

View Article Online View Journal

RSC Advances

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: D. Nauroozi, M. Pejic, P. Schwartz, M. Wachtler and P. Baeuerle, *RSC Adv.*, 2016, DOI: 10.1039/C6RA24064J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/rsc-advances

YAL SOCIETY CHEMISTRY

RSC Advances

ARTICLE

Received 00th January 20xx, D Accepted 00th January 20xx B

DOI: 10.1039/x0xx00000x

www.rsc.org/



Djawed Nauroozi,^{a*} Marijana Pejic,^b Pierre-Olivier Schwartz,^a Mario Wachtler,^b and Peter Bäuerle^{a*}.

The synthesis and polymerisation of dimethyl 2-vinylterephthalate **M1** for possible applications as anode material in organic secondary batteries are reported. **M1** exhibits a vinyl group as a polymerisable unit while the carboxylate moieties serve as cation (Li⁺, Na⁺) coordinating sites. The gram-scale synthesis of **M1** is described *via* three different routes in order to evaluate the route with the highest overall yield. Furthermore, different conditions for free radical polymerisation are investigated for obtaining polymer **P1** with high molecular weights in order to study the impact of immobilising the carboxylate redox-active centres in a polymer on the charge/discharge cycling stability when used in an organic battery. In order to synthesise suitable materials for battery investigated. Cyclic voltammetry measurements showed for **P1-Li** redox activity in the range of $0.5 - 1.2 \text{ V s Li}^+$ /Li which assigns it as a candidate for the anode. Under the present experimental conditions, the galvanostatic measurements of **P1-Li** exhibited a specific capacity of 64 mAh g⁻¹. It is further demonstrated that **P1-Li** shows an improved cycling stability of 83 % discharge capacity remaining after 100 cycles compared to the parent monomer (44 %).

Introduction

The concept of using organic molecules as candidates for energy storage applications has recently attracted increased attention both for environmental and economic reasons.¹⁻⁴ Compared to conventional inorganic electrode materials they offer a potentially low-cost production due to the low temperature procedures, their composition of naturally abundant chemical elements (C, H, N, O, S) that do not involve expensive metals, and their recyclability. Thus, organic materials represent a promising alternative to their inorganic counterparts.

The access to an inexhaustible pool of organic molecules further allows the design of electrode materials suitable for a wide range of redox potentials. Several classes of organic compounds such as conjugated polymers, stable organic radicals, organodisul-fides, and thioethers have already been studied.⁵⁻¹⁴ Recently, particular interest is focussed on organic carbonyls as they present a common functional group and are able to stabilise charges *via* delocalisation.^{3,15} Among carbonyl compounds, conjugated

dicarboxylates such as terephthalates have been shown to be suitable candidates for anodes due to their electrochemical reactivity at low potentials.¹⁶ However, most of the organic electrode materials with low molecular weight suffer capacity fading after a while due to their solubility in the electrolyte. An intuitive approach to overcome this disadvantage is to use the corresponding polymers.^{17,18} Several polymers that show stable performance over some hundred cycles have already been investigated as electrode materials.¹⁹⁻²¹ However, there are just a few examples of polymers that can be used as anodes.²²⁻²⁴

Poly(terephthalates) such as poly(ethylene terephthalate), known as PET, are among the most common polymers, which are used today. They are produced *via* condensation reaction of a carboxylic acid and an alcohol. In order to use poly(terephthalate) as an electrode active material though, the carboxylate moiety needs to be accessible for the insertion/de-insertion of metal cations (Li⁺ or Na⁺) during the charge/discharge process in a battery. We therefore sought the synthesis of a styrene derivative, 2-vinyl-terephthalate **M1** (Scheme 1), that allows the polymerisation of the terephthalate *via* the vinyl group while the carboxylate moiety remains accessible for the electrochemical processes.

In this work, we report synthesis of terephthalate-based monomer **M1** as well as the investigation of different conditions for free radical polymerisation in order to obtain the corresponding polymers in high molecular weights. The suitability and possible

^{a.} Institute of Organic Chemistry II and Advanced Materials, Ulm University, Albert-Einstein-Allee 11, D-89081 Ulm, Germany. E-mail: <u>djawed.nauroozi@uniulm.de</u>, <u>peter.baeuerle@uni-ulm.de</u>.

 ^{b.} ZSW – Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Helmholtzstr. 8, D-89081 Ulm, Germany.
 †Electronic Supplementary Information (ESI) available: See

DOI: 10.1039/x0xx00000x

DOI: 10.1039/C6RA24064J Journal Name

ARTICLE

application of the synthesised polymer as anode material are further investigated by electrochemical methods such as cyclic voltammetry and galvanostatic cycling.

