest capacity is 190 mA h g⁻¹ at 0.1C. In order to understand the reason the origination of high capacity of PMAQ, the cyclic voltammetry of PMAQ, AQ monomer as well as a polyimide without quinone groups (PI) were tested. The molecular structure of PMAQ and PI shows that they both have carbonyl groups of pyromellitic dianhydride, but PMAQ has another pair of carbonyl groups of anthraquinone. The CV curves in Fig. 4b show that PI (the molecular structure of PI is shown in Scheme S1) has two pairs of redox peaks, which both come from two carbonyl groups of pyromellitic dianhydride. Pl's reduction peak is 2.24 V and 1.91 V, respectively and oxidation peak locates at 2.24V and 2.43V. The reduction peak of AQ monomer locates at 2.18 V and oxidation peak is 2.4 V. Both the reduction peak and oxidation peak of AQ monomer are between that of PI. PMAQ has three pairs of redox peaks. The peaks labelled 1 and 3 are the same as PI (derive from the carbonyl groups of pyromellitic dianhydride). The peak labelled



Fig. 4 (a) Rate performance of PMAQ-SWNT composite; (b) cyclic voltammetry (CV) test of PI and PMAQ; (c) electrical conductivity and (d) electrochemical impedance spectroscopy of PMAQ-SWNT with different content of SWNT.

2 is the redox reaction of the carbonyl groups of anthraquinone. Based on the CV test, PMAQ can transfer three electrons reversibly. The carbonyl groups of both PMDA unit and AQ unit are active and can contribute to the capacity. It means that the electrochemical process consists of three steps.

As showed in Scheme 1, firstly, PMAQ get one electron and is reduced to PMAQ[•]. This happens at ca. 2.25 V, corresponds to 3' peak in CV curves. Then it get second electron and is reduced to PMAQ²⁻. This process can be ascribed to 2' peak in CV curves. At last it is reduced to PMAQ³⁻. This step happens at ca. 1.8V. It can be attributed to 1' peak in CV curves. It stores one lithium at each step and becomes to lithium enolate. The oxidation process is reverse. So the theoretical capacity of PMAQ is 191 mA h g⁻¹ based on the three electrons redox reaction. The experiment result is consistent with the three electrons process.



Scheme 1 Electrochemical redox reactions of PMAQ. Its reduction occurs in three steps, generating the radical anion (PMAQ[•]), then the dianion (PMAQ^{2°}), trianion (PMAQ^{3°}) with Li + association. Oxidation process is reverse.

To obtain a deeper insight into the reduction process, theoretical calculations are performed using density functional theory (DFT) with B3LYP functional and 6-31+G(d,p) basis set for the PMAQ system implemented in the G09 program.⁴¹ As seen from Fig. 5, for one, two and three-electron reductions of the PMAQ molecule, these three processes are energetically favorable with the negative electron affinity (EA) of -2.58 eV, -1.97eV and -0.93eV respectively. In addition, B3LYP-optimized geometries show that there are no large difference for the dihedral angle between PMDA and AQ moiety when going from the neutral PMAQ (45°) to PMAQ radical anion, dianion and trianion (34°, 43° and 42°, respectively). This indicates that the one, two and three-electron reduction processes are easily occurred accompanied with only a little changes of the geometries. Natural Bond Orbital (NBO) analysis shows that a negative charge mainly exists on the PMDA moiety for the PMAQ radical anion. For the PMAQ dianion, the negative charges are mostly localized on the PMDA moiety and a little on the AQ moiety. In the case of PMAQ trianion, two negative charges are localized on the PMDA moiety and one negative charge on the AQ moiety. However, for the four-electron reduction of PMAQ molecule, it is not stable due to a very large positive EA of 6.89 eV. The optimized geometry of PMAQ4- also shows that the PMDA and AQ moiety is almost perpendicular. This large geometry change is not favourable for the four-electron reduction. B3LYP/6-31+G(d,p)-calculated

energy barrier for the geometry change of one, two, three and four reduction process is -2.58 eV, -0.62 eV, 2.89 eV and 5.95 eV, respectively. For one and two electron reduction process, these two reactions are exothermic and make PMAQ⁻ and PMAQ²⁻ very stable. For three electron reduction process, the smaller energy barrier makes the process possible even though it is endothermic. However, for four reduction process, the energy barrier is almost twice larger than the three-reduction process, which leads to this reduction process very difficult and PMAQ⁴⁻ not stable. Our calculation results are in very agreement with the experimental findings and support that only one, two and three-reduction processes are energetically favourable.



