2,3,6,7,10,11-Hexamethoxytriphenylene (HMTP): A new organic cathode material for lithium batteries

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ABSTRACT

We propose a new organic cathode material for rechargeable lithium battery applications: 2,3,6,7,10,11-hexamethoxytriphenylene (HMTP). HMTP is composed of six methoxy functional groups substituted onto a central triphenylene moiety. The cell, incorporating 40 wt.% of organic cathode material, exhibits full specific capacity at current densities up to 3 C. The main advantage of HMTP as organic cathode material lies in a stable cell performance and negligible self discharge, even though the capacity is lower, ~66 mAh/g, compared to other organic cathode materials. Cells with the HMTP cathode showed > 95% retention of the initial discharge capacity after 50 cycles at 1 C and self-discharge was not observed during a full month of open circuit voltage measurements. The latter is due to the fact that the nature of the HMTP radical is fundamentally different from other organic cathode materials' radicals.

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1. Introduction

Current secondary lithium battery technology is based on variations of the C/LiCoO$_2$ concept developed by Sony Corporation almost two decades ago [1]. Despite their success in many applications, ranging from mobile phones to electric vehicles, there is a need for improvement; new electrode materials and new electrolytes are needed in order to increase, for example, power density, safety, and rate capability. Additionally, with environmental requirements, toxicity, recycling, and disuse of battery materials are becoming hot issues. By considering organic battery components there is potential for renewable and sustainable lithium batteries, e.g. by using biomass as starting material [2].

Research on light and flexible organic batteries has been intense, motivated by their potential applications in miniature electronic systems. For example, the use of the stable organic radical, poly(2,2,6,6-tetra-methylpiperidinyloxy-4-yl methacrylate) (PTMA), as a cathode active material for non-toxic, light, flexible and high rate capability batteries was first reported in 2002 by Nakahara et al. [3] and a PTMA-based cathode was applied by Nishide et al. [4,5]. The PTMA cathode has a capacity of 111 mAh/g, excellent high rate capability and stable cycle performance [6–10]. The main drawbacks reported are loss of contact between PTMA and the carbon material in the cathode during cycling [11,12], irreversible side reactions at high voltages [13], and self-discharge [14]. Significant work has focused on developing the PTMA concept toward higher theoretical capacity and ionic conductivity, by designing molecular structures with the nitroxide radical 2,2,6,6-tetra-methyl-1-piperidinyloxy (TMPTA) and similarly for spirobisnitroxides [15–20].

In this paper, we report on the application of a new organic cathode material; 2,3,6,7,10,11-hexamethoxytriphenylene (HMTP, Fig. 1a) with similar reduction–oxidation potentials as PTMA, and high rate capability and stable cycling. Each molecular unit contains six methoxy functional groups (CH$_3$O) substituted onto a central triphenylene group. HMTP in itself is not a new compound [21,22], however, the application of HMTP as a cathode material, the electrochemical characteristics, and the nature of the radical have to our knowledge not previously been reported.

2. Experimental

2.1. Synthesis of 2,3,6,7,10,11-hexamethoxytriphenylene (HMTP)

All starting materials were purchased from Aldrich and used as received without further purification. A solution of veratrol (13.82 g, 100 mmol) in dichloromethane (140 ml) was added drop-wise to a suspension of FeCl$_3$·H$_2$O in dichloromethane (300 ml) and concentrated sulfuric acid (0.7 ml). After complete addition, the reaction mixture was further stirred for 3 h at room temperature and then 400 ml of methanol was slowly added under vigorous stirring. The mixture was further stirred for 30 min and the precipitate was filtered off, washed with

