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Thianthrene-functionalized polynorbornenes as high-voltage materials for organic cathode-based dual-ion batteries

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Thianthrene-functionalized polynorbornenes were investigated as high-voltage organic cathode materials for dual-ion cells. The polymers show reversible oxidation reactions in solution and as a solid in composite electrodes. Constant current investigations displayed a capacity of up to 66 mAh g⁻¹ at a high potential of 4.1 V vs. Li/Li⁺.

In face of the climate change there is a strong and growing demand for storage of renewable energies. In conjunction with new techniques for their production, reliable electricity storage devices such as batteries and electrochemical capacitors are required.¹ Nowadays, the market is dominated by lead-acid batteries² and lithium-based battery systems.^{3,4} Rechargeable Li battery systems comprise the well-known Li-ion and Li-metal anode-based cell chemistries, with sulfur and oxygen being the most investigated cathodes for Li metal batteries in recent years.^{5–10} Another recently reported lithium battery system is the dual-ion cell, where graphites or other anion-accepting host materials are used as cathodes against graphite (e.g. in a dual graphite cell) or Li-metal anodes.^{11–14} The use of aqueous electrolytes has also been investigated.¹⁵ Beyond that, organic cathode materials have attracted great interest, as they can be prepared from renewable, sustainable or less-limited resources, being easy to recycle as well as potentially safer and cheaper to produce, leading to a low carbon footprint.^{16–18} Furthermore, high temperature annealing, a common procedure in the synthesis of ceramic cathode materials, is not required for the preparation of organic materials. A variety of organic cathode materials has been proposed and investigated,^{19,20} such as conducting polymers,^{21–24} organosulfur compounds,^{25–34} radical

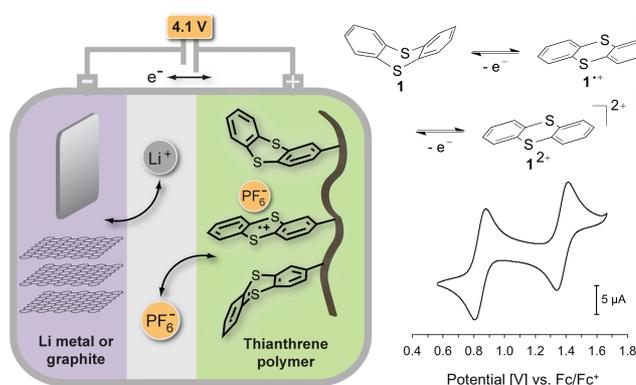


Fig. 1 Schematic of a battery with a thianthrene polymer as cathode-active anion-intercalating material (left); two-fold oxidation of thianthrene (**1**, top right) and cyclic voltammogram of **1** (1 mM in CH₃CN with 0.1 M *n*-Bu₄PF₆, glassy carbon electrode, scan rate 100 mV/s).

polymers,^{35–38} organic carbonyl compounds,^{39–42} and stable open-shell systems with high spin-delocalization.^{43–45} Some of these materials own capacities higher than that of LiCoO₂ (140 mAh g⁻¹), which is one of the most widely used cathode materials in Li-ion batteries.⁴⁶ In contrast to Li-ion deintercalating/intercalating inorganic cathode materials, organic compounds follow different reaction types such as doping/undoping,⁴⁷ bond breaking/ bond forming,⁴⁸ or oxidation/reduction of stabilized molecules embedded in a polymer structure. From the last-mentioned reaction, TEMPO-radical functionalized polymethacrylate (PTMA) is one of the most investigated organic radical materials for application in rechargeable batteries due to a fast redox process leading to high rate capabilities, while providing a stable capacity of 111 mAh g⁻¹.^{49,50} In order to compare this material with other cathode materials, it is important to understand the mechanism related to the redox reactions. The electrochemical process of PTMA is characterized by a one-electron transfer. During charging, the radical nitroxide groups of TEMPO are oxidized to oxoammonium cations leading to a build-up of positive charge. Charge balancing is achieved