Experimental

Methods and Instruments:

NMR spectra were recorded on a *Bruker* AMX 500 (¹H NMR: 500 MHz, ¹³C NMR: 125 MHz) or an Avance 400 spectrometer (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz), normally at 25 °C. Chemical shift values (δ) are expressed in parts per million using solvent signals (¹H NMR, $\delta_{\rm H}$ = 7.26 and ¹³C NMR, $\delta_{\rm C}$ = 77.0 for CDCl₃; ¹H NMR, δ_{H} = 2.50 and ^{13}C NMR, δ_{C} = 39.52 for DMSO-d6) as internal standards. Melting points were determined using a Büchi M-565. Elemental analyses were performed on an Elementar Vario EL (Ulm University). Cyclic voltammetry experiments were performed with an Autolab Potentiostat Galvanostat in a three-electrode singlecompartment cell with a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. Ferrocene (Fc) has been added as internal reference. The potentials have furthermore been recalculated to the Li⁺/Li reference electrode using 3.25 V for the oxidation potential of ferrocene vs Li⁺/Li. FT-IR spectra were measured with a Perkin Elmer Spectrum 2000. MS/CI experiments were performed using a Finnigan MAT, SSQ-7000 spectrometer.

The battery-related electrochemical investigations were carried out in three-electrode Swagelok-type cells using lithium metal (Sigma Aldrich) as the counter and reference electrodes, 3 glassfibre sheets (Whatman, GF/A) as separators, and 1 M LiPF₆ in a mixture of ethylene carbonate and dimethyl carbonate (EC:DMC) 1:1 by wt. (UBE Industries) as the electrolyte. The electrodes were prepared via a solvent-free preparation method using polytetrafluoroethylene (PTFE, Dyneon) as the binder. The active material (56.6 wt. %) and carbon black (SuperP-Li, Timcal; 33 wt. %) were homogenised by ball-milling (400 rpm, 10 min) before PTFE powder (10.4 wt.%) was added in a mortar to form a smooth paste. After calendering, composite electrode discs with diameters of 12 mm and a typical thickness of 170 - 190 µm were cut out of the film, pressed onto aluminium expanded metal mesh (3 t; 1 min), then dried overnight under dynamic vacuum at 80 °C, and finally stored under dry Ar. The cells were assembled in an Ar-filled glove box. Cyclic voltammetry was performed with a VMP3 electrochemical workstation from Biologic. The experiments were run with a scan rate of 0.1 mV s⁻¹ and a potential range of 0.5 -2.0 V vs Li⁺/Li. Galvanostatic cycling tests were performed with a CTS battery cycler from Basytec. The cells were charged and discharged with a constant current of 0.1 C for 100 cycles, within 0.5 - 2.0 V vs Li*/Li. The C-rates were calculated based on the theoretical capacity of the corresponding active material (theoretical capacity of **P1-Li** = 263 mAh g^{-1} , 1C rate = 263 mA g^{-1} , C/3 rate = 87.7 mA g⁻¹). All electrochemical measurements were carried out at room temperature and repeated in order to guarantee reproducibility. The specific currents and capacities are referred to the mass of active material.

Synthesis

Dimethyl 2-vinylterephthalate (M1): In a flame dried threenecked round bottom flask with a gas inlet tube, 3 g (5.46 mmol) of 5 were placed and dissolved in dry methanol. 1.23 g (10.92 mmol) potassium tert-butoxide dissolved in dry methanol (10 ml) was added and the colour of the solution turned to red. After 1 h, in a separate two-necked round bottom flask para-formaldehyde was placed and heated to 200 °C which sublimed to formaldehyde gas. The obtained formaldehyde gas was directed with argon flow to the first reaction flask through the gas inlet tube. After all paraformaldehyde was sublimed, the mixture was stirred for 14 h at room temperature, while the red mixture in the first flask turned to vellow. The mixture was extracted with dichloromethane, washed with water and brine. The organic phases were collected, dried over Na2SO4, and filtered. After removal of the solvent under reduced pressure a pale yellow solid was obtained, which was sublimed at a cold finger (75 torr, 80 °C) as a colourless solid in 75 % yield (0.90 g, 4.10 mmol). ¹**H-NMR** (CDCl₃ – 400MHz, ppm): δ = 8.24 (s, 1H), 7.99-7.86 (m, 2H), 7.41 (dd, 1H, J = 11.2 Hz, 6.4 Hz), 5.76 (d, 1H, J = 17.2 Hz), 5.43 (d, 1H, J = 10.7 Hz), 3.95 (s, 3H), 3.92 (s, 3H); 13 **C-NMR** (CDCl₃ – 400MHz, ppm): δ = 167.25, 166.24, 139.53, 134.80, 133.11, 132.31, 130.37, 128.32, 128.10, 117.77, 52.48, 52.43. **FT-IR** (KBr, 25 °C, cm⁻¹): γ = 2927, 1698, 1565, 1489, 1415, 1303, 1265, 922, 788, 763, 751. MS/Cl(+) m/z = 221; mp = 55 °C. Elemental Analysis: C12H12O4 (theoretical); C: 65.45; H: 5.49; C₁₂H₁₂O₄ (found); C: 65.72; H: 6.18.