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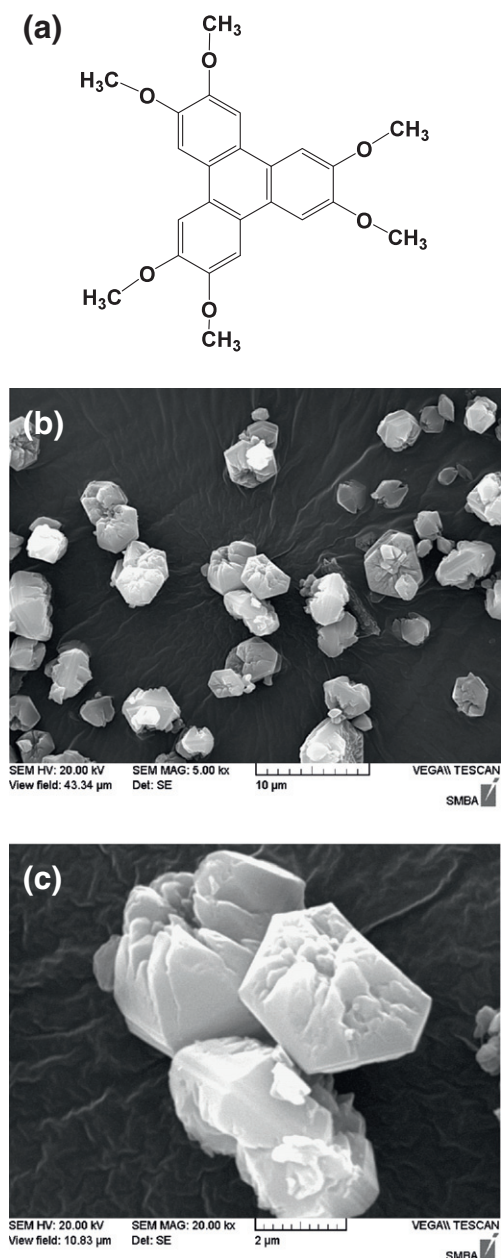
Fig. 1. (a) Molecular structure and SEM images (b, c) of the 2,3,6,7,10,11-hexamethoxy-triphenylene (HMTP) powder at two different magnifications.

methanol and dried under reduced pressure to give a slightly beige powder, purity >90% (TLC), mp ~312 °C, in 85% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δH (ppm): 4.135 (s, 18H, CH$_3$O), 7.831 (s, 6H, ArH); ^{13}C NMR (CDCl$_3$, 75.47 MHz): 55.88, 116.32, 124.38, and 158.62 ppm. IR (KBr) (cm^{-1}): 2986–2829 (m), 1621 (s), 1521 (s), 1466–1419 (s), 1307 (w), 1264 (s), 1207–1159 (s), 1049 (s), 1023 (m), 972 (w), 833 (s), 778 (s), 650 (w), 627 (m), 539 (w); Mass spectrometry (MS) [M]$^{+}$. Found: 408.0. The X-ray powder diffractogram on the bulk material reveals a crystal structure with space group $P6_3/m$ crystal structure [21].

2.2. Characterization and electrochemical tests

^{1}H and ^{13}C NMR spectra of the synthesized material were recorded on a Bruker 400 spectrometer (400 MHz for ^{1}H and 75.47 MHz for ^{13}C) using CDCl$_3$ as solvent. Scanning electron microscopy (SEM) imaging was done using FE-SEM (VEGA-II LMU, Tescan). Differential scanning calorimetry (DSC) was performed in the temperature range of 40 to 300 °C in hermetically sealed Al pans prepared in an Ar-filled glove box, and DSC traces were recorded during the subsequent heating up to 300 °C at a rate of 10 °C min^{-1}. The crystal structure of HMTP was characterized by powder X-ray diffraction (XRD: SIEMENS D5005) using *Cu Kα* radiation (35 mA/40 kV). EPR spectra of HMTP were collected at room temperature on a Varian E9 spectrometer with a microwave power of 0.8 mW, modulation amplitude of 0.1 mT and a microwave frequency of 9.4744 GHz.

To prepare the cathode, the organic active material (HMTP) in powder form, carbon black, and poly(vinylidene fluoride) (PVdF) binder were mixed in a ratio of 40:45:15 by weight. To 1 g of the mixture 9 ml N-methylpyrrolidone (NMP) solvent was added. The viscous slurry was cast on aluminum foil and dried at 80 °C under vacuum for 10 h. The film was cut into circular disks of area 0.95 cm^2 and a mass of ~2.5 mg (35 μm thickness without Al-foil) for use as the cathode. Electrochemical performance tests of HMTP were made using CR2030 coin type cells. The coin type Li/organic material cells were fabricated by stacking lithium metal anode and HMTP-based cathode with Celgard 2200 separator film. 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) in 1:1 volume ratio (supplied from Samsung Co.) was used as the electrolyte. A fixed volume (40 μl) of the liquid electrolyte was injected into the cell using a micro-syringe. A self-discharge test was performed by measuring the open circuit voltage (OCV) over one month.

3. Results and discussion

Representative SEM images of the neat HMTP powder are shown in Fig. 1(b, c). The size distribution of the particles is rather uniform and in the range of 2–5 μm. The particles are hexagonal with some disorder. Higher magnification reveals that the summits of the particles are open structures providing a large accessible surface area. The DSC trace, not shown, shows that the material is stable up to the melting point (312 °C) without any intermediate phase transitions or decomposition occurring.