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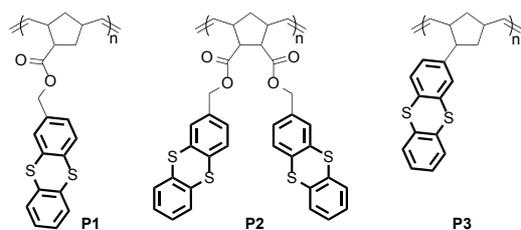
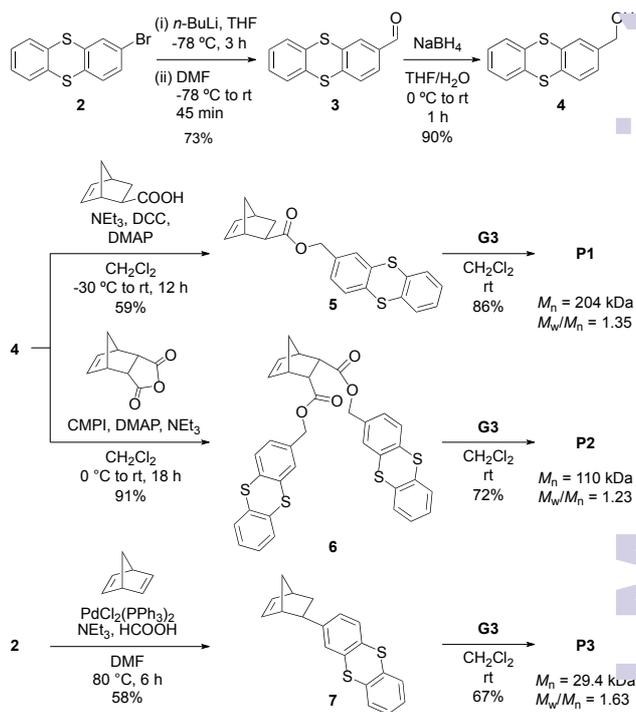


Fig. 2 Thianthrene-substituted polynorbornenes synthesized for this study.

through insertion of anions into the polymer structure such as PF_6^- from LiPF_6 -based electrolytes. On the anode side, Li^+ ions are intercalated into graphite or deposited onto lithium foil. Overall, this charge/discharge mechanism is typical for a dual-ion cell. Characteristic charge/discharge potentials for such redox systems are in the order of less than 4.0 V vs. Li/Li^+ (3.6 V vs. Li/Li^+ for PTMA).^{19,20,24,49} Even though radical polymer cathode-based batteries have high rate capabilities, the specific energy needs to be improved for being commercialized in rechargeable battery systems.²⁰ One approach to achieve higher specific energies is the increment of the working potential.^{19,20} On our search for redox-active molecules with high oxidation potentials vs. Li/Li^+ , we focused our attention on thianthrene, whose chemical oxidation to a radical cation (Fig. 1) has been known for almost 150 years.^{51,52} Thianthrene has been suggested as a chemical overcharge protection in Li-ion batteries,⁵³ however, to the best of our knowledge, these materials have not yet been investigated as electrode-active materials for charge storage. Electrochemically, thianthrene undergoes a two-step oxidation to a dication. The first oxidation potential of thianthrene lies at 0.84 V vs. Fc/Fc^+ (Fig. 1 and Table in Fig. 3), corresponding to 4.09 V vs. Li/Li^+ ,⁵⁴ making thianthrene a potential high-voltage organic cathode material. While the first oxidation was found to be a reversible reaction, the second oxidation (Fig. 1) could only be examined under extremely dry conditions.^{55–57} Another requirement for electrode materials is their insolubility in the electrolyte solution, which can be met even for organic cathodes by using a polymeric material. As such, organic redox polymers can be employed consisting of aliphatic polymer chains functionalized with redox-active side groups, which are promising candidates for use as electrode-active battery materials.⁵⁸ Polynorbornenes have been successfully employed in TEMPO-based organic cathode materials.⁵⁹ Herein, we present thianthrene-functionalized polynorbornenes **P1–P3** as a new class of anion-inserting organic cathode materials (see Fig. 1 and Fig. 2). The charge/discharge potential of these materials is in the order of 4.1 V vs. Li/Li^+ , which is, up to date, one of the highest published values for organic electrode materials, in particular considering that thianthrene is a fluorine-free compound.²⁰ These thianthrene polymers show no detectable solubility in the electrolyte solutions and are easily accessible in gram quantities in three to five synthetic steps.