Polymerisation of M1: In a flame dried Schlenk tube with a stir bar and under argon atmosphere 300 mg (1.36 mmol) of **M1** was placed and the tube was heated to 80 °C while **M1** was melted. 0.2 mol % (4 mg) of 2,2'-azobis(2-methylpropionitrile) was added to the molten **M1** and stirring was continued. After 30 min a resin was obtained and stirring was not possible any more. The temperature was increased to 150 °C and the tube was maintained at this temperature for 24 h. After cooling to room temperature the yellow solid was transferred into 50 ml MeOH. A white precipitate was formed immediately which was subjected to Soxhlet extraction with MeOH overnight. The obtained polymer was dried under vacuum and gave the polymer **P1** in 80 % (240 mg) as a colourless solid. ¹**H-NMR** (CDCl₃ – 400MHz, ppm): δ = 7.91-7.00 (3H), 4.01-3.51 (3H), 3.50-2.78 (3H), 1.98-1.00 (3H); **FT-IR** (KBr, 25 °C, cm⁻¹): γ = 2953, 2916, 2848, 1723, 1435, 1286, 1240, 1192, 1116, 753.

Synthesis of P1-COOH: 300 mg P1 were dissolved in a mixture of 15 ml THF/MeOH (2:1) and 220 mg (4 eq.) NaOH was added to the solution. The mixture was heated to reflux for 14 h. A precipitate was formed which was collected and washed excessively with MeOH. The product was obtained after drying under vacuum as a colourless powder in 80 % yield (210 mg). FT-IR (KBr, 25 °C, cm⁻¹): $\gamma = 2200$ -3500, 1702, 1568, 1495, 1419, 1233, 1125, 1054, 916, 880, 853, 757.

Synthesis of P1-Li using LiHMDS: 200 mg (1.0 mmol) P1-COOH were dissolved in 20 ml dry THF and 700 mg (4.2 mmol) lithium hexamethyldisilazide (LiHMDS) was added in portions. Then the mixture was heated to 60 °C for 14 h. The formed precipitate was collected and washed with hot THF. The product was obtained after

Journal Name

drying under vacuum as a pale yellow powder in 70 % yield (150 mg). FT-IR (KBr, 25 °C, cm⁻¹): γ = 1517, 1428, 864, 500.

Results and discussion

Synthesis of the monomer

The synthesis of monomer M_1 is shown in Scheme 1. Although molecules 1-5 as well as M1 are literature-known (s. ESI), for some of them a synthesis procedure and/or proper characterisation are missing, which is described here. In the first step, the commercially available 2-methylterephthalonitrile 1 was treated with NaOH in presence of diethylene glycol (DEG) to obtain 2-methylterephthalic acid 2 in quantitative yield. Subsequent esterification under acidic conditions gave methyl ester 3 quantitatively. Bromination of the methyl group using N-bromosuccinimide (NBS) and subsequent transformation to the corresponding phosphonium salt provided 5 that serves as a precursor for the following Wittig reaction.²⁵ Unfortunately, a convenient synthesis of monomer M1 with commercially available formaldehyde is not possible due to the presence of water in the methanol solutions of formaldehyde. To circumvent this obstacle, formaldehyde was generated in situ by decomposition of the para-formaldehyde polymer into the corresponding monomers at 200 °C. Thus, the formaldehyde was obtained as a gas, which could be easily directed to the reaction flask, where the phosphonium salt was already treated with potassium tertbutylate. This reaction gave the desired 2-vinylterephthalate M1 after 14 h reaction time at room temperature. Purification via flash chromatography and recrystallisation from ethyl acetate gave the monomer M1 in 75 % yield. Although the overall yield of this multistep synthesis is satisfying (65 % over 5 steps), other routes have also been investigated in order to reduce the number of synthetic steps and to gain better yields (details in Supporting Information). However, the overall yields of the two other routes were less than the one shown here.

