Angewandte
Zuschriften

Lithium batteries

DOI: 10.1002/ange.201302586

Quasi-Solid-State Rechargeable Lithium-Ion Batteries with a Calix[4]quinone Cathode and Gel Polymer Electrolyte**

*Weiwei Huang, Zhiqiang Zhu, Lijiang Wang, Shiwen Wang, Hao Li, Zhanliang Tao, Jifu Shi, Lunhui Guan, and Jun Chen**

Rechargeable lithium-ion batteries (LIBs), which are currently based on the exchange of Li/Li$^+$ between a graphite (Li$_x$C$_6$) anode and an inorganic lithium-transition-metal-oxide cathode, have been widely used in portable electronics.[1] However, the further application of LIBs in the areas of large-capacity and high-power electronics, electrical vehicles, and smart grids is still limited. Critical issues are the low capacity, low energy/power density, short life, high cost, and low safety of the batteries. Among various strategies, one interesting approach is to find redox-active organic materials with high capacities and low cost.[2] Recently, carbonyl organic compounds, such as $Li_2C_2O_6$ ($C_{theo} = 589\ mA\,h\,g^{-1}$) and pyrene-4,5,9,10-tetraone ($C_{theo} = 409\ mA\,h\,g^{-1}$) have been considered as promising materials for the cathode of LIBs primarily owing to their high theoretical gravimetric capacities.[2b,3] However, the electrochemical performance of those materials as the cathode of LIBs was always poor because they suffer from severe solubility in liquid organic electrolyte. As an attempt to solve this problem, it is found that grafting a soluble active "monomer" organic molecule to an insoluble inactive substrate, such as SiO$_2$ helps.[4] However, the tested molecule, which is a quinone derivative of calix[4]arene, only has a low theoretical capacity (189 mA h g^{-1}). Moreover, since the ion conduction and transport in electrolyte is so important in electrochemical energy conversion and storage,[5] the solubility problem of organic materials in electrolyte has been effectively mitigated by accommodating soluble quinonic cathode materials in quasi-solid-state cells.[6] For example, a capacity exceeding 200 mA h g^{-1} with excellent cyclability has been obtained for tetracyanoquinodimethane (TCNQ)-based all-solid-state cells with a silica room-temperature ionic liquid (RTIL) composite quasi-solid electrolyte.[6a] More recently, by using the same electrolyte, a capacity of approximately 300 mA h g^{-1} with a power density of 540 W h kg^{-1} has been achieved by 2,5-dihydroxy benzoquinone (DHBQ)-based solid-state cells.[6b]

Wright's group discovered the ionic conductivity of poly(ethylene oxide) (PEO) doped with alkali-metal salt complexes in 1973.[7] Armand and co-workers studied polymer electrolyte used for solid-state electrochemical devices a few years later.[8] Although this system offers very low ionic conductivity (ca. $10^{-8}\ S\,cm^{-1}$ at room temperature),[9] it stimulated the study of gel polymer electrolyte (GPE), which displays a much higher conductivity through the introduction of an organic aprotic dipolar solvent into the polymer matrix. To date, a series of polymer hosts, such as PEO, poly(propylene oxide) (PPO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVdF), and poly(vinylidene fluoride hexafluoro propylene) (PVdF-HFP) have been developed.[10] Among various polymer matrices, PEO-based polymers are the most thoroughly studied because the CH$_2$CH$_2$O unit in the PEO chain has a good solvating ability with respect to Li$^+$ ions and the polymer chain segments are highly mobile.[9,11] As a low-molecular weight polyether, poly(ethylene glycol) (PEG) which offers similar advantages has been investigated in LIBs.[12] Our group reported a poly(methacrylate) (PMA)/PEG-based GPE as the electrolyte of dye-sensitized solar cells (DSSCs), which shows satisfactory ionic conductivity that is benefited from its ability of entrapping large numbers of liquid electrolyte.[13] The question arises how about PMA/PEG-based GPE as the electrolyte of organic LIBs when using a traditional LIB electrolyte, such as LiClO$_4$ in dimethyl sulfoxide (DMSO) to replace the DSSCs liquid electrolyte, such as LiI and I$_2$, in a mixed solution of ethylene carbonate (EC) and propylene carbonate (PC)). Herein, we report the extension of a PMA/PEG-based GPE loading LiClO$_4$ in DMSO for organic LIBs using a high capacity carbonyl compound calix[4]quinone ($C_{28}H_{16}O_8$, C4Q, $C_{theo} = 446\ mA\,h\,g^{-1}$) as the cathode with desirable electrochemical performance (a capacity of ca. 380 mA h g^{-1} has been maintained after 100 cycles at 0.2C charge/discharge rate).

