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Empowering organic-based negative electrode material based on conjugated lithium carboxylate through molecular design

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TABLE OF CONTENT



Liz-ADC based composite electrode

ABSTRACT

In this article, we describe the design and gram-scale synthesis of a new anthracenebased negative electrode material for Li-ion batteries. Based on rational design, featuring a strong electronic delocalization and a long conjugation length, this material has power performance to date unmatched for a conjugated lithium carboxylate, displaying a gravimetric capacity of 150 mAh.g⁻¹ at a cycling rate of 20 Li⁺/h (10C) without any electrode engineering. Additionally, to the design, partial solubility of the fully reduced phase may also explain the electrochemical performances obtained at low and high rate.

INTRODUCTION

We are currently facing global climate change mainly caused by global warming. This increase is directly linked to the release of greenhouse gases by human activities, which is constantly increasing. To hamper this critical issue, a complete overhaul of our habits in terms of transport, energy production and consumption is required. This has already started with the growth of renewable energies. However, owing to the intermittency of these processes, it is essential to have efficient storage systems for delivering on-demand and transporting the energy thus produced.

Ion batteries are currently the most efficient systems addressing these specifications. Nevertheless, the electroactive compounds used as an electrode in these systems are exclusively inorganic materials based on Co, Mn, Fe, Ni, V, which are exhaustible, difficult to recycle and sometimes toxic.¹ In parallel to the eco-conception of electroactive materials^{2–4} and the recycling of current Li-ion batteries constitutants,⁵ a promising solution to overcome these problems is to use renewable resources such as organic compounds, from inedible agroresources and/or "green" sustainable synthesis processes taking into account the resource aspect and ecological sustainability, to create sustainable, efficient and easy recycling electrical energy storage systems.⁶ For now, Organic batteries field benefits of more than ten years of intensive

research and is still an active research area. ^{7–9} Positioned between sulfur and intercalation compound in the battery materials landscape,¹⁰ performances of organic electrode materials have strongly evolved representing a serious alternative in support to inorganic compounds and to the constantly growing demand for more sustainable batteries. These last years, several improvements were realized like high potential and high power positive electrode materials^{11–13} and high specific capacity.^{14–20} From our side, we focused on the enhancement of the rate capability of conjugated lithium carboxylate, used as a negative electrode. Based on our previous studies on naphthalene,²¹ perylene²² and biphenyl²³ derivatives, it is now established that kinetic properties of the materials depend on the electronic conjugation of the aromatic ring on one hand and of the length and nature of the spacer and the associated crystallographic opening of the material structure on the other hand.

On this basis, we capitalize our expertise to design a new material to improve the power performances of the family of conjugated lithium carboxylate derivatives. The anthracene core, well-known in the optoelectronic field, was selected as a basis to welcome electroactive function. Anthracene derivatives caught interest in the last ten years since the discovery of remarkable electroluminescence, photoluminescence and semiconducting properties.²⁴ This family of molecules is nowadays integrated into various application fields like electronics,²⁵ sensing²⁶ or supramolecular chemistry.²⁷ They have also been used as an emitter and electrical transport layer in organic light-emitting diodes (OLED) in which they serve as building blocks for the design of new robust materials.²⁸ To make it electroactive at low potential, we have developed the synthesis of the 2,6-anthracene dicarboxylate lithium (Li₂-ADC) which has a strong electronic delocalization and in the same time has a slightly larger size than the dilithium 4,4'-Biphenyl dicarboxylate also known as Li₂-BPDC (Figure 1).

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Figure 1: Evolution of the distance between the two end carboxylates (carbon-carbon distance) and electrostatic map, obtained using Spartan 18 software, in different centrosymmetric aromatic organic conjugated lithium carboxylate used as a negative electrode material. In the electrostatic maps, electron-poor and electron-rich regions are indicated respectively in blue and red.

Li₂-ADC was synthesized at gram scale from cheap and commercially available 2,6-diamino anthraquinone and exhibits outstanding rate capability with 160 mAhg⁻¹ at 20 Li⁺/h (10C) rate which is the higher value reported in the literature at te best of our knowledge.