Polymerisation experiments

The solubility of organic molecules in electrolytes is among the most serious obstacles for their use in batteries. On the one hand, the electrode capacity decreases as it dissolves, on the other hand, the dissolved redox-active molecules can act as redox shuttles



Scheme 1: Synthesis of vinyl terephthalate monomer **M1**. For the polymerisation conditions towards P1, see text and Table1.

resulting in a self-discharge of the cell. An intuitive approach to circumvent this problem is the transformation of the electrodeactive material into a polymer. With the use of M1 we intended to prepare stable polymers P1 that show low solubility in the electrolyte mixtures of a battery (Scheme 1, last step). Hence, different conditions for a free radical polymerisation reaction of monomer M1 with 2,2'-azobis(2-methylpropionitrile) (AIBN) as radical starter have been investigated. All polymerisation conditions as well as the corresponding characterisation data for the obtained polymers are summarised in Table 1. The GPC chromatograms are shown in Figure 1. First attempts to polymerise M1 in THF as solvent at 60 °C gave polymers with molecular weights of around M_n = 18 kDa corresponding to approximately 90 repeating units (Figure 1, black curve). In order to obtain polymers with higher molecular weights, we tried to improve the polymerisation process by changing the solvent from THF to dioxane or N-methylpyrrolidone (NMP), which allow performing the reaction at higher temperatures, 100 °C and 150 °C, respectively. However, both solvents gave polymers with molecular weights of approximately 15 kDa (Figure 1, orange and turquoise curves). The same trend was observed when different radical starters such as dibenzoyl peroxide (DBPO) or the water soluble 2,2'-azobis(2-methylpropionamidine) dihydrochloride were used (data and chromatograms not shown).

Benefiting from the low melting point of **M1** (mp = 55 °C), a solventless free radical polymerisation was tested. For this purpose, **M1** was melted in a dried tube and the melt was stirred continuously. Then, the radical starter was added and the stirring continued for 8 h. In this fashion, we obtained in a first attempt a polymer that showed a bimodal distribution in the GPC chromatogram with molecular weights of 400 kDa and 25 kDa, respectively (Figure 1, green curve). The promising formation of polymers with longer chains using this method prompted us to test other conditions in order to obtain monomodal polymers with high



Figure 1: GPC chromatograms of polymerisation experiments of **M1**.

Published on 17 November 2016. Downloaded by Freie Universitaet Berlin on 18/11/2016 07:10:02

 Table 1: Polymerisation conditions of M1 and characterisation data of the corresponding polymers. 2,2'-Azobis(2-methylpropionitrile) was used as radical starter in all cases. PDI = Polydispersity index; DP = Degree of polymerisation.

Entry	Solvent	Concentration [mol/L]	т [°С]	Time [h]	M _n [kDa]	PDI	DP
1	Dioxane	0.45	100	24	15	1.5	70
2	NMP	0.45	150	24	16	1.5	70
3	THF	0.45	60	24	18	1.6	90
4	-	bulk	80	8	400	1.3	1800
					25	4.6	115
5	-	bulk	80	24	200	5.6	900
6	-	bulk	80-150	24	550	2.6	2500

molecular weights. In another attempt, simple elongation of the reaction time led to a polymer with a monomodal distribution in the GPC chromatogram with approx. 200 kDa (blue curve).

Along with the variation of reaction times a gradual increase of the temperature from 80 °C to 150 °C during the polymerisation reaction was tested as well. Much to our satisfaction, polymers with molecular weights of around 550 kDa and a polydispersity Index (PDI) of 2.6 were obtained (Figure 1, pink curve). Triggered by the obtained results, reaction times of longer than 24 h were also investigated; however, no significant improvement in obtaining longer chains was observed. It is noteworthy that upon repeating the synthesis of **P1**, both the solventless as well as the solutionbased polymerisations gave reproducible results.

The obtained polymers were characterised by ¹H NMR spectroscopy. Figure 2 shows both the ¹H NMR spectra of the monomer **M1** and the corresponding polymer **P1**. The spectrum of the monomer **M1** (top) displays the aromatic signals of the protons of the phenyl ring at 7.93 ppm and 8.24 ppm, respectively. In addition to the signals for the methyl ester groups at 3.94 ppm and 3.92 ppm, two doublets can be observed at 5.43 ppm and 5.76 ppm, respectively, as well as a quartet at 7.41 ppm that correspond to the vinylic protons. These proton signals are undoubtedly



Figure 2: ${}^{1}H$ NMR spectra (400 MHz, CDCl₃) of the monomer **M1** (top) and the corresponding polymer **P1** (bottom).

missing in the ¹H NMR spectrum of the polymer **P1** indicating the reaction of the vinylic group (Figure 2, bottom). In addition, a broad signal at 1.80-1.25 ppm is observed that corresponds to the protons of the aliphatic chain. It is also interesting to notice that the methyl ester signals are much more separated in the polymer NMR (3.82 ppm and 3.24 ppm) compared to the monomer, supposedly because of the closer vicinity of the alkyl chain to the carboxylate groups. At the same time, the aromatic signals are merged into each other and give a broad signal centred at 7.46 ppm.