In Fig. 2a we present the CV of our cell, where a single pair of well-defined redox peaks is observed and no change in the peak voltages was observed during cycling. The average redox voltage of the cell is 3.7 V with a small peak voltage separation, 0.4 V, between the anodic and the cathodic peaks. These observations suggest that the charge transfer process at the cathode is fast and efficient, even when compared with a PTMA cathode based cell with 40% relative content of organic material [11]. Repeated cycling results in an almost identical peak current and, moreover, the areas under the respective anodic and cathodic peaks are constant, indicating a high Coulombic efficiency of the redox process and highly reversible electrochemical reactions of the HMTP cathode. By close inspection of the CV, in Fig. 2a, an additional redox pair can be discerned at slightly higher voltages possibly indicating a multistep intercalation process.

The charge–discharge and cycling behavior of the HMTP-based cathode versus Li metal is shown in Fig. 2b and in the inset the cycling performance at a current density 0.05 mA/cm^2 and 1 C rate, in the voltage range of 2.0–4.2 V is shown. During the first charging (Li extraction) process, the voltage increases rapidly to ~3.8 V followed by a long plateau to about 45 mAh/g and then a gradual increase to the high cut-off voltage value resulting in a storage capacity of ~67 mAh/g. Thus a slight over-lithiation is indicated as compared to the theoretical storage capacity for one Li ion per HMTP, ~66 mAh/g. The capacity is low compared to other organic cathode materials [6–10]. The discharge curve shows a similar plateau as during charging. The irreversible capacity loss between the first charge and discharge reaction is only ~1 mAh/g, thus revealing a high Coulombic efficiency for the redox process, in agreement with the observations from the CV, Fig. 2a. A rather low polarization of about 0.3 V between charging and discharging plateaus (at 0.5 mol Li$^+$ insertion) reflects a low cell resistance.
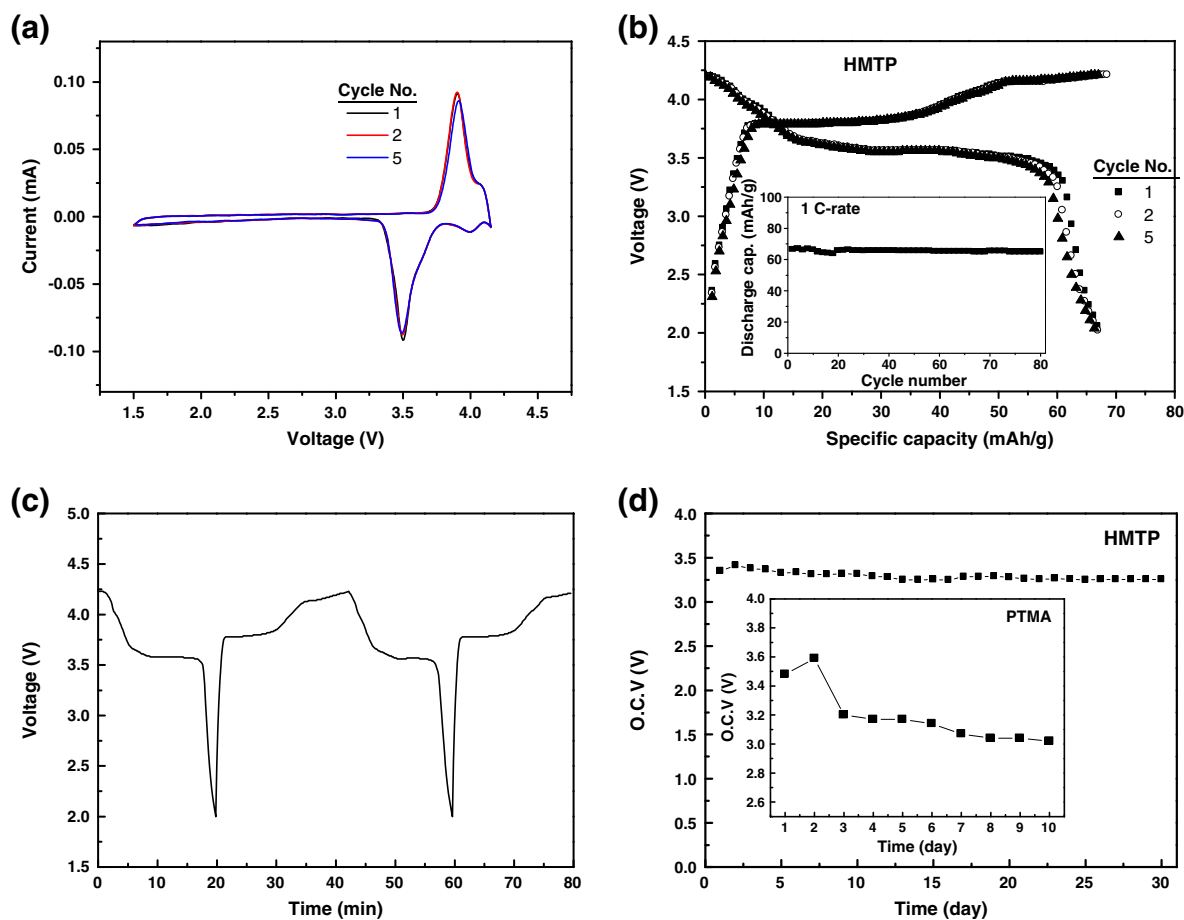
Fig. 2. (a) Cyclic voltammograms (scan rate: 1 mV/s), (b) galvanostatic charge–discharge cycle curves (1 C rate, cut-off voltage 2.0–4.2 V) and (c) discharge–charge cycles of the HMTP-based cell, at 3 C rate. Inset of (b) shows the cycle performance of a Li/HMTP-based cathode cell at 1 C rate. (d) Open circuit voltage (OCV) of a HMTP based battery during one month (initial voltage and charge capacity: 3.4 and SOC ~90%, see text for further information). Inset shows OCV of PTMA during ten days (initial voltage and charge capacity: 3.5 V and SOC ~90%).