P1–P3 were synthesized as shown in Scheme 1 starting from 2-bromothianthrene (**2**).⁶⁰ For the synthesis of monomers **5** and



Scheme 1 Synthesis of thianthrene-substituted polymers **P1–P3**.

6, bromide **2** was transformed into aldehyde **3**⁶¹ followed by reduction with NaBH_4 employing a protocol by Zeynizadeh and Behar⁶² to afford 2-thianthrenemethanol (**4**). Monomer **5** was accessed through esterification of alcohol **4** with exo-norbornene carboxylic acid,⁶³ while monomer **6** was synthesized by reaction of **4** with 5-norbornene-2,3-dicarboxylic anhydride and 2-chloro-1-methylpyridinium iodide (CMPI) as the coupling reagent. Monomer **7** was synthesized through a palladium-catalysed hydroarylation reaction of bromide **2** with norbornadiene. For the ring-opening metathesis polymerization (ROMP) of monomers **5**, **6** and **7**, two different catalysts were employed: Grubbs' second generation catalyst⁶⁴ and its modified version with 3-bromopyridine ligands (**G3**, for structure see SI).⁶⁵ In Scheme 1 the results of polymerizations on large scale are shown using **G3**. Due to its fast-initiating nature, **G3** has proven to be an excellent choice for norbornene polymerizations leading to low polydispersity indexes (PDIs).⁶⁶ Indeed, using **G3** polymers **P1** and **P2** were obtained with low PDIs between 1.18 and 1.35, while **G2** yielded significantly higher PDIs (for details see SI). For **P3**, the PDIs were generally higher; likely due to the steric bulk induced by the direct substitution of the norbornene ring with thianthrene. However, also in this case **G3** yielded a lower PDI compared to **G2**.

The oxidation potentials of **P1–P3** were determined using cyclic voltammetry (CV) in CH_2Cl_2 solution (Fig. 3a–c and Table in Fig. 3). In all cases, a reversible oxidation of the thianthrene side group was observed at potentials between 0.67 and 0.76 V vs. Fc/Fc^+ , which corresponds to a slight shift to lower potentials compared to thianthrene (0.84 V vs. Fc/Fc^+). This is likely due to an inductive effect of the substituents on the thianthrene core.