Post-functionalisation of polymer P1

For the synthesis of the Li-salt **P1-Li** that would serve as battery material, the esters of the polymer **P1** were first hydrolysed to the corresponding carboxylic acids. After deprotonation, Li⁺-ions were inserted *via* two synthetic routes (Scheme 2). The first route (Scheme 2, Route A) follows a literature-known procedure,¹⁶ where the hydrolysis of the ester groups and the insertion of the Li⁺-ions occur in one step by using LiOH. For this purpose, the polymer was dissolved in THF and LiOH was added to the solution. After 12 h reaction time, a precipitate was observed indicating the formation of the polymer Li-salt **P1-Li**. As the product is well soluble in water, but shows low solubility in THF, the water phase was dropped into an excess amount of THF. The obtained precipitate was subjected to centrifugation and collected by decantation. Since LiOH is soluble in a certain amount of water as well, this procedure was repeated several times in order to obtain the pure polymer **P1-Li**.

To ensure the purity of the material and to synthesise the Lisalt in a more convenient way, another route was sought (Scheme 2, Route B). Following a two-step synthesis, the ester polymer **P1** was first hydrolysed with NaOH in a THF/MeOH mixture. Under these conditions, the desired polymer with two carboxylic acid groups **P1-COOH** precipitated from the solution. The pure compound was obtained after an excessive wash of the precipitate with MeOH in a yield of 80 %. Treatment of **P1-COOH** with LiHMDS in dry THF at 50 °C overnight led to the formation of the target **P1-**Li. The obtained material was washed excessively with hot THF in order to get rid of the formed by-products. Published on 17 November 2016. Downloaded by Freie Universitaet Berlin on 18/11/2016 07:10:02



Scheme 2: Synthesis of the polymer Li-salt P1-Li via two different routes.

To validate the insertion of the Li⁺-ions, the two polymers P1 and P1-Li were characterised by IR-spectroscopy (Figure 3). The polymer P1 showed two characteristic bands at 1723 cm⁻¹ and 1286 cm⁻¹ that correspond to the stretching vibration of the carbonyl (C=O) and the alkyl grou ps of the polymer backbone (C-C), respectively. These two bands are markedly shifted in case of the polymer lithium salt P1-Li. The carbonyl band is shifted by about 200 cm⁻¹ to lower wavenumbers and can be observed at 1517 cm⁻¹, while the band for the C–C-bond vibrations are shifted by about 150 cm⁻¹ to higher wavenumbers and can be observed at 1428 cm⁻¹. These significant shifts indicate the change of the vibrational character in the two materials. Moreover, a significant band can be additionally observed at approximately 500 cm⁻¹ in the IR spectrum of P1-Li corresponding to the Li-O deformation vibration, which confirms the successful substitution reaction of the Li⁺-ions. This band is clearly missing in the ester-functionalised polymer P1.

Electrochemical characterisation of M1 and P1 in solution

Monomer **M1** and the corresponding polymer **P1** were characterised electrochemically by means of cyclic voltammetry (CV). The measurements were performed in a 0.1 M solution of the compound in THF with n-tetrabutylammonium hexafluoro-



View Article Online DOI: 10.1039/C6RA24064J

ARTICLE

Figure 3: IR-spectroscopic analyses of the ester polymer P1 (top) and the Li-salt polymer P1-Li (bottom).

phosphate (TBAPF₆) as electrolyte. The cyclic voltammogram of the monomer **M1** (Figure 4, left) showed a reversible reduction wave at -2.35 V vs Fc⁺/Fc (\sim 0.9 V vs Li⁺/Li) with two electrons involved referring to the reduction of the methyl esters. In case of the polymer **P1** (Figure 4, right), the cyclic voltammogram showed a reduction process at -2.53 V vs Fc⁺/Fc (\sim 0.72 V vs Li⁺/Li) which is about 300 mV cathodically shifted compared to the monomer. The observed redox process showed a broad wave for the reduction which is common for polymers. The re-oxidation of the same polymer showed an impetuous drop of current at -2.49 V vs Fc⁺/Fc that recovers again and continues giving a broad wave. Assuming that the polymer exists as a coil, this observation may be related to the faster re-oxidation of the outer units of the polymer due to their easier accessibility while that of the units inside the coil needs more time because of the diffusion dependency.