The cycling performance of the organic HMTP cathode cell at room temperature and at 1 C rate is shown in the inset of Fig. 2b. The discharge capacity decreases slightly during the first 6 cycles after which it stabilizes. The average discharge capacity fade for the cell with the HTMP cathode, calculated on the basis of the initial and 50th cycle capacities, is less than 0.1% per cycle. The discharge/charge cycle at a current density of 3 C (0.15 mA/cm^2) is shown in Fig. 2c. Even at such a high current density very efficient and fast charge/discharge processes are possible in the HMTP-based cell; each process took about 20 min, which is the theoretical time at this rate. Thus, it is clear that the cathode assembly does not hinder the rapid electron transfer reaction of the organic material, responsible for the fast electrochemical process.

Fig. 2d shows the open circuit voltage (OCV) for a HMTP based battery as a function of storage time. The inset shows for comparison the OCV of a PTMA based organic battery (17 μm electrode thickness, loading of PTMA, carbon black, PVdF binder is 40:50:10). Comparing the OCV of HMTP and PTMA is not straightforward since a PTMA based cell is assembled in a discharged state and a HMTP based cell is charged from the "beginning". In the OCV test of PTMA we charged the cell to ~90% SOC (~100 mAh/g) and subsequently, within 10 min, the initial voltage dropped to ~3.5 V, corresponding to reaching the plateau voltage value. In order to have a comparable setting the HMTP cell was charged to ~90% SOC (~60 mAh/g) after the first discharge and the resulting OCV voltage ~3.4 V also corresponds to the plateau voltage value of the discharge in a charge–discharge cycle. Thus, all OCV tests were performed at a starting state corresponding to the beginning of the plateau region of the discharge curve for

each material. The OCV test over time is thus a qualitative demonstration of a very low degree of self-discharge and at the same time a high stability of HMTP toward the electrolyte. This is in contrast to PTMA which shows a more pronounced self-discharge as was also previously pointed out [14].

We propose that a one electron reduction process of HMTP during discharge leads to the formation of a radical anion; HMTP•. To verify this idea and monitor for unpaired electrons, EPR experiments were performed. The neat HMTP material gave no measurable EPR signal, while the reduced HMTP gave a single isotropic line with a g value of 2.0039, which is close to the value of 2.0023 for a free electron, thus indicating an unpaired electron delocalized over the entire molecule. The peak-to-peak line width of the first-derivative signal was 0.2 mT and no hyperfine coupling to the HMTP hydrogen nuclear spins was observed. Based on the EPR results we conclude that HMTP is distinctly different from most other common organic cathode materials containing free radicals such as PTMA, spirobisnitroxides, and TMPTA, where the charge is always localized [3,17,19,20]. The delocalization should stabilize the HMTP• radical and thus lead to a reduced self-discharge, in agreement with the result of the OCV test.

4. Conclusions

A new organic cathode material has been prepared from 2,3,6,7,10,11-hexamethoxytriphenylene (HMTP), which is a structure of methoxy functional groups around a triphenylene moiety. The electrochemical redox reaction of HMTP shows high reversibility. A very good cycle performance of a complete cell in the present study

also demonstrates the efficiency of the HMTP based cathode. A long time test at OCV shows that HMTP is less prone to self-discharge compared to other organic cathode materials. The reason to this we believe is the delocalization of the free electron over the whole molecule, in contrast to other organic cathode materials containing free radicals, where the charge is localized. In addition, the stable crystalline structure of HMTP seems to prevent dissolution into the liquid electrolyte, which is otherwise reported as a problem for organic electrodes. Thus, the HMTP based cathode materials may open new opportunities for organic, light, flexible and stable secondary lithium batteries.

Acknowledgments

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