Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2015

Phenothiazine-functionalized redox polymers for a new cathode-active material

Ali A. Golriz,[a,b] Takeo Suga[c,*], Hiroyuki Nishide[d,*], Rüdiger Berger[a], Jochen S. Gutmann[b,e*]

[a] *Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany. E-mail: berger@mpip-mainz.mpg.de; Fax: +49-(0)6131-379-100; Tel: +49-(0)6131-379-114*

[b] *Department of Chemistry and Center for Nanointegration Duisburg- Essen (CENIDE), University Duisburg-Essen, Universitätsstr. 5, D-45117 Essen, Germany. E-mail: jochen.gutmann@uni-due.de; Fax: +49-(0) 201-183-4934; Tel: +49-(0) 201-183-2566*

[c] *Waseda Institute for Advanced Study, Waseda University, Tokyo 169-8555, Japan. E-mail: takeosuga@toki.waseda.jp*

[d] *Department of Applied Chemistry, Waseda University, Tokyo, 169-8555, Japan. E-mail: nishide@waseda.jp; Fax: +81-3-3209-5522; Tel: +81-3-3200-2669*

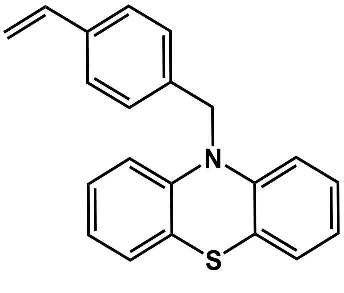
[e] *Deutsches Textilforschungszentrum Nord-West e.V., Adlerstr. 1, D-47798 Krefeld, Germany*

Materials

Potassium *tert*-butoxide (PTBO; Sigma Aldrich, 95%), 1-(chloromethyl)-4-vinylbenzene (CVB; Sigma Aldrich, 95%), dilithium tetrachlorocuprate (Li_2CuCl_4; Sigma Aldrich, 0.1 M in THF), dry tetrahydrofuran (THF; Acros, 99.8%), 1-bromo-3-chloropropane (BCP; Acros, 98%), hexane (Fisher Scientific, 95%), dichloromethane (DCM; TCI Japan, 99.5%), acetonitrile (ACN; TCI Japan, 99.5%), vapour grown carbon fiber (VGCF; Show Denko Japan), tetrabutylammonium perchlorate (TBAPC; TCI Japan, 98%), polyvinyldiflouridine (PVDF; Sigma Aldrich, average Mw ≈ 530000 g/mol) and 1-methyl-2-pyrrolidone (NMP; TCI Japan, 99%) were used as received. 4-bromostyrene (PBS; Sigma Aldrich, 97%) was distilled prior to use. Azobisisobutyronitrile (AIBN; Sigma Aldrich, 98%) was crystallized from ethanol and dried under vacuum prior to use and kept under argon atmosphere in the refrigerator.