Figure 1 a shows the fabrication process of the PMA/PEG-based GPE. The synthesis details are described in the Experimental Section. Figure 1 b,c show photographs of the as-prepared PAM/PEG hybrid and PMA/PEG-based GPE with LiClO$_4$/DMSO loading, both are a homogeneous semi-

---

[*] Dr. W. Huang,[+] Dr. Z. Zhu,[+] Dr. L. Wang, Dr. S. Wang, H. Li, Prof. Dr. Z. Tao, Prof. Dr. J. Chen
Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry; Synergetic Innovation Center of Chemical Science and Engineering, Nankai University
Tianjin 300071 (China)
E-mail: chenabc@nankai.edu.cn
Prof. Dr. J. Shi
Key Lab Renewable Energy & Gas Hydrate, Inst Energy Convers, Chinese Academy of Sciences
Guangzhou 510640 (China)
Prof. Dr. L. Guan
State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter Chinese Academy of Sciences
Fujian 350002 (China)

[+] These authors contributed equally to this work.

[**] This work was supported by Programs of National 973 (2011CB935900), NSFC (21231005), and 111 Project (B12015).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302586.

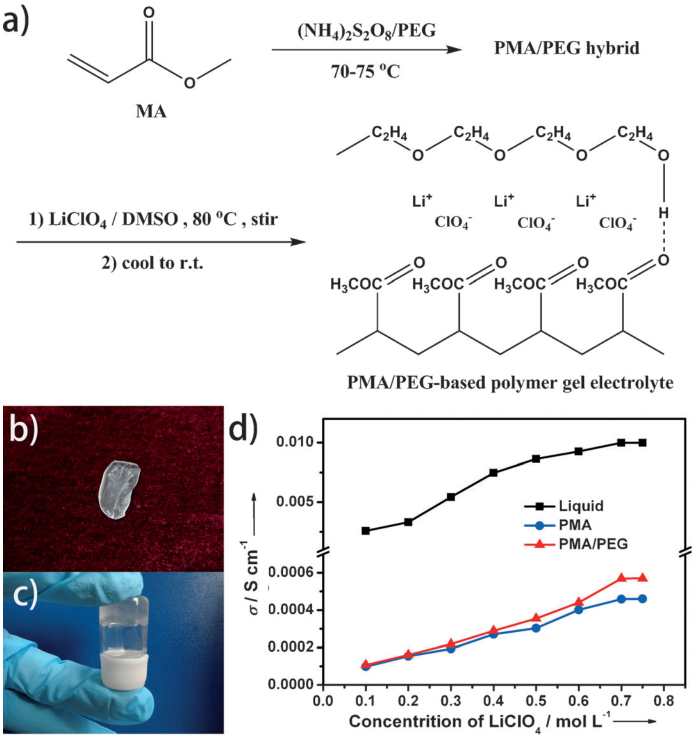
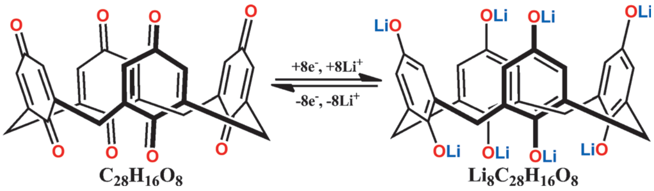