Figure 4: Cyclic voltammograms of monomer **M1** (left) and the corresponding polymer **P1** (right). Measurements were performed in 0.1 M solutions of the compounds in THF with TBAPF₆ as electrolyte; scan rate = 200 mV s⁻¹; working electrode area: 0.79 mm²; referenced against Fc⁺/Fc (*).

This journal is $\ensuremath{\mathbb{C}}$ The Royal Society of Chemistry 20xx

Page 6 of 9





Figure 5: Electrochemical results of **P1-Li** in 1 M LiPF₆ / EC:DMC (1:1 by wt.) of all electrodes containing **P1-Li** (56.6 wt. %), PTFE (10.4 wt. %) and carbon black (33 wt. %). (a) CV (0.1 mV s⁻¹, 5 cycles). (b) Galvanostatic charge-discharge cycling (C/3) of **P1-Li** (blue) compared to dilithium terephthalate (red). Capacity plots (charge capacity: closed symbols; discharge capacity: open symbols) and potential profiles of cycle 1, 2, 10, 50, 100, 150 and 200 (inset).

Measurements on polymers with different molecular weights of 18 kDa and 200 kDa led to the same observation (see SI, Figure 2). A similar electrochemical investigation of the Li-salt **P1-Li** was not possible because of the insolubility of the material in any common organic solvent. Nevertheless, considering the structural similarity of the Li-salt and the methyl ester derivative, the reduction of **M1** as well as of **P1** at low potentials underlines the principal suitability of this class of compounds as anode material in batteries. It is worth emphasising that the polymer salt **P1-Li** is completely insoluble in any organic solvent. In particular, the insolubility in common battery electrolytes such as ethylene carbonate/dimethyl carbonate underlines the superiority of polymeric materials in terms of cycling stability in comparison with the corresponding monomers, which is discussed below.

Electrochemical investigations of P1-Li as anode material for organic batteries

The CV of the polymeric anode material **P1-Li** shows a redox range of 0.5 - 1.2 V vs Li⁺/Li (Figure 5a) (consistent with the results of **P1** in Figure 4). Only few organic compounds have been described which work at such low potentials upon insertion/de-insertion mechanism, and almost all of them are of low molecular weight.^{16,26} One example of a polymeric compound is diethyl terephthalate-functionalised polythiophenes, which have been reported recently²⁷- unfortunately no specific capacities are given. **P1-Li** is another polymer active in this potential region. Generally, a low anode potential is the key to obtaining large voltages and high energies of the full cell.

On repeated cycling there is a major change taking place between the first and the second CV cycle, whereas from the second cycle onwards the CV curves change only little. Obviously, some kind of formation process takes place during the first charge, giving rise to significant irreversible capacity. The galvanostatic charge-discharge profile of **P1-Li** shown in Figure 5b (blue curve) confirms the high irreversible loss in the 1st cycle. One reason is the high amount of carbon black (33 wt.%) in the electrode, which is indispensable for sufficient conductivity within the electrode, because this kind of active materials is usually non-conductive. It is known that carbon black itself exhibits a large irreversible capacity below 1 V vs Li⁺/Li caused by its high surface area and functionalities, which offer many possibilities for reductive side reactions.^{28,29} These side reactions are visualised in the CV (Figure 5a, black curve) by the increased reductive currents during the 1st cycle.

The reversible capacity amounts to 58 mAh g^{-1} (at the C/3 rate used for the galvanostatic cycling test), which is 22% of the theoretical capacity of **P1-Li** (263 mAh g^{-1}) (Figure 5b, blue curve). Apparently not all of the material takes part in the electrochemical reaction. A possible reason could be an insufficient electronic conductivity within the electrode. As **P1-Li** is an electronic insulator, only those areas of the material will electrochemically react which are in contact with the carbon black. Especially for large particles the reaction may therefore be limited to the particle surface. We expect the reversible capacity to increase by decreasing the particle size and by optimising the distribution of and contact between the carbon black and the active material. Generally, literature-known polymers which are used as cathode materials often exhibit lower specific capacities than the calculated theoretical capacities of their particular units.^{30,31}

To test the effect of immobilising the redox-active unit in a polymer, we compared the electrochemical performance of **P1-Li** to that of the related literature-known monomeric dilithium terephthalate. Dilithium terephthalate was synthesised as previously described,¹⁶ and processed into electrodes and tested under the same preparation and cycling conditions as **P1-Li**. The CV measurements (see SI, Figure 3) indicate higher capacities than for the polymer **P1-Li**, and a significant irreversible capacity. This is