RESULTS AND DISCUSSION

Unlike the previously described materials based on naphthalene, perylene and biphenyl,^{21–23} 2,6-anthracene dicarboxylic acid (ADC) is not commercially available. Multiple strategies and synthetic routes have been explored to obtain Li₂-ADC on a multiple gram scale. The most efficient synthetic pathway in our hands starts from 2,6-diaminoanthraquinone. Li₂-ADC was prepared in a 7-step sequence with a 30% overall yield (Scheme 1). Two functional group transformations were identified as key steps: the introduction of carboxylic groups from amino derivatives (from diaminoanthraquinone to 3) and the reduction of anthraquinone to anthracene (from 3 to 6).^{29–32}



<u>Scheme 1</u>: Preparation of 2,6-anthracene dicarboxylic acid from 2,6-diaminoanthraquinone. (i) *t*-BuONO, CuBr₂, ACN, 80°C, 96%. (ii) CuCN, NMP, 180°C, 6h, 98%. (iii) H₂SO₄, water, 160°C, 80%. (iv) Zn, NH₄OH, 80°C, 95%. (v) CH₃I, Li₂CO₃, DMF, RT, 78%. (vi) DDQ, Toluene, 115°C, 70%. (vii) NaOH, EtOH, 70°C, 88%.

Targeted lithium carboxylate (Li₂-ADC) was then obtained by refluxing the diacid in an EtOH solution of lithium hydroxide, enabling crystallization of the titled compound (**8**) (Figure 2a). Complete lithiation was evidenced by ¹H NMR with shielding the characteristic peaks of the carboxylic acid (Figure 2b). Signals corresponding to the isolated protons 1 and 9 (Figure 2a) are shielded after the deprotonation, shifting from 8.89 and 8.83 ppm to 8.47 and 8.45 ppm, respectively (Figure 2b). The peaks corresponding to the protons 3 and 4 are also affected with shifts from 8.21 to 7.98 ppm and 7.98 to 7.89 ppm, respectively (Figure 2b). Solid-state ¹³C NMR analysis confirms the total conversion of the carboxylic acid groups to lithium carboxylate with a shift of the peaks corresponding to the carbonyl groups from 170 ppm to 176 ppm (Figure 2c). A change in the ¹³C NMR chemical shifts of the aromatic carbon atoms is also observed, evolving from large peaks to 4 narrower peaks. FT-Infrared spectroscopy analysis leads to the same conclusions with the disappearance of the broad peak corresponding to O-H group between 2000 cm⁻¹ and 3500 cm⁻¹ in the carboxylic acid form to 1420 cm⁻¹ for the lithium carboxylate (Figure 2d).



Figure 2: (a) Synthesis of dilithium 2,6-anthracene dicarboxylate (Li₂-ADC) from 2,6-anthracene dicarboxylic acid (ADC). Comparison between ADC (blue curves) and Li₂-ADC (red curves) by (b) liquid-state ¹H NMR (400 MHz) in DMSO-*d*₆, (c) solid-state ¹³C NMR (500 MHz) using CP-MAS sequence and (d) FTIR in transmission mode.

The lithiation process also leads to structural notable modifications as evidenced by powder Xray diffraction (Figure 3a). While only three very large diffraction peaks are observed for the acid form, indicating a strong disorder in the initial structure, the diffraction pattern of the corresponding lithiated form reveals intense and highly resolved peaks. Scanning electron microscopy also shows an important morphological change. The carboxylic acid ADC is organized into rods 10 μ m long and 3 μ m wide (Figure 3b) while the dilithium salt forms mainly agglomerates of small particles whose size is in the order of 400-700 nm (Figure 3c). This change in textural parameters can be explained by the partial dissolution of acid in ethanol followed by precipitation of the lithium salt which is very poorly soluble in this solvent.



Figure 3: Comparison between Li₂-ADC (red curve) and ADC (black curve) by (a) powder X-ray diffraction and (b and c) by Scanning Electron Microscopy.

