Lithium Batteries

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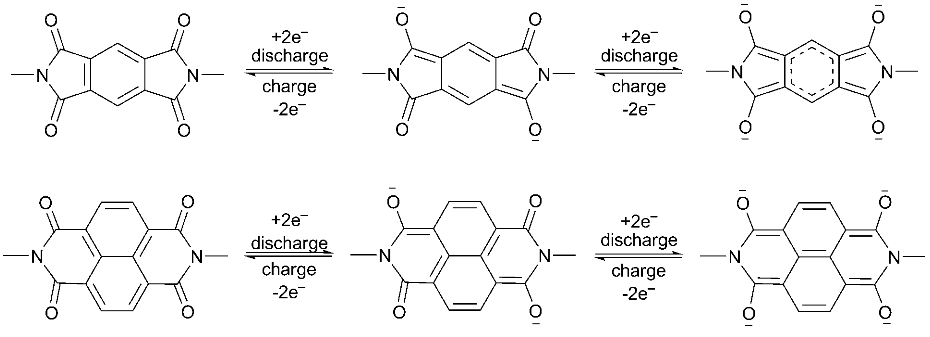
Polyimides: Promising Energy-Storage Materials**

Zhiping Song, Hui Zhan, and Yunhong Zhou*

A clean and sustainable energy supply is essential for the future of human beings and is thus a crucial issue in the 21st century. Regarding energy conversion and storage, lithium batteries have played an indispensable role over the past 20 years and will do so for the foreseeable future because of their advantages in energy density and cyclability. Nowadays, the lithium battery market, especially given the development of electric automobiles, has grown rapidly, and scientists are now urged to focus on not only energy density, but also power density, safety, and sustainability. Recently, Armand, Tarascon, and co-workers introduced the concept of a "sustainable battery" or "green battery",[1–5] aiming to evoke researchers' concern over the resource issues and environmental issues that may be caused by large-scale production and use of Li-ion batteries based on conventional inorganic electrodes. The key technique for a "sustainable Li-ion battery" is to develop renewable organic electrodes, which may eventually be synthesized from biomass.

In fact, the concept of an organic electrode material is not new. Dichloroisocyanuric acid was studied as a cathode material for a lithium battery as early as the 1960s.[6] Some conducting polymers such as polyaniline and polypyrrole have already been commercialized.[7] However, relative to the application of organic materials in the field of light-emitting diodes (LEDs), photovoltaic (PV) devices, and field-effect transistors (FETs),[8] the development of organic electrode materials for rechargeable lithium batteries lags far behind. In the 1980s and 1990s, there was a search for organic polysulfide cathode materials.[7] However, this research diminished after 2000, because of their poor electrochemical performance and low stability. Recently, researchers have shifted their interest toward organic materials based on the carbonyl group, such as anhydrides and quinones, and achieved significant progress.[2,4,5,9,10]

In recent years, our group has been looking for novel organic cathode materials[10] with a performance comparable to that of conventional inorganic materials. In our opinion, to avoid the unwanted dissolution in the electrolyte and achieve fast kinetic properties, constructing polymer cathodes with a stable, inactive framework, and highly electroactive functional group is key. A small molar mass of the monomer unit and facile preparation are also important factors. On the basis of these principles, a type of known polymers, polyimide (PI), is proposed herein. PI is an important engineering plastic[11,12] with high mechanical strength and excellent thermal stability. Other than being used as a structural material[13,14] or as a skeleton of functional groups,[15,16] its application as an electrode material has rarely been mentioned, possibly because of its insulating characteristics. However, our recent studies show that, like dianhydride,[9] the aromatic imide group can also be electrochemically reduced and oxidized in a reversible manner (Scheme 1).



Scheme 1. Electrochemical redox mechanism of polyimides based on PMDA or NTCDA.