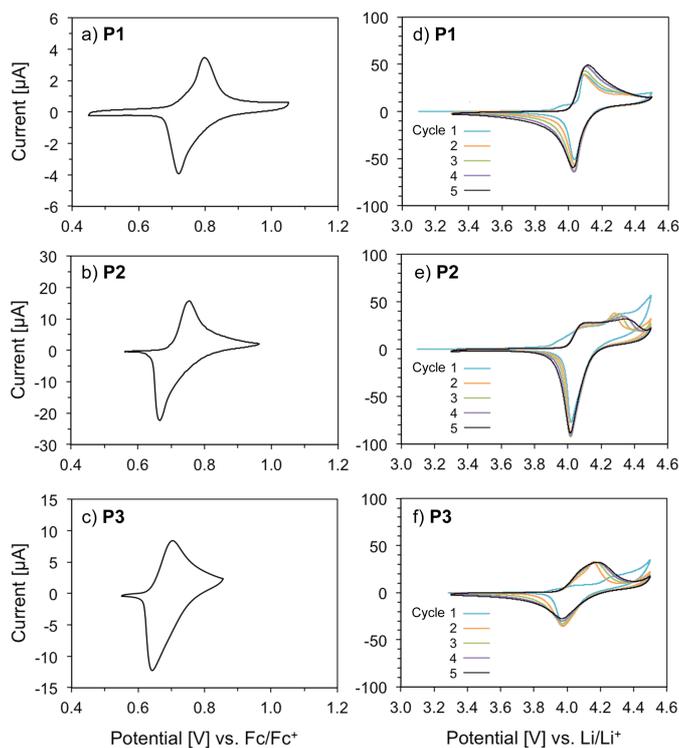


Fig. 3 Cyclic voltammograms of **P1-P3**: a)-c) in solution,^a d)-f) in composite electrodes,^b Table: Half-wave potentials [V] (related to anion coordination/insertion) for the first oxidation of thianthrene (**1**) and **P1-P3** in solution^a and in composite electrodes.^b (^a ~1 mM in CH₂Cl₂, 0.1 M *n*-Bu₄PF₆, scan rate 100 mV/s; ^b polymer/hard carbon/PVdF (10:80:10 wt%), EC/DMC (1:1), 1 M LiPF₆, scan rate 500 μV/s, counter/reference electrode: Li foil; ^c calculated using the potentials measured by Laire et al.⁵⁴)

		1	P1	P2	P3
vs. Fc/Fc ⁺	Solution ^a	0.84	0.76	0.71	0.67
	Solution ^{a,c}	4.09	4.01	3.96	3.92
vs. Li/Li ⁺	Composite cell ^b	-	4.06	4.05	4.07

To investigate the electrochemical performance of thianthrene polymers **P1-P3** as cathode-active materials in dual-ion batteries, composite electrodes with an amorphous carbon host material and PVdF binder were prepared and measured against metallic lithium. Cyclic voltammograms of the composite electrodes of **P1-P3** are shown in Fig. 3. The oxidation potentials lie between 4.05 and 4.07 V vs. Li/Li⁺ and are in good agreement with those measured in solution (Table in Fig. 3). In all cases, the first cycle differs from cycles 2-5, which is likely due to reorganization processes in the composite electrode.⁶⁷ All three polymers show good reversibility of oxidation and reduction and therefore for the insertion and deinsertion of the PF₆⁻ anion into the polymer structure. Among these, the highest current flow combined with the highest oxidation potential in solution was observed for **P1**. Hence, this material was chosen for further investigations. A composite electrode containing 50 wt% **P1**, 47 wt% carbon black (Super P Li) and 3 wt% PVdF binder was investigated regarding its charge/discharge performance vs. metallic lithium. The charge/discharge profiles of the resulting electrode cycled at 1C (full charging and discharging in 2 h) show a stable potential plateau at 4.1 V vs. Li/Li⁺ during charging and 4.05 V vs. Li/Li⁺ during discharging (Fig. 4, left),

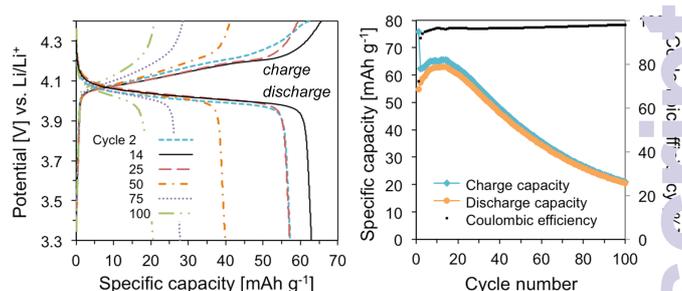


Fig. 4 Charge/discharge curves (left) and constant current cycling data (right) of a **P1** composite electrode at 1C (**P1**/Super P Li/PVdF (50:47:3 wt%), EC/DMC (1:1), 1 M LiPF₆, Li counter/reference electrode, potential range 3.3-4.4 V vs. Li/Li⁺).