Fig. 5 (a) B3LYP/6-31+G (d, p)-calculated electron affinity (EA) of PMAQ anions; (b) B3LYP/6-31+G (d, p)-optimized geometries of PMAQ anions. Dihedral angles between PMDA and AQ moiety and Natural Bond Orbital (NBO) charge populations are also shown.

The electronic conductivity and electrochemical impedance spectroscopy (EIS) were further tested to explain the outstanding rate performance of PMAQ-SWNT. The electronic conductivity was tested using a four-probe measurement. In Fig. 4c, the pure polymer PMAQ film, made from PMAQ and PTFE (98:2 in weight) but without conductive carbon, has a very low electronic conductivity that even cannot be tested by our apparatus (detection limit is ca. 10⁻⁹ S cm⁻¹). After mixing with 10 wt% SWNTs, the electronic conductivity increases to 33 S cm⁻¹. When the content of SWNT is up to 30 wt%, the electronic conductivity increases to 138 S cm⁻¹, and the pure SWNT film has a high electronic conductivity of 415 S cm⁻¹. The SWNT network make the PMAQ change from insulator to semiconductor, the electronic conductivity is increased more than 11 orders of magnitude. This result indicates that the SWNT can construct interpenetrated conductive network and significantly increase the electronic conductivity of PMAQ-SWNT film, therefore can improve rate performance.

The Nyquist plots is shown in Fig. 4d, obtained for the PMAQ-SWNT films electrodes with a frequency range from 0.01 Hz to

100 kHz. The plots can be divided to three parts and different parts show different process. The high-to-medium frequencies part reflects the resistance for Li ion migration through the surface films and film capacitance. The semicircle reflect charge-transfer resistance and interfacial capacitance. The diameter of semicircle reflects the charge-transfer resistance. In addition to the charge-transfer resistance across the surface film/ particle interface, other factors such as interparticle electronic resistance may influence the diameter of the semicircle. At very low frequencies, it is a sloping line which reflects solid-state diffusion, behaves similarly to a finite space-type Warburg impedance.⁴²

In the plots, the diameter of semicircle reflects the charge transfer resistance R_{ct}, so that a smaller semicircle implies a faster charge transport. In order to compare the diameter of these three samples, we further did the simulation using equivalent circuit (shows in Fig. 3d).The charge transfer resistance R_{ct} of the PMAQ-10%SWNT, PMAQ-20%SWNT and PMAQ-30%SWNT film is 42.6 Ω , 24.6 Ω and 8.3 Ω , respectively. The result indicates that PMAQ-30% SWNT film has the smallest charge transfer resistance. PMAQ-30% SWNT film has high electronic conductivity and small charge transfer resistance, which resulting in excellent rate performance.

Therefore, SWNTs not only connect PMAQ particles together but also perform as a current collector, ensuring excellent electron transport kinetics without the introduction of conductive carbon and metal current collector. Conductive SWNTs provide a highly conductive pathway for electrons and significantly increase the electronic conductivity. The rate performance of SWNTs was further tested to study whether the SWNT have contribution to the flexible organic cathode film (Fig. S5), the result indicates that the SWNT have little contribution to the capacity and can be ignored.

Based on the above electrochemical performance, we can conclude that PMAQ-30% SWNT displays the best electrochemical performance among all the samples. So we further did the cycling performance test at 0.1C (the first 5 cycles) and 0.5C (the last 300 cycles). As shown in Fig. 6a, PMAQ-30% SWNT film exhibits good cycling stability, consistent with the fact that the polymer has enhanced cyclability. PMAQ-SWNT film has an initial capacity of 164 mA h g⁻¹ and retains 91.5% after 300 cycles. Fig. S6 shows typical galvanostatic charging/discharging curves of the PMAQ-30% SWNT film. The PMAQ-30% SWNT film exhibits almost the same charge and discharge profiles after 100 cycles and 200 cycles. The charge/discharge profile only shifts to the left a little after 300 cycles. The results reveal that the PMAQ-30% SWNT has excellent electrochemical reversibility and very stable cycling performance. It is worth noting that both PMAQ-10% SWNT and PMAQ-20% SWNT have high cycling stability. As show in Fig. S7, the capacity of PMAQ-10% SWNT remains 84.2% after 300 tests and PMAQ-20% SWNT retains 91.3% after 300 cycles. It indicates that increasing the content of active material will not obviously affect the cycling performance. This is very different compared with organic small molecules electrode materials. When small molecules act as active cathode, the dissolution can't be avoided. If the

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amount of small molecules is increased, the capacity deteriorate.³⁴ But polymer cathode material is stable in electrolyte, therefore it shows high cycling stability even when the content of polymer is increased to 90 %.