The process can be generalized as enolization and its reverse process of the carbonyl group, which can be promoted by a conjugated structure, either aromatic[9] or aliphatic.[5] When PI is used as the cathode material for rechargeable lithium batteries, its reduction and oxidation are accompanied by the association and disassociation of Li^+ ions with oxygen. Ideally, each formula unit is able to transfer four electrons through two steps (Scheme 1), which may allow a theoretical specific capacity of more than 300 $mAh\,g^{-1}$. To confirm our expectations, we studied five polyimide samples. All of them exhibit electrochemical activity and some of them present promising performance.

Polyimide can be synthesized by simple polycondensation from dianhydride and diamine (Scheme 2).[12] We chose different dianhydrides and diamines as the starting materials, and five typical polyimides were obtained through different paths, which are designated as PI-1 to PI-5 (Table 1). The detailed synthetic process can be found in the Supporting Information.

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[*] Z. Song, Dr. H. Zhan, Prof. Y. Zhou
Department of Chemistry, Wuhan University
Wuhan, Hubei 430072 (P. R. China)
Fax: (+86) 27-6875-4067
E-mail: zhanhui3620@126.com

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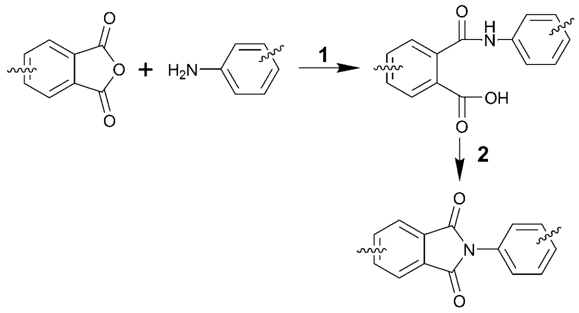
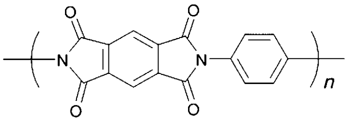
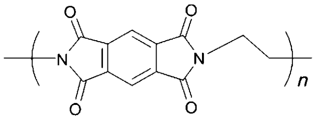
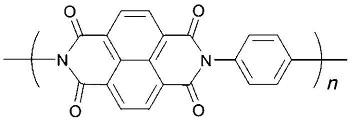
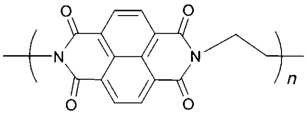
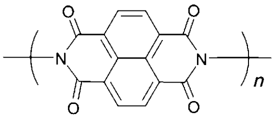


Scheme 2. Typical two-step synthetic route to polyimide: 1) solution polymerization and 2) heat treatment.

Table 1: General description of the five polyimide samples.[a]

Name	Structure	Preparation method	Color	Yield [%]	Theoretical capacity [$mA h g^{-1}$]
PI-1		AD	yellow	99	369.4
PI-2		BC	dark orange	83	442.7
PI-3		BC	light brown	81	315.0
PI-4		AC	brown	86	366.8
PI-5		BC	dark yellow	54	405.8

[a] The preparation methods A, B, C, and D are detailed in the Supporting Information. The theoretical capacity is calculated based on a four-electron transfer redox process for each formula unit.

Our preparation method has been widely used and its feasibility has also been substantially demonstrated.[12] The products were structurally characterized by IR spectroscopy. In general, IR spectra (Figure 1) for PI-1 and PI-2 resemble each other, whereas those for PI-3, PI-4, and PI-5 are similar, reflecting the similarity of their structures. However, for PI-5, the absorption band near 1700 cm^{-1} is quite different from that for PI-3 and PI-4. The characteristic IR bands are assigned in Table 2. The literature values of PI-1[17] were used as a reference for our PI-1 and PI-2 samples. The literature values of another NTCDA-based polyimide M5 (NTCDA = 1,4,5,8-naphthalenetetracarboxylic dianhydride),[15] and the experimental values of our DANTCBI monomer (DANTCBI = *N*,*N'*-diamino-1,4,5,8-naphthalenetetracarboxylic bisimide), whose structure has been already clearly determined by ^{1}H NMR spectroscopy and elemental analysis (see the Supporting Information) were used as references for PI-3, PI-4, and PI-5. We can see that almost all the characteristic absorption bands of the imide group are found in our samples, suggesting the successful synthesis of the target products.