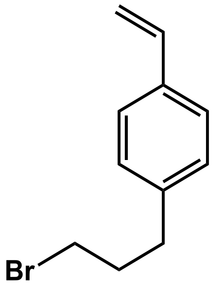
Synthesis

1.1. *Synthesis of 10-(4-vinylbenzyl)-10H-phenothiazine (VBPT)*



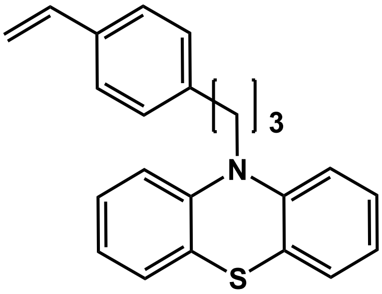
13.2 g phenothiazine (0.067 mol) were dissolved in 200 ml dry THF and 7.85 g PTBO (0.07 mmol) were added to the solution and stirred for 3 hours at room temperature under argon. Then, 17.5 ml CVB (0.12 mmol) were added to the dispersion using a dropping funnel and the mixture was refluxed over night. 100 ml distilled water were added and the organic phase was extracted twice with Na_2SO_4 solution. Subsequently, the water phase was extracted three times with DCM. Finally the organic phases were washed twice with distilled water, dried over $MgSO_4$, and the solvent was removed under vacuum. The residue was crystallized three times from ethanol to obtain 15.36 g (74%) of light yellow crystals as the product. M.p. 121-124 °C. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.29 (d, 2H), 7.18 (d, 2H), 7.01 (d, 2H), 6.87 (t, 2H), 6.77 (t, 2H), 6.59 (dd, 1H), 6.52 (d, 2H), 5.67 (d, 1H), 5.16 (d, 1H), 4.97 (s, 2H).^{13}C-NMR (300 MHz, $CDCl_3$): δ 144.1 (C-N), 136.1 (C_{quart}), 126.9 (CH_{aromat}), 126.5 (CH_{aromat}), 126.3 (CH_{aromat}), 122.9 (C-S), 122.2 (CH_{aromat}), 115.1 (CH_{aromat}), 113.5 (C=C), 52.2 (CH_2).

1.2. *Synthesis of 1-(3-bromopropyl)-4-vinylbenzene (BPVT)*



A Grignard mixture of 1.34 g magnesium and 10 g (0.055 mol) PBS was made in 50 ml THF. In another beaker, a mixture of 17.2 g BCP (0.11mol) and 7.6 ml 0.1M Li_2CuCl_4 in 50 ml THF was prepared and cooled to 0 °C. The Grignard was slowly dropped to the latter mixture and the reaction continued at room temperature over night. Finally, 100 ml 2n HCl solution was added to the reaction. The water phase was separated and washed twice with ether. The organic phases were then unified, washed three times with water, dried over $MgSO_4$, and the solvent was removed under vacuum. The resulting oil was purified by distillation to result in a colorless oil. (5.88 g, 60%, b.p.: 70-75 °C). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.37 (d, 2H), 7. 16 (d, 2H), 6.72 (m, 1H), 5.71 (d, 1H), 5.22 (d, 1H), 3.56 (t, 2H), 2.81 (t, 2H), 2.11 (p, 2H).

1.3. *Synthesis of 10-(3-(4-vinylphenyl)propyl)-10H-phenothiazine (VPPP)*



4.3 g phenothiazine (0.022 mol) was dissolved in 50 ml THF. 2.6 g PTBO (0.023 mol) were added to the solution and the reaction stirred for 3h at room temperature. 3.9 g BPVT (0,022 mol) were added to the reaction which was then refluxed for 48 hours. After adding 100 ml water to the reaction, the water phase was separated and washed three times with DCM. The organic phase was washed once with sodium bisulfate solution and twice with water, dried over $MgSO_4$, and the solvent was removed under vacuum. The crude product was purified twice over column chromatography using a mixture of 9 : 1 petroleum ether/DCM and 10:1 hexane/ethyl acetate, respectively. A light yellow colored powder was obtained as the product. (5.23 g, 71%). ^1H-NMR (250 MHz, $CDCl_3$): δ 7.31 (d, 2H), 7. 18 (m, 6H), 6.96 (t, 2H), 6.86 (d, 2H), 6.66 (dd, 1H), 5.70 (d, 1H), 5.20 (d, 1H), 3.89 (t, 2H), 2.77 (t, 2H), 2.13 (t, 2H).

1.4. *Synthesis of the polymers*

The synthesis was carried out using 1 g of the monomer VBPT (VPPP) dissolved in 4 ml of anisole (THF). Using the adequate amount of the initiator AIBN, the monomers were polymerized via standard radical polymerization molecular with weights M_n of 25000 g/mol.

PVBPT: GPC (M_n =273000 g/mol, PDI = 2.32), 1H-NMR (250 MHz, CDCl3):δ 6.88 (br, 4H), 6.55 (br, 4H),6.35(br, 2H), 6.17 (br, 2H), 4,69 (br, 2H),1.77 (br, 1H),1,18 (br, 2H).