which is in good agreement with the potentials observed in the CV measurements (Fig. 3). In a constant current cycling measurement (Fig. 4, right), the **P1** composite electrode achieved its highest specific capacity of 66 mAh g⁻¹ after 15 cycles.⁵⁰ This value corresponds to 90% of the theoretical capacity of **P1**, which amounts to 73 mAh g⁻¹. The Coulombic efficiency is high and lies above 96% from cycle 9 up. The capacity fading from cycle 15 up is likely due to irreversible processes in the electrode material, such as an irreversibility of the anion intercalation. The highest measured specific capacity of 66 mAh g⁻¹ at 4.1 V corresponds to a specific energy of 274 Wh kg⁻¹. In comparison, the specific energies of PTMA and LiCoO₂ are 389⁵² and 534 Wh kg⁻¹, respectively. However, compared to recently investigated dual-ion intercalation battery systems,¹¹⁻¹⁴ a capacity of > 66 mAh g⁻¹ at potentials > 4.0 V vs. Li/Li⁺ combined with potentially high rate capabilities make these polymers highly interesting as cathode-active organic materials for dual-ion battery systems. In conclusion, we have synthesized and investigated three thianthrene-substituted polynorbornenes as potential high voltage materials for organic cathode-based dual-ion batteries. Electrochemical measurements indicate reversible oxidations of the thianthrene side groups in all polymers. Derivative **1** was investigated as cathode-active material in a dual-ion battery setup against lithium metal. Composite electrodes displayed a maximum capacity of 66 mAh g⁻¹ at an unprecedented high charge/discharge potential of 4.1 V vs. Li/Li⁺.

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Notes and references

- D. Lindley, *Nature*, 2010, **463**, 18–20.
- M. Winter and J. O. Besenhard, *Chemie unserer Zeit*, 1999, **33**, 252–266.
- J. O. Besenhard and M. Winter, *Pure Appl. Chem.*, 1998, **70**, 603–608.
- R. Wagner, N. Preschitschek, S. Passerini, J. Leker and M. Winter, *J. Appl. Electrochem.*, 2013, **43**, 481–496.