Figure 1. a) Illustration of the preparation process of the PMA/PEG-based gel polymer loading $LiClO_4$/DMSO electrolyte. Photographs of b) a PMA/PEG hybrid and c) a PMA/PEG-based gel polymer loading $LiClO_4$/DMSO electrolyte in the inverted glass bottle bottom. d) Effect of the $LiClO_4$ concentration on the ionic conductivity of the liquid and gel polymer electrolyte.

transparent motionless mixture. Figure 1d shows the variation of ionic conductivity of PMA/PEG-based electrolyte as a function of the concentration of $LiClO_4$ in DMSO at room temperature. For comparison, the ionic conductivities of the liquid electrolyte and PMA-based GPE have also been tested. It is clearly seen that the presence of PEG can enhance the conductivity of the GPE through its ability to act as an absorbent of the liquid electrolyte.[13] Although the conductivity of the gel electrolyte (10^{-4}–0.57×10^{-3} S cm^{-1}) is about 20-fold lower than that of the liquid electrolyte, it is still acceptable for the basic requirement of LIBs (on the order of 10^{-3} S cm^{-1} at room temperature).[14] The conductivity of the liquid and quasi-solid-state electrolyte increases with increasing the concentration of $LiClO_4$, because the higher salt concentration results in more charge carriers. When the concentration of $LiClO_4$ reaches 0.7 mol L^{-1}, the conductivity nearly attains the maximum value. Among the GPEs investigated, the PMA/PEG-based hybrid loading with a liquid electrolyte of 0.7 mol L^{-1} $LiClO_4$ in DMSO solution gives the highest ionic conductivity of 0.57×10^{-3} S cm^{-1}. Therefore, it has been used as the electrolyte for quasi-solid-state lithium cells.

Why choose calix[4]quinone as the active material of the cathode of LIBs? Although high theoretical gravimetric capacities of carbonyl compounds could be obtained by the combination of large number of carbonyl groups and a low molecular weight, the practical capacity is always low because of the low utilization of the available active sites.[3a,b] Over the past few years, much attention has been focused on calixarenes because of their ability to bind ions or molecules into their cavities.[15] However, the quinone derivatives of calixarenes could be more appealing owing to the oxidative properties of the quinone moieties.[2c,16] We note that a calixarene derivative, calix[4]quinone, which bears four quinone units, has a large theoretical capacity of 446 mA h g^{-1}. More importantly, as the molecular macrocyclic C4Q is composed of a cyclic array of *p*-quinone linked by a methylene groups, the carbonyl groups are not sterically encumbered, and are thus available to take up the full quota of 8 Li (Scheme 1). Hence, C4Q has been chosen as the cathode material of LIBs.

The target molecule C4Q was obtained from calix[4]arene (commercially available) through three steps: diazocoupling reaction, reduction, and oxidation (Scheme S1, see Supporting Information).[17] Elemental analysis, infrared spectrum (Figure S1), NMR (Figure S2), and mass spectra (Figure S3) were used to characterize the as-prepared C4Q, which was in the form of pale yellow powders and lamellar morphology (Figure S4). The full utilization of carbonyl groups is shown by the electrochemical measurement of C4Q cathode for LIBs either in liquid electrolyte (1 M $LiPF_6$ in a mixed solvent of EC and dimethyl carbonate (DMC) (1:1 in volume); Figure S5) or in the as-prepared PMA/PEG-based GPE with $LiClO_4$/DMSO loading (Figure 2). As shown in Figure S5, the C4Q cathode in the liquid electrolyte delivered an initial capacity of 431 mA h g^{-1} (96.6 % of the theoretical capacity) at 0.2C, but only preserved approximately 100 mA h g^{-1} after five cycles owing to C4Q dissolution, as demonstrated by UV/Vis absorption spectra (Figure S6).