PVPPP: GPC: (M_n = 25800 g/mol, PDI = 1.96), 1H-NMR (250 MHz, CDCl3): δ7.07 (br, 4H), 6.62 (br, 4H), 6.25 (br, 4H), 2.47 (br, 2H), 1.90 (br, 4H), 7.07 (br, 4H), 1.17 (br,3H).

Methods

The CV and CA experiments were performed on a BAS Inc. ALS660B potentiostat system with indium tin oxide (ITO), Ag/AgCl and Pt-wire as WE, RE and CE, respectively. The polymer films were spin-coated on ITO at 1000 rpm/s for 30 s using a 10 and 20 g/L solution of the polymer. For PVBPT and PVPPP, DCM was used as solvent, whereas for PVMPT, THF under heating resulted in the desired solution. 0.1 M and 1 M TBAPC in ACN served as electrolyte. Glassy carbon (GC) and ITO platelets (2.5 cm x 2.5 cm) were cleaned with DCM and n-propanole prior to use.

The UV/Vis measurements were performed on a Jasco V-660. For electrochemical measurements, a standard potentiogalvanostat (Nikko Keisoku DPGS-1) was used. Pt-wire attached to the polymer film spin-coated on ITO served as WE. As RE and CE, Ag/AgCl and Pt-wire were used.

Electron spin resonance (ESR) spectra were obtained with a JEOL JES-TE200 ESR spectrometer at 100 kHz field modulation. A Pt-wire electrode covered with the polymer was placed in the ESR tube as WE. An isolated Pt-wire and a further isolated Pt-wire coated with silver were placed in the ESR tube as CE and RE, respectively. The potential was applied using a potentiogalvanostat (Nikko Keisoku DPGS-1). To calculate the g-value, manganese isotope with spin quantum number $S = 5/2$ and g-value of 2.0024 ± 0.003 from Magnettech was taken as a standard. For the spin density measurements, galvinoxyl free radical was used as a reference.

The polymer composite was prepared as follows: 50 mg PVDF were dissolved in 450 mg NMP after ultra sonification. 80 mg VGCF were mixed with 10 mg of the polymer (PVBPT or PVPPP) and 100 mg of the PVDF solution. After adding a few drops of NMP, the composite was well mixed in a mortar. The obtained paste was spread out over a GC-plate or aluminum foil. The weight of the GC-plate was determined beforehand. The prepared paste was left to dry over night under vacuum at 60 °C. For the CP measurements on GC, the weight was measured after drying to determine the polymer amount. For battery preparation, the dried paste on aluminum foil was punched out as circles with the same size and the pieces were weighed before use. The weight of aluminum foil without composite was determined from punched circles of the same size.

The battery assembly was performed in a glovebox using the aluminum pieces with the dried polymer composite paste. The aluminum piece was laid on the steel bottom part of the coin cell covered with the electrolyte solution (1 M $LiPF_6$ in 50/50 v%/v% EC/DEC) and a fitting ring. Then, the cathode was separated with a thin teflon membrane cut off in a circular shape. A piece of lithium metal was put on the teflon membrane and covered with a steel platelet and a feather. Finally, the coin cell was closed with the upper part and sealed under pressure. The battery coin cell was tested with respect to short circuits, showing an open circuit potential of over 2.8 V.

Figures

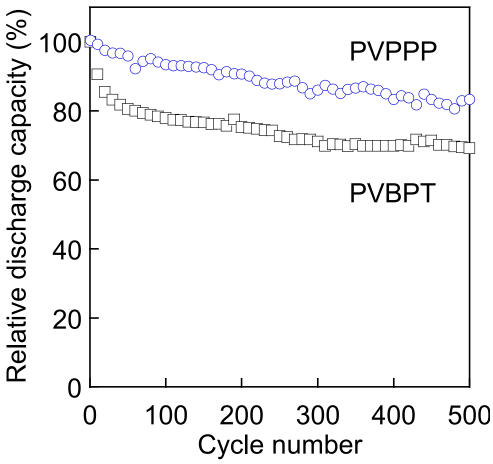


Figure S1 Cycle stability of coin cell batteries with lithium anode and either PVBPT or PVPPP cathode. Charging and discharging current: 10C-rate.