In terms of storage performances, Li₂-ADC has an electrochemical signature similar to the one generally obtained with lithium carboxylate with the presence of a low potential 2e⁻-plateau traducing a bi-phasic type lithium insertion/deinsertion reaction (Figure 4). The reduction potential is situated at 0.81 V (vs. Li⁺/Li) indicating that the addition of an aromatic ring (from naphthalene to anthracene) has little influence on the redox potential. The particularity of Li2-ADC comes from the exceptional power behaviour compared to the set of conjugated lithium carboxylate-based materials described so far.^{22,23,33–39} Indeed, up to 5 Li⁺/h (maximum speed for the Li₄-PTC for instance), Li₂-ADC exhibits complete electrochemical activity (reversibility of 2 Li⁺, specific capacity of 190 mAh.g⁻¹) associated with a quite low polarization of about 160mV despite a high regime and lack of optimization of the electrode (Figure 4a and 4b). At even higher cycling rate, namely, 10 Li^+/h and 20 Li^+/h , the electrochemical activity is always present with an outstanding reversible capacity on the first cycles of 166 mAh.g⁻¹ and 162 mAh.g⁻¹ respectively, despite an increase on the polarization reaching about 320 mV (Figure 4c and 4d). To the best of our knowledge, these performances were never obtained for a conjugated lithium carboxylate-based material without electrode formulation and recall the story about Li₄-PTC.^{22,40}



Figure 4: Galvanostatic potential-composition profiles for Li2-ADC manually grind with 40% carbon mass Super P at regime of (a) 2 Li⁺/h, (b) 5 Li⁺/h, (c) 10 Li⁺/h and (d) 20 Li⁺/h rate.

It is interesting to note the absence of the bump of potential observed at the end of oxidation for Li₂-BPDC and belonging with the solvent intercalation.²³ This fact is probably the consequence of the greater distance between the two carboxylates for Li₂-ADC that would accommodate even better to the penetration of the solvated ion and/or electrolyte in material structure. After 50 cycles, Li₂-ADC still displays impressive capabilities especially at very high speeds with specific capacities of 144 mAh.g⁻¹, 134 mAh.g⁻¹ and 133 mAh.g⁻¹ at speeds of 5 Li⁺/h, 20 Li⁺/h and 10 Li⁺/h respectively (Figure 5).



Figure 5: Evolution of the gravimetric capacity at different regimes (from 0.4 Li⁺/h to 20 Li⁺/h) as a function of the number of cycles and illustration of the origin of both rate capability rise and loss of capacity at a low rate.

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Despite such performances at a high rate, the cycling of Li₂-ADC at a lower rate reveals a decrease in capacity at a regime of 2 Li⁺/h (111 mAh.g⁻¹) and becoming drastically significant at 0.4 Li⁺/h (37 mAh.g⁻¹) independently of the electrolyte concentration or type used. One possible explanation of this gradual fading, also observed for previously reported high rate cycling materials based on lithium carboxylate, could be the solubility of the materials (never observed for lithium carboxylate). In the present case, since a solvent change was realized for the lithiation reaction (ethanol instead of methanol), this fact can make sense. To verify solubility of the material at the reduced state (Li₄-ADC phase), a specific electrochemical cell including Li₂-ADC/composite was assembled and reduced until 0.5V at a low rate (0.4Li⁺/h). The cell was allowed to stand for 48h at this state before being opened. The separators were then collected and compared with pure and impregnated separators with LP30. Since anthracene derivatives are fluorescent (emission of a blue fluorescence when exposed to UV-light),⁴¹ separators were exposed to such type of radiation (335nm precisely) to perceive any fluorescent compound. While pure and impregnated separators are uncolored, the separator recovered from the cell shows a blue fluorescence signal attributed to the anthracene derivative. This observation indicated that the reduced state of the molecular compound tends to solubilize in the electrolyte and can explain the capacity fading at a low rate. The same experiments were realized on separators of cycled cells at a high rate. No fluorescence was detected in the separators which indicated that no materials were dissolved in the electrolyte at a high rate, presumably because of the cycling kinetics. At a sufficient rate, the dissolution of the reduced phase is not sufficient to cause capacity fading. Based on this fact, it might be possible to have only surface solubility of the material (and directly followed by reprecipitation on the surface of the materials particle or insoluble part). This could lead to explain the excellent power performances by the boosting of the electron transfer from the conductive additive particle to the material and vice-versa though a molecular shuttling effect (Figure 5).