Scheme 1. Molecular formula and proposed electrochemical redox reactions of $C_{28}H_{16}O_8$ (C4Q) to give $Li_8C_{28}H_{16}O_8$, showing a theoretical capacity of 446 mA h g^{-1}.

Figure 2 shows the electrochemical performance of the C4Q cathode in PMA/PEG-based GPE. Figure 2a shows the cyclic voltammogram (CV) curves of C4Q electrode between 1.5 and 3.5 V at a scan rate of 0.1 mV s^{-1}. A reduction peak at around 2.78 V with a broad shoulder at 2.41 V is assigned to the reduction of the carbonyl groups. A broad oxidation peak at about 3.01 V corresponds to the re-oxidation of the alkoxide groups. This value is close to the computational result (2.903 V; Computational details in Supporting Information, Table S1–S4 and Figure S7). Careful observing of the CV curves shows that the broad redox peak contains over-

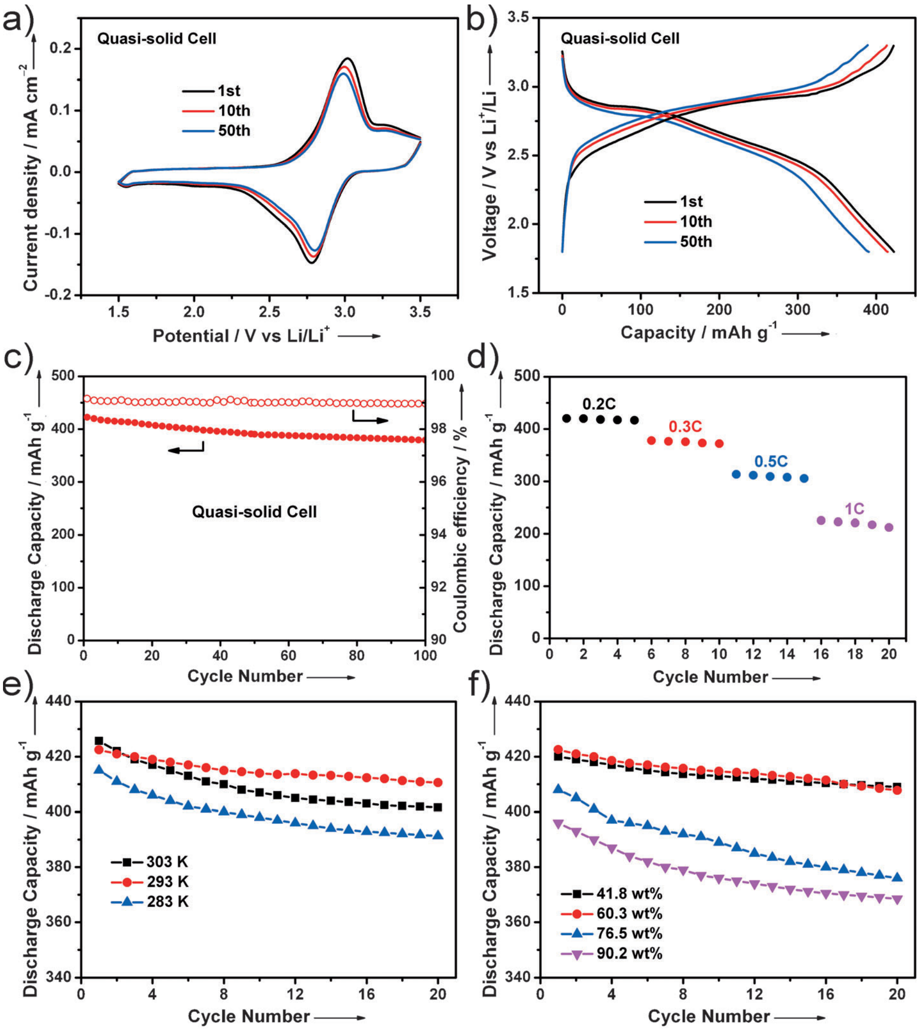


Figure 2. The electrochemical performance of the quasi-solid-state cells with the C4Q cathode in PMA/PEG-based GPE with $LiClO_4$/DMSO loading: a) the (1st, 10th, 50th) cyclic voltammetry profiles at a scan rate of 0.1 mV s^{-1}; b) the initial three discharge–charge profiles at 0.2C rate; c) the cycling performance between 1.8 V and 3.3 V at 0.2C rate; d) 0.2C to 1C rate capability; e) the cycling performance of the cathode at 0.2C containing 60 wt % C4Q at the temperatures of 303 K, 293 K, and 283 K; f) the cycling performance of the cathode at 303 K with C4Q content of 41.8 wt %, 60.3 wt %, 76.5 wt % and 90.2 wt %.

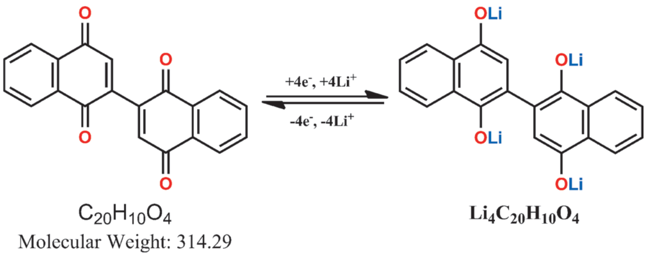
lapping peaks, which might be related to the multi-step reaction processes. In addition, all the CV peak potentials stayed almost unchanged during cycling, suggesting that all the redox reactions were reversible. Furthermore, the nearly unchanged peak current intensity upon cycling implies the outstanding cycling stability of the quasi-solid-state cells. Figure 2b shows the typical discharge/charge curves of the quasi-solid-state cell cycled at 0.2C rate. The discharge curve presents two sloping plateaus at about 2.55 and 2.85 V, which are basically tallying with the CV and computation results. The