The mechanical performance of electrode is very important for the application of flexible electrode used in flexible battery. Therefore, the stress-strain curves were tested as showed in Fig. 6b. The Young's modules and tensile strength of SWNT film are ca. 586 MPa and 10.91 MPa, respectively, and the final strain is 4.46%. The Young's modules and tensile strength of PMAQ-SWNT film is ca. 810.8 MPa and 7.01 MPa, respectively, and the final strain is 3.58%. Compared with pure SWNT film, the tensile strength and final strain decrease a little. SWNT has good mechanical performance and the interpenetrated network of SWNT can strengthen the PMAQ-SWNT composite. Therefore, PMAQ-SWNT film possesses good mechanical properties.



Fig. 6 (a) Cycling performance of PMAQ-30%SWNT; (b) stress-strain curve of PMAQ-30%SWNT and SWNT film.

Conclusions

In conclusion, a thin flexible organic cathode film PMAQ-SWNT was prepared with a novel polyimide PMAQ and highly conductive SWNT. PMAQ is the first organic electrode material that integrate the high capacity of quinone unit and high thermal stability of polyimide unit together. PMAQ particles were embedded by interpenetrating carbon nanotube network. CV test reveals that PMAQ-SWNT can transfer three electrons reversibly, with a theoretical capacity of 191 mA h g $^{-1}$. Theoretical calculation results also demonstrate that three electrons reduction process is energetically favourable. This means that anhydride and quinone can be connected in one polymer and the carbonyl groups of different monomers both can contribute to the capacity. The flexible electrode is binder free and doesn't need metal current collector. The SWNT can significantly increase the electronic conductivity of PMAQ. When the content of the SWNT reach 30%, it delivers a capacity of 190 mA h g^{-1} at 0.1 C. It also shows superior rate performance, remaining 120 mA h g⁻¹ at 20 C. PMAQ-SWNT also has good cycling stability and flexibility. The strategy can connect carbonyl groups of different aromatic molecules together and the material shows advantages of each unit. We expect the strategy can be extended to other aromatic molecules and make these materials be used in flexible batteries.

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References

- 1 J. A. Rogers, T. Someya and Y. Huang, *Science*, 2010, **327**, 1603.
- A. J. Baca, J.-H. Ahn, Y. Sun, M. A. Meitl, E. Menard, H.-S. Kim,
 W. M. Choi, D.-H. Kim, Y. Huang and J. A. Rogers, *Angew. Chem. Int. Ed.*, 2008, **47**, 5524.
- 3 Y. Sun, W. M. Choi, H. Jiang, Y. Y. Huang and J. A. Rogers, *Nat. Nanotechnol.*, 2006, **1**, 201.
- 4 G. Zhou, F. Li and H. M. Cheng, *Energy Environ. Sci.*, 2014, **7**, 1307.
- 5 Z. Song, T. Ma, R. Tang, Q. Cheng, X. Wang, D. Krishnaraju, R. Panat, C. K. Chan, H. Yu and H. Jiang, *Nat. Commun.*, 2014, **5**.
- J.-S. Kim, D. Ko, D.-J. Yoo, D. S. Jung, C. T. Yavuz, N.-I. Kim, I.-S. Choi, J. Y. Song and J. W. Choi, *Nano Lett.*, 2015, **15**, 2350.
- 7 S.-H. Kim, K.-H. Choi, S.-J. Cho, S. Choi, S. Park and S.-Y. Lee, Nano Lett., 2015, 15, 5168.
- 8 M. F. El-Kady, V. Strong, S. Dubin and R. B. Kaner, Science, 2012, 335, 1326.
- 9 Y. H. Lee, J. S. Kim, J. Noh, I. Lee, H. J. Kim, S. Choi, J. Seo, S. Jeon, T. S. Kim, J. Y. Lee and J. W. Choi, *Nano Lett.*, 2013, **13**, 5753.
- 10 M. Armand and J. M. Tarascon, Nature, 2008, 451, 652.
- 11 H. Nishide and K. Oyaizu, *Science*, 2008, **319**, 737.
- 12 Y. Liang, Z. Tao and J. Chen, Adv. Energy Mater., 2012, 2, 742.
- 13 P. Novak, K. Muller, K. S. V. Santhanam and O. Haas, *Chem. Rev.*, 1997, **97**, 207.
- 14 P. Poizot and F. Dolhem, *Energy Environ. Sci.*, 2011, **4**, 2003.
- 15 Z. Song and H. Zhou, *Energy Environ. Sci.*, 2013, **6**, 2280.
- 16 N. Oyama, T. Tatsuma, T. Sato and T. Sotomura, Nature, 1995, 373, 598.
- 17 T. Sarukawa and N. Oyama, J. Electrochem. Soc., 2010, 157, F23.
- 18 K. Oyaizu and H. Nishide, Adv. Mater., 2009, 21, 2339.
- 19 T. Suga, H. Ohshiro, S. Sugita, K. Oyaizu and H. Nishide, *Adv. Mater.*, 2009, **21**, 1627.
- 20 T. Suga, S. Sugita, H. Ohshiro, K. Oyaizu and H. Nishide, *Adv. Mater.*, 2011, **23**, 751.
- 21 Y. Mao, Q. Kong, B. Guo, X. Fang, X. Guo, L. Shen, M. Armand, Z. Wang and L. Chen, *Energy Environ. Sci.*, 2011, 4, 3442.
- 22 T. Matsunaga, T. Kubota, T. Sugimoto and M. Satoh, *Chem. Lett.*, 2011, **40**, 750.
- 23 K. Sakaushi, G. Nickerl, F. M. Wisser, D. Nishio-Hamane, E. Hosono, H. Zhou, S. Kaskel and J. Eckert, *Angew. Chem. Int.* Ed., 2012, **51**, 7850.
- 24 Y. Hanyu and I. Honma, Sci. Rep., 2012, 2.
- 25 Y. Morita, S. Nishida, T. Murata, M. Moriguchi, A. Ueda, M. Satoh, K. Arifuku, K. Sato and T. Takui, *Nat. Mater.*, 2011, 10, 947.
- 26 H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot and J. M. Tarascon, *ChemSusChem*, 2008, **1**, 348.
- 27 T. Nokami, T. Matsuo, Y. Inatomi, N. Hojo, T. Tsukagoshi, H. Yoshizawa, A. Shimizu, H. Kuramoto, K. Komae, H. Tsuyama and J.-i. Yoshida, J. Am. Chem. Soc., 2012, 134, 19694.
- 28 W. Walker, S. Grugeon, O. Mentre, S. Laruelle, J. M. Tarascon and F. Wudl, *J. Am. Chem. Soc.*, 2010, **132**, 6517.
- 29 S. Wang, L. Wang, K. Zhang, Z. Zhu, Z. Tao and J. Chen, *Nano Lett.*, 2013, **13**, 4404.