- 5 A. Manthiram, Y. Fu, S.-H. Chung, C. Zu and Y.-S. Su, *Chem. Rev.*, 2014, **114**, 11751–11787.
- 6 M. A. Rahman, X. Wang and C. Wen, *J. Appl. Electrochem.*, 2014, **44**, 5–22.
- 7 A. Kraytsberg and Y. Ein-Eli, *J. Power Sources*, 2011, **196**, 886–893.
- 8 Y.-X. Yin, S. Xin, Y.-G. Guo and L.-J. Wan, *Angew. Chemie Int. Ed.*, 2013, **52**, 13186–13200.
- 9 W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang and J.-G. Zhang, *Energy Environ. Sci.*, 2014, **7**, 513–537.
- 10 V. Etacheri, R. Marom, R. Elazari, G. Salitra and D. Aurbach, *Energy Environ. Sci.*, 2011, **4**, 3243–3262.
- 11 T. Placke, P. Bieker, S. F. Lux, O. Fromm, H.-W. Meyer, S. Passerini and M. Winter, *Zeitschrift für Phys. Chemie*, 2012, **226**, 391–407.
- 12 X. Qi, B. Blizanac, A. DuPasquier, P. Meister, T. Placke, M. Oljaca, J. Li and M. Winter, *Phys. Chem. Chem. Phys.*, 2014, **16**, 25306–25313.
- 13 S. Rothermel, P. Meister, G. Schmuelling, O. Fromm, H.-W. Meyer, S. Nowak, M. Winter and T. Placke, *Energy Environ. Sci.*, 2014, **7**, 3412–3423.
- 14 T. Placke, O. Fromm, S. F. Lux, P. Bieker, S. Rothermel, H.-W. Meyer, S. Passerini and M. Winter, *J. Electrochem. Soc.*, 2012, **159**, A1755–A1765.
- 15 N. Alias and A. A. Mohamad, *J. Power Sources*, 2015, **274**, 237–251.
- 16 P. Poizot and F. Dolhem, *Energy Environ. Sci.*, 2011, **4**, 2003–2019.
- 17 M. Armand and J. Tarascon, *Nature*, 2008, **451**, 652–657.
- 18 J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359–67.
- 19 Z. Song and H. Zhou, *Energy Environ. Sci.*, 2013, **6**, 2280–2301.
- 20 Y. Liang, Z. Tao and J. Chen, *Adv. Energy Mater.*, 2012, **2**, 742–769.
- 21 J. F. Mike and J. L. Lutkenhaus, *J. Polym. Sci. Part B Polym. Phys.*, 2013, **51**, 468–480.
- 22 J. F. Mike and J. L. Lutkenhaus, *ACS Macro Lett.*, 2013, **2**, 839–844.
- 23 H. E. Katz, P. C. Searson and T. O. Poehler, *J. Mater. Res.*, 2010, **25**, 1561–1574.
- 24 P. Novák, K. Müller, K. S. V. Santhanam and O. Haas, *Chem. Rev.*, 1997, **97**, 207–282.
- 25 J. Y. Zhang, L. B. Kong, L. Z. Zhan, J. Tang, H. Zhan, Y. H. Zhou and C. M. Zhan, *J. Power Sources*, 2007, **168**, 278–281.
- 26 L. Zhan, Z. Song, N. Shan, J. Zhang, J. Tang, H. Zhan, Y. Zhou, Z. Li and C. Zhan, *J. Power Sources*, 2009, **193**, 859–863.
- 27 L. Z. Zhan, Z. P. Song, J. Y. Zhang, J. Tang, H. Zhan, Y. H. Zhou and C. M. Zhan, *J. Appl. Electrochem.*, 2008, **38**, 1691–1694.
- 28 J. Tang, Z.-P. Song, N. Shan, L.-Z. Zhan, J.-Y. Zhang, H. Zhan, Y.-H. Zhou and C.-M. Zhan, *J. Power Sources*, 2008, **185**, 1434–1438.
- 29 J. Tang, L. Kong, J. Zhang, L. Zhan, H. Zhan, Y. Zhou and C. Zhan, *React. Funct. Polym.*, 2008, **68**, 1408–1413.
- 30 L. Zhan, Z. Song, J. Zhang, J. Tang, H. Zhan, Y. Zhou and C. Zhan, *Electrochim. Acta*, 2008, **53**, 8319–8323.
- 31 J. Zhang, L. Kong, L. Zhan, J. Tang, H. Zhan, Y. Zhou and C. Zhan, *Electrochem. Commun.*, 2008, **10**, 1551–1554.
- 32 J. Zhang, Z. Song, L. Zhan, J. Tang, H. Zhan, Y. Zhou and C. Zhan, *J. Power Sources*, 2009, **186**, 496–499.
- 33 T. Sarukawa and N. Oyama, *J. Electrochem. Soc.*, 2010, **157**, F23–F29.
- 34 S. E. Burkhardt, S. Conte, G. G. Rodriguez-Calero, M. a. Lowe, H. Qian, W. Zhou, J. Gao, R. G. Hennig and H. D. Abruña, *J. Mater. Chem.*, 2011, **21**, 9553–9563.
- 35 E. P. Tomlinson, M. E. Hay and B. W. Boudouris, *Macromolecules*, 2014, **47**, 6145–6158.