quasi-solid-state cells showed an initial discharge capacity of 422 mA h g^{-1} (Figure 2b), 89.8 % of which has been maintained after 100 cycles (Figure 2c). The maintained capacity of 379 mA h g^{-1} is more than two-times that of commonly used inorganic $LiCoO_2$ or $LiFePO_4$ cathodes. For carbonyl compounds, this is the second-highest capacity, which is next to that of $Li_2C_6O_6$ with an initial capacity of 580 mA h g^{-1} at an average potential of 2.2 V.[2b] It is noted that $Li_2C_6O_6$ exhibited a rapid capacity fading in liquid electrolyte (a capacity lower than 300 mA h g^{-1} was maintained after 14 cycles). The slow capacity decay of the present quasi-solid-state cells means that the gel polymer electrolyte delays the dissolution of C4Q for a certain time. In addition, the Coulombic efficiency is close to 99 % during the whole cycling test, which is important for practical use. The rate performance of the quasi-solid cells has also been tested (Figure 2d). Although the reversible capacity falls relatively fast with the increasing of the discharge/charge rate, it still delivers a capacity of approximately 220 mA h g^{-1} at a rate of 1C. This high capacity and reversibility of the quasi-solid-state cells with C4Q cathode shows a wide application potential.

To further characterize the quasi-solid-state cells, the effect of either the working temperature or the active C4Q content on the electrode properties was investigated. Figure 2e displays the cycling performance of the cathode containing 60 wt % C4Q at the changed temperatures (303 K, 293 K, and 283 K). After 20 cycles, the capacities were 391, 411, and 401 mA h g^{-1} at 283, 293, and 303 K with corresponding capacity retention of 94.2 %, 97.4 % and 94.1 %, respectively. This result illustrates that in the tested temperature range, high temperature would induce an enhancement in the capacity at the expense of the cyclability, which is consistent with an early report.[5a] However, all cells maintain nearly 94 % of their initial capacity after 20 cycles. This preliminary study verifies the reasonable cyclability of the quasi-solid-sate cells.