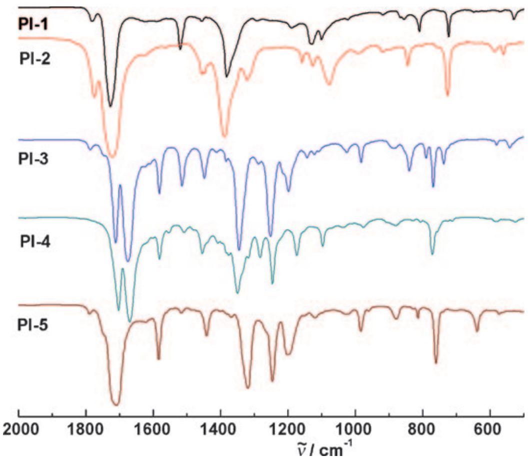


Figure 1. FTIR spectra of the five polyimide samples (KBr pellets).

The electrochemical performance of the five polyimides was tested by using CR2016-type coin cells. In our previous research, poly(anthraquinonyl sulfide) (PAQS) showed an excellent cyclability and rate capability. However, its working voltage of 2.1 V is somewhat low.[10] Therefore, in this study, our first concern was the working voltage of the resulting materials. Figure 2a shows the typical charge/discharge curves of the resulting samples. All the samples show a coulomb efficiency close to 100%, which satisfies the basic requirements for cathode materials. In Figure 2a, the average discharge voltage and the voltage hysteresis between charge and discharge for each polyimide are also listed. Although all the samples give sloping profiles, regular changes in the average discharge voltage still can be observed. For example, PI-1 and PI-2 both show average discharge voltages at around 2.05 V, whereas PI-3 and PI-4 show higher values of about 2.35 V. Among all the samples, PI-5 shows the highest average discharge voltage of 2.50 V. Another rough tendency is that the voltage gap decreases from PI-1 and PI-2 to PI-3, PI-4, and PI-5. As the polyimide-containing NTCDA unit tends to improve the discharge voltage and reduce the voltage gap, we conclude that the voltage profiles of our polyimides are more associated with the dianhydride component than with the diamine component. Among all the samples, PI-5 shows the best electrochemical performance, mainly because of its better conjuga-

Table 2: Characteristic IR band assignments of the five polyimide samples.

Group	PI-1[17]	PI-1	PI-2	DANTCBI	M5[15]	PI-3	PI-4	PI-5
imide C=O, ν_{as}	1780	1782	1774	1700	1712	1716	1703	1709
imide C=O, ν_s	1720	1727	1722	1644	1668	1676	1670	
imide C-N, ν	1380	1382	1388	1367	1348	1345	1350	1319
imide C=O, δ	725	723	726	759		769	771	761
pPDA benzene	1500	1520				1514		
naphthalene				1559	1581	1582	1582	1584
N–N				1103				1120

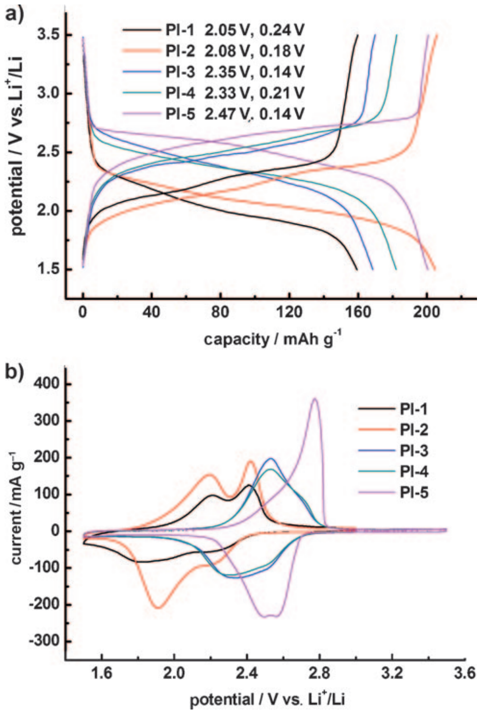
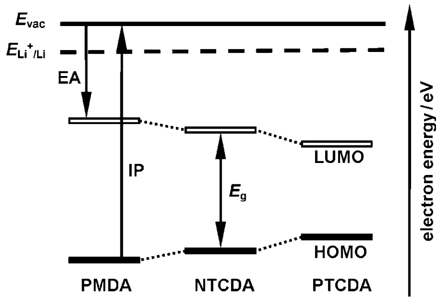