ARTICLE

reflected in the galvanostatic measurements (Figure 5b). Figure 5b shows, furthermore, that although the polymer (blue) provides a lower initial specific capacity than dilithium terephthalate (red), its cycling stability is significantly improved, resulting in much slower capacity decay. The ratio of the discharge capacities of the 100th cycle to that of the 1st cycle is 85% for P1-Li and only 40% for dilithium terephthalate. The inferior cycling stability of the lowmolecular-weight terephthalate is presumably associated with the dissolution of the active material into the electrolyte.¹⁶ As well swelling of the material / electrode due to uptake of solvent from the electrolyte may contribute to the capacity fade via loss of electronic contact within the electrode material. In the case of P1-Li the corresponding active units are incorporated into a polymer backbone preventing their dissolution. Thus, regarding long term cycling the polymer P1-Li seems to be the more suitable candidate for battery applications. Last but not least, the polymer P1-Li shows a better rate capability than monomeric dilithium terephthalate (see SI, Figure 4).

Conclusions

The monomer dimethyl 2-vinylterephthalate M1, which was synthesised in this work, exhibits a vinyl group as a polymerisable unit while the carboxylate moieties serve as cation coordinating sites. Synthesis of M1 was performed via three different routes in order to evaluate the route with the highest overall yield. However, in our hands the route with the highest number of synthetic steps gave the highest overall yield. Different conditions were evaluated to obtain polymers of M1 via free radical polymerisation. Solutionbased polymerisation with different solvents gave polymers with merely low molecular weights of 18 kDa in average. Taking advantage of the low melting point of M1 it was possible to perform the polymerisation reaction in the bulk. Under these conditions polymer P1 with high molecular weights of 550 kDa could be obtained with reaction times of 24 h and reaction temperatures of approx. 150 °C. With the aim to use polymers as electroactive materials in organic batteries, P1 was postfunctionalised to the corresponding lithium salt P1-Li via two different routes. The route with stepwise hydrolysis and Li-insertion using LiHMDS was more convenient in terms of better yields and sophisticated purification.

P1-Li was investigated electrochemically using cyclic voltammetry and galvanostatic measurements. The CVs of **P1-Li** showed redox activity in a potential range of 0.5 - 1.2 V vs Li⁺/Li which assigns the material as a candidate for anode. **P1-Li** showed high irreversible losses in the first cycle, which is symptomatic for most organic materials. Galvanostatic charge-discharge cycling reveals a specific capacity of 58 mAh g⁻¹ for **P1-Li** (at a C/3 rate) which is only 22 % of the theoretical capacity. However, the polymer displays a good cycling stability, still showing a discharge capacity of 85% after 100 cycles. Especially the comparison with the parent monomer dilithium terephthalate with only 40% discharge capacity after 100 cycles reveals the superiority of the polymer in terms of cycling stability.

This class of polymers seems to be promising for application as anode material in battery applications. Nonetheless, further investigations on how to reduce the irreversible capacity (especially in the first cycle) and on how to increase the practical reversible capacity are needed before it can be used in commercial cells.

Acknowledgements

The authors are indebted to the German Federal Ministry of Education and Research (BMBF) for financial support within the project "LiEcoSafe" (contract no. 03X4636A/B). Dr Günther Götz and Dr Elena Mena-Osteritz (Ulm University) are sincerely acknowledged for fruitful discussions, and Dagmar Weirather-Köstner (ZSW) for complementary electrochemical measurements. The authors thank Zeynab Nikpoor for the graphical illustration of the TOC Figure.