In general, on account of the low intrinsic electrical conductivity, organic cathode materials need much more conductive additive (e.g., more than 40 wt % carbon black) than that of commonly used inorganic electrode materials. This is at the expense of the energy density of the electrode. Thus the composition of the electrode is another key parameter governing practical applications. As a further study, cathodes containing different amounts of the C4Q active materials (41.8 wt %, 60.3 wt %, 76.5 wt %, and 90.2 wt %) were assembled into cells and tested at 0.2C and 293 K. As shown in Figure 2 f, the electrode containing

60.3 wt % C4Q displays comparable capacity and cycling stability to the electrode containing 41.8 wt % C4Q. This shows that cathodes with a C4Q content of 41.8 wt % to 60.3 wt % possesses satisfactory electrode performance. Unfortunately, when further increasing the content of C4Q (76.5 wt % and 90.2 wt %), both capacity and cyclability decreased. After 20 cycles, the capacities of the two cathodes were 376 mA h g^{-1} and 368 mA h g^{-1}, respectively. It is noteworthy that even for the electrode containing 90.2 wt % C4Q, 93 % of the initial capacity remained after 20 cycles. This superior performance of the electrode is ascribed to the favorable electronic conductivity support (ca. 2.57 S cm^{-1}) constructed by carbon black spheres, single-walled carbon nanotubes, and PVdF binder (Figure S8).

To demonstrate the stabilization effect of PMA/PEG-based GPE with $LiClO_4$/DMSO loading as the electrolyte, another organic molecular 2,2′-bi(1,4-naphthoquinone) (BNQ) has been tested (Scheme 2). The cycling performance of the liquid and quasi-solid cells is shown in Figure S9. The two cells deliver a similar initial capacity of around 330 mA h g^{-1}, which is about 96.8 % of the theoretical capacity (341 mA h g^{-1}). However, after 30 cycles, the capacities for the liquid and quasi-solid cells are 163 and 322 mA h g^{-1}, respectively. This result further confirms that the design and application of PMA/PEG-based GPE can be applied to other soluble carbonyl compounds. More in-depth and optimization research is in progress.



Scheme 2. Structures and proposed electrochemical redox reactions of $C_{20}H_{10}O_4$ (BNQ) to $Li_4C_{20}H_{10}O_4$, corresponding to a theoretical capacity of 341 mA h g^{-1}.

In summary, quasi-solid-state organic LIBs with high capacity and good cyclability have been designed by using a $C_{28}H_{16}O_8$ (C4Q) cathode and a PMA/PEG-based GPE with $LiClO_4$/DMSO loading. The quasi-solid-state cells with a cathode containing 62 wt % C4Q exhibited an initial discharge capacity of 422 mA h g^{-1} with an average potential of 2.64 V. Moreover, 379 mA h g^{-1} remained after 100 cycles at 0.2C charge–discharge rate. Further investigation verified that the PMA/PEG-based GPE was suitable for other organic compounds, such as $C_{20}H_{10}O_4$ (BNQ). These results could widen the application potential of LIBs employing organic carbonyl compounds with multi-electron reactions as high capacity cathodes and PMA/PEG-based gel polymer loading $LiClO_4$/DMSO as quasi-solid-state electrolytes.