Figure 2. Typical a) voltage profiles and b) CV curves of the five polyimide samples. Conditions: a) cutoff voltage = 1.5–3.5 V, current rate = C/10; 1C = the theoretical capacity supplied in Table 1; b) scan rate = 0.1 mV s^{-1}, cutoff voltage = 1.5–3.0 V for PI-1 and PI-2, cutoff voltage = 1.5–3.5 V for PI-3, PI-4, and PI-5.

tion. These results reveal that the working voltage and the reversibility of these polyimides are acceptable for practical use.

The difference in the electrochemical behavior of these polyimide samples also can be explained from a theoretical view. Organic cathode materials are usually good electron acceptors. We can use electron affinity (EA) to represent their electron-accepting ability. According to molecular orbital theory, a lower LUMO energy means a larger EA and better oxidizability, and thus higher reduction potential. Correspondingly, a higher HOMO energy means a smaller ionization potential (IP) and better reducibility. In addition, the LUMO–HOMO gap, usually represented by E_g, is related to the electronic conduction. The EA and IP values of a series of dianhydrides calculated by Andrzejak et al. by a DFT method[18] can be used for a qualitative comparison of the energy level of PMDA, NTCDA, and PTCDA (Scheme 3; PMDA = pyromellitic dianhydride; PTCDA = 3,4,9,10-perylenetetracarboxylic dianhydride). The EA value becomes larger from PMDA to NTCDA and then PTCDA, whereas the IP value changes in the reverse order. According to the fact that the final polyimide tends to retain the redox activity of the dianhydride precursor, larger EA values of the adopted dianhydride precursor may in turn lead to better oxidizability of the polyimide derivatives. Therefore, the increased average discharge voltage of PI-3, PI-4, and PI-5 is reasonable. In contrast, the decreasing value of E_g from PMDA to PTCDA is accompanied by an increased electronic conduction reducing the polarization of the latter. This is why polyimides containing a NTCDA moiety show better redox reversibility than those containing PMDA. Based on this analogy, we can predict that a PTCDA precursor may lead to the best performance, disregarding the difficulty of preparation and reduced theoretical capacity.



Scheme 3. Energy level diagram for the three dianhydrides. E_{vac} = electron energy level in vacuum.

Another point that needs to be considered is the experimental capacity of the polyimides. According to the redox mechanism shown in Scheme 1, ideally, each formula unit will transfer two electrons in each step. Since two steps are involved, at least two charge/discharge plateaus should appear in the charge/discharge profile. However, the experimental results do not support this reaction mode. In Figure 2 a, the capacity delivered from the polyimides within 1.5–3.5 V is approximately half of the theoretical value shown in Table 1, suggesting that only two-electron transfer is involved. The difference between the theoretical and experimental mode can be explained by the molecular structure of these polymers. The electrochemical reduction with four-electron transfer can be obtained by a deep discharging to below 1.5 V. Unfortunately, this deep discharge process is accompanied by serious structural damage, such as the collapse of the polymer framework and inactivation of the polymer. A similar result was also reported by Han et al.[9] This process is possibly caused by the repulsion between injected negative charges in the conjugated dianhydride unit.