References

- ¹ Y. Liang, Z. Tao, J. Chen, *Adv. Energy Mater.*, 2012, **2**, 742.
- ² Z. P. Song, H. S. Zhou, *Energy Environ. Sci.*, 2013, **6**, 2280.
- ³ P. Poizot, F. Dolhem, *Energy Environ. Sci.*, 2011, **4**, 2003.
- ⁴ M. Armand, J. M. Tarascon, *Nature*, 2008, **451**, 652.
- ⁵ K. Sakaushi, E. Hosono, G. Nickerl, T. Gemming, H. Zhou, S. Kaskel,
- J. Eckert, Nat. Commun., 2013, **4**, 1485.
- ⁶ L. Zhan, Z. Song, J. Zhang, J. Tang, H. Zhan, Y. Zhou, C. Zhan, *Electrochim. Acta*, 2008, **53**, 8319.
- ⁷ L. Zhan, Z. Song, N. Shan, J. Zhang, J. Tang, H. Zhan, Y. Zhou, Z. Li,
 C. Zhan, *J. Power Sources*, 2009, **193**, 859.
- ⁸ N. Oyama, T. Tatsuma, T. Sato, T. Sotomura, *Nature*, 1995, **373**, 598.
- ⁹ S. R. Deng, L.-B. Kong, G.-Q. Hu, T. Wu, D. Li, Y.-H. Zhou, Z.-Y. Li, *Electrochim. Acta*, 2006, **51**, 2589.
- ¹⁰ T. Janoschka, M. D. Hager, U. S. Schubert, *Adv. Mater.*, 2012, **24**, 6397.
- ¹¹ T. Jähnert, M. D. Hager, U. S. Schubert, J. Mat. Chem. A, 2014, 2, 15234.
- ¹² K. Oyaizu, H. Nishide, *Adv. Mater.*, 2009, **21**, 2339.
- ¹³ K. Nakahara, K. Oyaizu, H. Nishide, *Chem. Lett.*, 2011, **40**, 222.
- ¹⁴ P. Novák, K. Müller, K. S. V. Santhanam, O. Haas, *Chem. Rev.*, 1997, **97**, 207.
- ¹⁵ B. Häupler, A. Wild, U. S. Schubert, *Adv. Energy Mater.*, 2015, **5**, 1402034.
- ¹⁶ M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribiére, P. Poizot, J.-M. Tarascon, *Nature Mater.*, 2009, 8, 120.
- ¹⁷ L. M. Zhu, W. Shi, R. R. Zhao, Y. L. Cao, P. X. Ai, A. W. Lei, H. X. Yang, *J. Electroanal. Chem.*, 2013, **688**, 118.
- ¹⁸ J. Heinze, B. A. Frontana-Uribe, S. Ludwigs, *Chem. Rev.*, 2010,
 110, 4724.
- ¹⁹ Z. Song, Y. Qian, X. Liu, T. Zhang, Y. Zhu, H. Yu, M. Otani, H. Zhou, *Energy Environ. Sci.*, 2014, **7**, 4077.
- ²⁰ Z. Song, Y. Qian, T. Zhang, M. Otani, H. Zhou, *Adv. Sci.*, 2015, 2, 1500124.

DOI: 10.1039/C6RA24064J Journal Name

- ²¹ Z. Song, Y. Qian, M. L. Gordin, D. Tang, T. Xu, M. Otani, H. Zhan,
- H. Zhou, D. Wang, Angew. Chem. Int. Ed., 2015, 54, 13947.
- ²² L. Chen, W. Li, Y. Wang, Y. Xia, *RSC Adv.*, 2014, **4**, 25369.
- ²³ W. W. Deng, S. M. Liang, X. Y. Wu, J. F. Qian, Y. L. Cao, X. P. Ai, J.
 W. Feng, H. X. Yang, *Sci. Rep.*, 2013, **3**, 2671.
- ²⁴ H. Qin, Z. P. Song, H. Zhan, Y. H. Zhou, *J. Power Sources*, 2014, **249**. 367.
- ²⁵ G. Wittig, U. Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318.
- ²⁶ a) W. Walker, S. Grugeon, H. Vezin, S. Laruelle, M. Armand, F.
- Wudl, J.-M. Tarascon, *J. Mater. Chem.*, 2011, **21**, 1615. b) T. Yasuda, N. Ogihara, *Chem. Commun.*, 2014, **50**, 11565.
- ²⁷ L. Yang, X. Huang, A. Gogoll, M. Strømme, M. Sjödin, *Electrochim. Acta*, 2016, **204**, 270.
- ²⁸ L. Fransson, T. Eriksson, K. Edström, T. Gustafsson, J. O. Thomas, J. Power Sources, 2001, **101**, 1.
- ²⁹ K. Takei, N. Terada, K. Kumai, T. Iwahori, T. Uwai, T. Miura, *J. Power Sources*, 1995, **55**, 191.
- ³⁰ J. Xiang, C. Chang, M. Li, S. Wu, L. Yuan, J. Sun, *Cryst. Growth Des.*, 2008, **8**, 280.
- ³¹ T. L. Gall, K. H. Reiman, M. C. Grossel, J. R. Owen, *J. Power Sources*, 2003, **119–121**, 316.

Solvent-free polymerisation of vinyl terephthalate was used to obtain high molecular weight polymers, whose corresponding Li-salts underlined the superiority of polymers regarding long term stability in comparison with the monomeric counterparts.