Experimental Section

The target molecular calix[4]quinone ($C_{28}H_{16}O_8$) was synthesized from the purchased material calix[4]arene ($C_{28}H_{24}O_4$) (Sigma-Aldrich) in three steps: diazocoupling reaction, reduction, and oxidation[11] (Scheme S1, see experimental details in Supporting Information). Elemental analysis, IR (Figure S1), NMR (Figure S2) and MS (Figure S3) spectra were used to characterize the structure of the as-synthesized calix[4]quinone which was in the form of pale yellow powders. 2,2′-bi(1,4-naphthoquinone) (BNQ) was synthesized according previous reports.[18,19]

In a typical preparation of poly(methyl acrylate)/poly(ethylene glycol) (PMA/PEG)-based gel polymer electrolyte, ammonium persulfate (polymerization initiator, 1 wt % methyl acrylate) was dissolved in PEG-600 (4 g) at room temperature.[12] Then, the mixture was added to distilled methyl acrylate (7.26 g) under vigorous stirring at 70 °C under a nitrogen atmosphere. After polymerization, a homogeneous mixture was formed. The content of PEG in this hybrid is 35 wt % [PMA/PEG (65/35)]. Predetermined amounts of $LiClO_4$ solution were dissolved in DMSO. After that, 27 wt % PMA/PEG (65/35) hybrid was added into the $LiClO_4$ solution. Finally, the resulting mixture was heated at 80 °C under vigorous stirring until no solid was observed. After allowing to cool to room temperature, a uniform motionless gel polymer electrolyte was obtained. The ionic conductivity of the as-prepared GPE was measured with a Parstat 2273 potentiostat/galvanostat analyzer (Princeton Applied Research & AMETEK Company) over a frequency range of 10 Hz–100 kHz at room temperature.

Electrode properties were evaluated using CR2032 coin-type cells. The cathode was composed of a mixture of 62 wt % of active material ($C_{28}H_{16}O_8$), 30 wt % of porous carbon black spheres (40 nm, 320 $m^2 g^{-1}$, 0.36 Ω cm), 3 wt % single-walled carbon nanotubes,[20] 5 wt % of polyvinylidene fluoride (PVdF) binder. The mixture was suspended in *N*-methyl-2-pyrrolidinone (NMP) to form a slurry, which was coated on an aluminum foil using a doctor blade. The electrode was dried in vacuum at 80 °C overnight to remove NMP. Lithium foil and Celgard 2300 porous membrane were used as the counter electrode and separator, respectively. The PMA/PEG-based gel polymer electrolyte with $LiClO_4$/DMSO loading was used. All the cell assembly procedures were conducted in an argon-filled glove box with moisture content and oxygen level below 1 ppm. The cyclic voltammograms (CV) were performed on a Parstat 263 A electrochemical workstation (AMTECT Company). The charge–discharge experiments were carried out with a LAND battery testing system. The specific capacity was calculated on the basis of the amount of the active material, excluding the mass of the carbon and PVDF.

Received: March 28, 2013
Revised: May 27, 2013

Keywords: calix[4]quinone · cathode · lithium batteries · quasi-solid-state electrolyte

---

[1] a) M. Armand, J. M. Tarascon, *Nature* **2008**, *451*, 652–657; b) P. G. Bruce, B. Scrosati, J.-M. Tarascon, *Angew. Chem.* **2008**, *120*, 2972–2989; *Angew. Chem. Int. Ed.* **2008**, *47*, 2930–2946.

[2] a) M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribiere, P. Poizot, J. M. Tarascon, *Nat. Mater.* **2009**, *8*, 120–125; b) H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot, J. M. Tarascon, *ChemSusChem* **2008**, *1*, 348–355; c) Y. Liang, Z. Tao, J. Chen, *Adv. Energy Mater.* **2012**, *2*, 742–769.

[3] a) Y. Liang, P. Zhang, J. Chen, *Chem. Sci.* **2013**, *4*, 1330; b) Y. Liang, P. Zhang, S. Yang, Z. Tao, J. Chen, *Adv. Energy Mater.* **2013**, *3*, 600–605; c) Z. Song, H. Zhan, Y. Zhou, *Angew. Chem.* **2010**, *122*, 8622–8626; *Angew. Chem. Int. Ed.* **2010**, *49*, 8444–

8448; d) X. Han, C. Chang, L. Yuan, T. Sun, J. Sun, *Adv. Mater.* **2007**, *19*, 1616 – 1621.