Figure 2b shows the cyclic voltammetry (CV) results of the five polyimide samples. The results are quite consistent with the charge/discharge profiles. That is, PI-1 and PI-2 show similar peak potentials, whereas the CV profiles of PI-3 and PI-4 almost coincide with each other. Compared with those of PI-1 and PI-2, the redox peaks of PI-3 and PI-4 shift to a more positive potential and become sharper. Among all the polyimide samples, PI-5 shows the highest redox potential and narrowest peak. From the CV profiles it is clear that all the redox processes consist of two continuous steps, which are possibly associated with the formation of the radical anion (I^-) and then the dianion (I^{2-}), respectively, in a similar manner as that for quinone.[10] A previous study on NTCDA,[19] one of our dianhydride precursors, confirms its multistep reversible reduction process, as well as the much lower reduction potential of the third step generating the radical trianion (I^{3-}). From Figure 2b, it is noted that two pairs of well-resolved redox peaks appear above 1.5 V for PI-1 and PI-2. However, for other polyimides derived from NTCDA, we cannot clearly distinguish the two pairs of redox peaks because of the fast transformation between the radical anion and dianion, which has also been observed on PAQS.[10]

Figure 3a compares the cycling performances of the samples. The PMDA-based PI-1 and PI-2 samples show a large capacity loss (ca. 5 and 8 mA h g^{-1}, respectively) between the first and the second cycle, and continuous capacity fading in the following cycles. The capacities of the NTCDA-based PI-3 and PI-4 samples become stable within the first few cycles and then remain almost constant in subsequent cycling. The capacity of PI-5 gradually decreases with cycle number, and moderate cycling stability was observed. There seems to be some relationship between the cycling behavior and the structure of the dianhydride precursor, and we are still investigating this phenomenon.

As well as cyclability, rate capability is another important factor that needs to be considered when constructing cathode materials for lithium batteries, especially for organic materials, which have suffered from slow reaction kinetics in previous studies.[7] The rate performance of our polyimides was tested under different current rates of C/20, C/10, C/5, and C/2. Figures 3b–d show the results of three typical samples of PI-2, PI-4, and PI-5; samples of PI-1 and PI-3 are not displayed since their performance is very similar to that of PI-2 and PI-4, respectively. Usually, higher current rate results in larger polarization and smaller capacity. Within the potential range 1.5–3.5 V, PI-2 shows greatly increased polarization and serious capacity degradation at C/2 (not shown). PI-4 and PI-5 show much better rate capability. Their capacity retentions are both more than 90% even though the current rate increases from C/20 to C/2. It is also noticeable in Figures 3b–d that the cycling stability seems to be improved at the higher current rate of C/5. After tens of cycles, the capacity at a rate of C/5 even exceeds that at C/20.

The electrochemical parameters of all the resulting samples are collected in Table 3. PI-4 and PI-5 show the best performance among the five PI samples. PI-4 shows the best cyclability and PI-5 shows the highest energy density, comparable to that of $LiCoO_2$. It can be generalized that the polyimide derived from NTCDA has a better performance, which should be explained by its better conjugation and lower LUMO energy level. The capacity data in Table 3 also verify our opinion about the two-electron transfer in a practical redox process. Therefore, it is hard to improve the capacity of analogous polyimides by a large margin. However, if we can improve the cyclability of PI-5 to the level of PI-4, it will still be a great achievement. Another strategy is to use another dianhydride containing an electron-withdrawing group, such as cyano,[20] as the precursor, which can lower the LUMO energy of the final polyimide product and make it more reducible, and thus the reduction voltage and energy density can both be boosted.