CONCLUSIONS

We presented here the rational design of a new conjugated lithium carboxylate including an anthracene unit as negative electrode materials for lithium-ion batteries. Owing to the strong electronic delocalization of the anthracene unit coupled with the high conjugation distance between the two carboxylates (opening of the material), this material exhibits an excellent rate capability with 77% of the theoretical gravimetric capacity after 50 cycles at 20 Li⁺/h rate without any formulation engineering. Additionally to the specific design, the outstanding power performances may also be attributed to the partial solubility of the molecular material at the reduced state promoting an electronic shuttle effect between conductive additive particle and active material.

EXPERIMENTAL SECTION

Reagents and Chemicals

All the compounds used were purchased either from Alfa Aesar or Sigma-Aldrich. All the solvents were purchased from Fischer scientific. Deuterated dimethylsulfoxide (DMSO-*d6*) was purchased from Euriso-top. All solvents and reagents were used as received.

Instrumentation

FT-IR (Fourier Transform Infra-Red) spectra were recorded in transmission mode at room temperature using a Nicolet AVATAR 370 DTGS spectrometer from Thermo Electron Corporation. Spectra were acquired over a range of 4000 to 400 cm⁻¹ with a resolution of 2 cm⁻¹. ¹H liquid NMR (Nuclear Magnetic Resonance) spectra were recorded on a Bruker 300 MHz spectrometer, chemical shifts are reported in parts per million (ppm) and coupling constants (*J*) values are given in hertz. The solid-state ¹³C-NMR experiments were carried out at room temperature on a Bruker Avance I wide-bore spectrometer operating at a ¹H Larmor frequency of 300 MHz, with a Bruker 4 mm double resonance CPMAS probe-head. The magic

angle spinning rate was 12.5 kHz. All 13 C chemical shifts presented in this manuscript were referenced with respect to the CH₂ resonance of adamantane at 38.48 ppm with respect to neat TMS.

X-Ray Powder Diffraction patterns (XRPD) were acquired using a Bruker D8 diffractometer equipped with a Cu anti-cathode (K_{α} radiation, operating at 40 kV–40 mA). Patterns were collected in the 2 θ range of 10–60° with a step size of 0.03°. The particles morphology and their size were estimated by Scanning Electron Microscopy (SEM) using an environmental FEI Quanta 200 FEG-microscope.

Electrochemical performances were determined using 2 electrodes Swagelok-type cell assembled in an argon-filled glovebox. For this, a typical working electrode was composed of *ca.* 10 mg of active material (60%) manually mixed with 40 % of Super P carbon. It was separated from a lithium foil playing both the role of counter and reference electrode by two Whatman fibreglass sheets soaked with LiPF₆ (1M) in ethylene carbonate-dimethyl carbonate (EC-DMC) 1/1 (v/v) mixture (LP30 electrolyte, certified battery purity grade, Merck). The different galvanostatic measurements were recorded between 3 V and 0.4 V (vs. Li⁺/Li) using a Biologic VMP potentiostat/galvanostat.

Synthesis of Li₂-ADC

2,6-dibromo-9,10-anthraquinone (1):29

Copper (II) Bromide (21.09 g, 94.42mmol) was dissolved in 90 mL of anhydrous acetonitrile and *tert*-butyl nitrite (26.2 mL, 220.36mmol) was slowly added under stirring. The mixture was heated to 70°C and 2,6-diaminoanthraquinone (1) (15 g, 62.96mmol) were added over for 10 minutes. Strong release of nitrogen is observed. When the nitrogen evolution has stopped, the mixture was cooled at room temperature and was poured into an aqueous solution of HCl (20% v/v) under vigorous stirring during 20 minutes. Then the precipitate was recovered by filtration and was washed several times with water to give a yellow-brown product (22.10 g, 96% yield).