- 30 M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribiere, P. Poizot and J. M. Tarascon, *Nat. Mater.*, 2009, 8, 120.
- 31 Z. Song, H. Zhan and Y. Zhou, *Angew. Chem. Int. Ed.*, 2010, **49**, 8444.
- 32 Y. Liang, P. Zhang and J. Chen, Chem. Sci., 2013, 4, 1330.
- 33 Z. Song, H. Zhan and Y. Zhou, *Chem. Commun.*, 2009, DOI: 10.1039/b814515f, 448.
- 34 M. Lee, J. Hong, H. Kim, H.-D. Lim, S. B. Cho, K. Kang and C. B. Park, *Adv. Mater.*, 2014, **26**, 2558.
- 35 L. W. Qu, Y. Lin, D. E. Hill, B. Zhou, W. Wang, X. F. Sun, A. Kitaygorodskiy, M. Suarez, J. W. Connell, L. F. Allard and Y. P. Sun, *Macromolecules*, 2004, **37**, 6055.
- 36 B. K. Zhu, S. H. Xie, Z. K. Xu and Y. Y. Xu, *Compos. Sci. Technol.*, 2006, **66**, 548.
- 37 A. S. Mathews, I. Kim and C.-S. Ha, J. Appl. Polym. Sci., 2006, 102, 3316.
- 38 D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, *Polyimides*, Springer, 1990.
- 39 P. R. Young, J. R. J. Davis, A. C. Chang and J. N. Richardson, Journal of Polymer Science Part a-Polymer Chemistry, 1990, 28, 3107.
- 40 Z. Song, T. Xu, M. L. Gordin, Y.-B. Jiang, I.-T. Bae, Q. Xiao, H. Zhan, J. Liu and D. Wang, *Nano Lett.*, 2012, **12**, 2205.
- 41 F. Gaussian 09 D.01, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A., Journal.
- 42 D. Aurbach, M. D. Levi, E. Levi, H. Teller, B. Markovsky, G. Salitra, U. Heider and L. Heider, J. Electrochem. Soc., 1998, 145, 3024.

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A novel polyimide derivative PMAQ is prepared by condensation polymerization and carbonyl groups on different repeating units both contribute to the capacity.