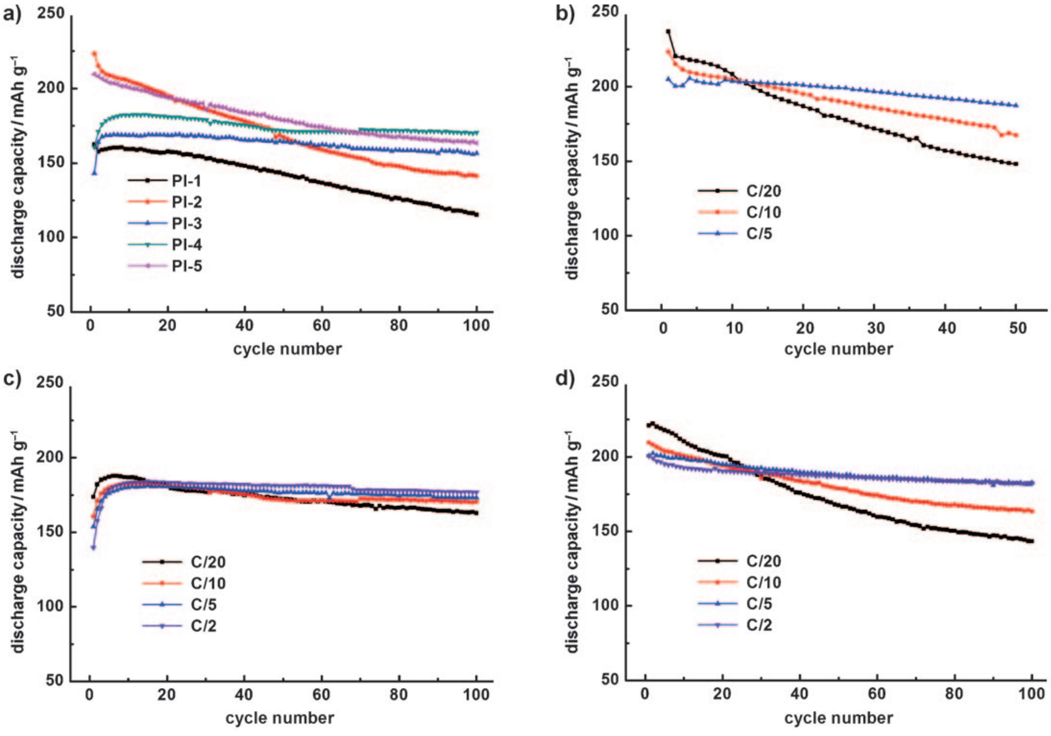


Figure 3. Cycling performance of a) the five polyimide samples under C/10, and b) PI-2, c) PI-4, d) PI-5 under different current rates. In (b), the cycling capacity within 50 cycles is given because of the poor cyclabilty of the PI-2 sample.

In conclusion, we propose the use of polyimides as cathode

Table 3: Electrochemical parameters of the five polyimide samples.

Sample	Theoretical capacity [mAh g^{-1}]	Average discharge voltage [V]	Practical capacity [mAh g^{-1}]		
			C/20		C/5
			max	max	100th cycle
PI-1	369	2.05	181	155	129
PI-2	443	2.08	237	206	171
PI-3	315	2.35	170	163	156
PI-4	367	2.33	188	181	173
PI-5	406	2.47	222	202	183

materials for rechargeable lithium batteries for the first time. Although they are regarded as insulators, the five polyimide samples are all electrochemically active; they all benefit from the good reaction reversibility of the imide group and the stable polymer framework. The two-electron transfer of each monomer unit results in a specific discharge capacity of around 200 mAh g^{-1}, a discharge voltage of 2.0–2.5 V, and a coulomb efficiency close to 100%. Moreover, the intrinsic stability and insolubility of the polyimide ensures that it is not dissolved in the electrolyte, and thus allows cyclability. The use of polyimide is also considered safe because of its excellent thermal stability and nonflammability.[12] Since polyimide is hydrolyzable under specified conditions, it is environmentally friendly and conforms to the requirements of a "green battery". PI has a totally different structure (based on anhydride) than previously reported organic cathode materials such as PAQS.[10] It shows many advantages over PAQS in terms of higher working voltage, higher capacity, and higher energy density. PI also enables better regulation of the electrochemical properties through modifying the molecular structure. Moreover, PI is much easier to mass-produce because of its facile preparation and low cost.

However, several problems remain unresolved. For example, although the PI cathode itself is quite safe and stable, it has to be combined with a lithium metal anode, which raises concerns regarding the reliability or safety of the whole battery. This will possibly be solved by recent advances in electrolyte additive or lithium protection, such as those reported for the Li/S system.[21] Besides, the development of lithium-containing anodes, such as lithium nitride,[22] may enable us to avoid using metallic lithium anodes. The electrochemical performance of PI also needs to be further improved, which may be achieved by optimizing the preparation conditions or molecular structure.