[4] B. Genorio, K. Pirnat, R. Cerc-Korosec, R. Dominko, M. Gaberscek, *Angew. Chem.* **2010**, *122*, 7380 – 7382; *Angew. Chem. Int. Ed.* **2010**, *49*, 7222 – 7224.

[5] a) B. Scrosati, F. Croce, G. B. Appetecchi, L. Persi, *Nature* **1998**, *394*, 456 – 458; b) N. Sata, K. Eberman, K. Eberl, J. Maier, *Nature* **2000**, *408*, 946 – 949; c) K. Xu, *Chem. Rev.* **2004**, *104*, 4303 – 4418; d) A. S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, W. van Schalkwijk, *Nat. Mater.* **2005**, *4*, 366 – 377; e) J. Maier, *Nat. Mater.* **2005**, *4*, 805 – 815.

[6] a) Y. Hanyu, I. Honma, *Sci. Rep.* **2012**, *2*, 453; b) Y. Hanyu, Y. Ganbe, I. Honma, *J. Power Sources* **2013**, *221*, 186 – 190.

[7] D. E. Fenton, J. M. Parker, P. V. Wright, *Polymer* **1973**, *14*, 589.

[8] M. B. Armand, J. M. Chabagno, M. Duclot, in The Second International Meeting on Solid Electrolytes (Extended Abstracts), St. Andrews, Scotland, **1978**, p. 6.

[9] Y. V. Baskakova, O. g. V. Yarmolenko, O. N. Efimov, *Russ. Chem. Rev.* **2012**, *81*, 367 – 380.

[10] a) J. Y. Song, Y. Y. Wang, C. C. Wan, *J. Power Sources* **1999**, *77*, 183 – 197; b) A. Manuel Stephan, *Eur. Polym. J.* **2006**, *42*, 21 – 42.

[11] E. Quartarone, *Solid State Ionics* **1998**, *110*, 1 – 14.

[12] a) W. Wieczorek, P. Lipka, G. Żukowska, H. Wyciślik, *J. Phys. Chem. B* **1998**, *102*, 6968 – 6974; b) M. Marcinek, A. Bac, P. Lipka, A. Zalewska, G. Żukowska, R. Borkowska, W. Wieczorek, *J. Phys. Chem. B* **2000**, *104*, 11088 – 11093.

[13] J. Shi, S. Peng, J. Pei, Y. Liang, F. Cheng, J. Chen, *ACS Appl. Mater. Interfaces* **2009**, *1*, 944 – 950.

[14] E. Quartarone, P. Mustarelli, *Chem. Soc. Rev.* **2011**, *40*, 2525 – 2540.

[15] a) H. J. Schneider, *Angew. Chem.* **2009**, *121*, 3982 – 4036; *Angew. Chem. Int. Ed.* **2009**, *48*, 3924 – 3977; b) M. Liu, W. Liao, C. Hu, S. Du, H. Zhang, *Angew. Chem.* **2012**, *124*, 1617 – 1620; *Angew. Chem. Int. Ed.* **2012**, *51*, 1585 – 1588.

[16] Y. O. Kim, Y. M. Jung, S. B. Kim, B. H. Hong, K. S. Kim, S. M. Park, *J. Phys. Chem. B* **2004**, *108*, 4927 – 4936.

[17] Y. Morita, T. Agawa, E. Nomura, H. Taniguchi, *J. Org. Chem.* **1992**, *57*, 3658 – 3662.

[18] T. N. Van, B. Kesteleyn, N. D. Kimpe, *Tetrahedron* **2001**, *57*, 4213 – 4219.

[19] T. Ogata, I. Okamoto, E. Kotani, T. Takeya, *Tetrahedron* **2004**, *60*, 3941 – 3948.

[20] L. Guan, K. Suenaga, S. Iijima, *Nano Lett.* **2008**, *8*, 459 – 462.