- 36 T. Janoschka, M. D. Hager and U. S. Schubert, *Adv. Mater.*, 2012, **24**, 6397–6409.
- 37 K. Nakahara, K. Oyaizu and H. Nishide, *Chem. Lett.*, 2011, **40**, 222–227.
- 38 H. Nishide, K. Koshika and K. Oyaizu, *Pure Appl. Chem.*, 2009, **81**, 1961–1970.
- 39 S. Wang, L. Wang, Z. Zhu, Z. Hu, Q. Zhao and J. Chen, *Angew. Chem. Int. Ed.*, 2014, **53**, 5892–5896.
- 40 H. Chen, M. Armand, M. Courty, M. Jiang, C. P. Grey, F. Dolhem, J. Tarascon, P. Poizot and J. Verne, *J. Am. Chem. Soc.*, 2009, **131**, 8984–8988.
- 41 M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribière, P. Poizot and J.-M. Tarascon, *Nat. Mater.*, 2009, **8**, 120–125.
- 42 X. Han, C. Chang, L. Yuan, T. Sun and J. Sun, *Adv. Mater.*, 2007, **19**, 1616–1621.
- 43 Y. Morita, S. Nishida, T. Murata, M. Moriguchi, A. Ueda, M. Satoh, K. Arifuku, K. Sato and T. Takui, *Nat. Mater.*, 2011, **10**, 947–951.
- 44 Y. Morita, T. Aoki, K. Fukui, S. Nakazawa, K. Tamaki, S. Suzuki, A. Fuyuhiko, K. Yamamoto, K. Sato, D. Shiomi, A. Naito, T. Takui and K. Nakasuji, *Angew. Chem. Int. Ed.*, 2002, **41**, 1793–1796.
- 45 Y. Morita, S. Nishida, J. Kawai, K. Fukui, S. Nakazawa, K. Sato, D. Shiomi, T. Takui and K. Nakasuji, *Org. Lett.*, 2002, **4**, 1985–1988.
- 46 J. Rana, R. Kloepsch, J. Li, T. Scherb, G. Schumacher, M. Winter and J. Banhart, *J. Mater. Chem. A*, 2014, **2**, 9099–9110.
- 47 M. Armand, *Le J. Phys. Colloq.*, 1983, **44**, C3–551–C3–557.
- 48 M. Liu, S. J. Visco and L. C. De Jonghe, *J. Electrochem. Soc.*, 1999, **136**, 2570–2575.
- 49 H. Nishide and T. Suga, *Electrochem. Soc. Interface*, 2005, **14**, 32–36.
- 50 Capacities reported per mass of active material.
- 51 J. Stenhouse, *Proc. R. Soc. London*, 1868, **17**, 62–67.
- 52 J. Stenhouse, *Justus Liebigs Ann. Chem.*, 1869, **149**, 247–255.
- 53 D.-Y. Lee, H.-S. Lee, H.-S. Kim, H.-Y. Sun and D.-Y. Seung, *Korean J. Chem. Eng.*, 2002, **19**, 645–652.
- 54 C. O. Laoire, E. Plichta, M. Hendrickson, S. Mukerjee and K. M. Abraham, *Electrochim. Acta*, 2009, **54**, 6560–6564.
- 55 J. Beck, T. Bredow and T. R. Tjahjanto, *Zeitschrift für Naturforsch.*, 2009, **64b**, 145–152.
- 56 L. A. Tinker and A. J. Bard, *J. Am. Chem. Soc.*, 1979, **101**, 2316–2319.
- 57 O. Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537–541.
- 58 R. Gracia and D. Mecerreyes, *Polym. Chem.*, 2013, **4**, 2206–2214.
- 59 T. Sukegawa, A. Kai, K. Oyaizu and H. Nishide, *Macromolecules*, 2013, **46**, 1361–1367.
- 60 H. Morita, Y. Oida, T. Ariga, S. Fukumoto, M. C. Sheikh, T. Fujii and T. Yoshimura, *Tetrahedron*, 2011, **67**, 4672–4679.
- 61 J. M. Lovell and J. A. Joule, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2391–2395.
- 62 B. Zeynizadeh and T. Behyar, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 307–315.
- 63 J. K. Pontrello, M. J. Allen, E. S. Underbakke and L. L. Kiessling, *J. Am. Chem. Soc.*, 2005, **127**, 14536–14537.
- 64 M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953–956.
- 65 J. A. Love, J. P. Morgan, T. M. Trnka and R. H. Grubbs, *Angew. Chemie Int. Ed.*, 2002, **41**, 4035–4037.
- 66 T.-L. Choi and R. H. Grubbs, *Angew. Chemie Int. Ed.*, 2003, **42**, 1743–1746.
- 67 J.-W. Jeon, Y. Ma, J. F. Mike, L. Shao, P. B. Balbuena and J. L. Lutkenhaus, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9654–62.