Experimental Section

CR2016-type coin cells consisting of the cathode composite and lithium foil anode separated by a Celgard 2400 membrane were used for cycling tests. The cathode contained 60 wt% polyimide, 30 wt% conductive carbon (Printex XE2), and 10 wt% polytetrafluoroethylene (PTFE) binder. The electrolyte was 1 M $LiN(CF_3SO_2)_2$ (LiTFSI) solution in a mixed solvent of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (2:1 w/w). The cells were assembled in an argon-filled MB200B glove box (M. Braun GmbH, Germany). The charge/discharge experiments were performed on a LAND battery test system (China) in the potential range 1.5–3.5 V using different current rates. CV measurements were conducted on a three-electrode cell on a CHI660A electrochemical workstation (CH Instruments Inc., USA). The working electrode had the same composition as mentioned above; lithium foil acted as both the reference and counter electrode. Scanning parameters are specified in the text. All the electrochemical tests were performed at room temperature.

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[1] M. Armand, J.-M. Tarascon, *Nature* **2008**, *451*, 652–657.
[2] H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot, J.-M. Tarascon, *ChemSusChem* **2008**, *1*, 348–355.
[3] J.-M. Tarascon, *ChemSusChem* **2008**, *1*, 777–779.
[4] H. Chen, M. Armand, M. Courty, M. Jiang, C. P. Grey, F. Dolhem, J.-M. Tarascon, P. Poizot, *J. Am. Chem. Soc.* **2009**, *131*, 8984–8988.
[5] M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribière, P. Poizot, J.-M. Tarascon, *Nat. Mater.* **2009**, *8*, 120–125.
[6] D. L. Williams, J. J. Byrne, J. S. Driscoll, *J. Electrochem. Soc.* **1969**, *116*, 2–4.
[7] P. Novák, K. Müller, K. S. V. Santhanam, O. Haas, *Chem. Rev.* **1997**, *97*, 207–281.
[8] Y. Shirota, H. Kageyama, *Chem. Rev.* **2007**, *107*, 953–1010.
[9] X. Han, C. Chang, L. Yuan, T. Sun, J. Sun, *Adv. Mater.* **2007**, *19*, 1616–1621.
[10] Z. Song, H. Zhan, Y. Zhou, *Chem. Commun.* **2009**, 448–450.
[11] C. E. Sroog, *J. Polym. Sci. Part C* **1967**, *16*, 1191–1209.
[12] M. K. Ghosh, K. L. Mittal, *Polyimides: fundamentals and applications*, Marcel Dekker, New York, **1996**.
[13] T. Agag, T. Koga, T. Takeichi, *Polymer* **2001**, *42*, 3399–3408.
[14] Z. Ahmad, J. E. Mark, *Chem. Mater.* **2001**, *13*, 3320–3330.
[15] Y. Yin, O. Yamada, K. Tanaka, K.-I. Okamoto, *Polym. J.* **2006**, *38*, 197–219.
[16] N. Asano, M. Aoki, S. Suzuki, K. Miyatake, H. Uchida, M. Watanabe, *J. Am. Chem. Soc.* **2006**, *128*, 1762–1769.
[17] Y. Iinuma, K. Kishimoto, Y. Sagara, M. Yoshio, T. Mukai, I. Kobayashi, H. Ohno, T. Kato, *Macromolecules* **2007**, *40*, 4874–4878.
[18] M. Andrzejak, G. Mazur, P. Petelenz, *J. Mol. Struct.* **2000**, *527*, 91–102.
[19] C. De Luca, C. Giomini, L. Rampazzo, *J. Electroanal. Chem.* **1990**, *280*, 145–157.
[20] S. Chopin, F. Chaignon, E. Blart, F. Odobel, *J. Mater. Chem.* **2007**, *17*, 4139–4146.
[21] D. Aurbach, E. Pollak, R. Elazari, G. Salitra, C. S. Kelley, J. Affinito, *J. Electrochem. Soc.* **2009**, *156*, A694–A702.
[22] D. H. Gregory, *Chem. Rec.* **2008**, *8*, 229–239.