¹H NMR (400 MHz, CDCl₃), δ in ppm: 8.43 (d, J = 2.00 Hz, 2H), 8.17 (d, J = 8.30 Hz, 2H), 7.94 (dd, J = 2.00 Hz, J = 8.30 Hz, 2H); ¹³C NMR (100.62 MHz, CDCl₃), δ in ppm: 181.43, 137.55, 134.47, 131.90, 130.52, 130.34, 129.29. IR (KBr): 3091, 3065, 1673, 1573, 1313, 1282, 1160, 1065, 826, 730.

2,6-dicyano-9,10-anthraquinone (2):³⁰

A mixture of Copper (I) Cyanide (17.61 g, 196.72mmol) and 2,6-dibromo-9,10-anthraquinone (1) (18 g, 49.18 mmol) were added in 220 mL of NMP and stirred. The mixture was heated to 190°C for 8 hours, then cooled at room temperature and then precipitated in water (300 mL). A solid dark compound was filtered and washed with a saturated EDTA solution to eliminate residual Copper. After washing with EDTA solution until complete discoloration, the powder was washed again with water to give a brown solid (12.5 g, 98.5% yield) and was used without further purification.

¹H NMR (400 MHz, DMSO-*d*₆), δ in ppm: 8.61 (d, *J* = 35.5 Hz, 2H), 8.34 (s, 2H), 7.73 (s, 1H). IR (KBr): 3091, 3043, 2230, 1678, 1600, 1317, 1295, 1195, 860, 730

2,6-Anthraquinone dicarboxylic acid (3):³⁰

2,6-dicyano-9,10-anthraquinone (**2**, 12 g, 46.47mmol) was stirred in 53 mL of water and then (158 mL, 4.92mol) of sulphuric acid (95%) was slowly added under vigorous stirring. The mixture was heated to 160°C for 6h and was cooled to room temperature. The mixture was poured into 160 mL of water under stirring for 20 minutes then filtered and washed with water to give a pale brown powder (11 g, 80% yield).

¹H NMR (400 MHz, CDCl₃), δ in ppm: 8.54 (s, 2H), 8.31 (d, *J* = 6.8 Hz, 2H), 8.20 (d, *J* = 7.7 Hz, 2H). ¹³C NMR (100.62 MHz, CDCl₃), δ in ppm: 181.27, 165.76, 135.76, 135.37, 134.52, 132.94, 127.38. IR (KBr): 3343, 3047, 2634, 2360, 1695, 1604, 1478, 1430, 1273, 969, 869, 713

9,10-dihydro-anthracene-2,6-dicarboxylic acid (4):³¹

A mixture of 2,6-anthraquinone dicarboxylic acid (**3**, 9 g, 30.38 mmol) and 90 mL of ammonium hydroxide (28% in water) was stirred and zinc powder (12.5 g, 191.4 mmol) was added before heating to 80°C and maintained at this temperature until the end of the reaction. The mixture was stirred for 24h and an additional 10 mL of ammonium hydroxide was added through this period until the red colour disappeared. Then, the mixture was filtered to remove zinc powder and was acidified with 35% concentrated aqueous HCl. A yellow precipitate was recovered by filtration and washed with water and dried under vacuum to give 7.75 g (95% Yield).

¹H NMR (400 MHz, DMSO-*d*₆), δ in ppm: 12.84 (s, 2H), 7.93 (s, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 4.07 (s, 4H). ¹³C NMR (100.62 MHz, DMSO-*d*₆), δ in ppm: 167.30, 141.59, 136.40, 128.76, 128.16, 127.47, 127.32, 39.52, 35.27. IR (KBr): 3434, 3017, 2804, 2000, 1704, 1617, 1569, 1408, 1265, 930, 752

Dimethyl-9,10-dihydro-2,6-anthracenedicarboxylate (5):

In 110 ml of DMF, 8 g of 9,10-dihydro-anthracene-2,6-dicarboxylic acid (4) (29.82 mmol) and 13.2 g of lithium carbonate (178.9 mmol) were added under vigorous stirring. Then 11.2 ml of methyl iodide (178.9 mmol) was added and the mixture was stirred at room temperature for 48 h. The mixture was poured in 300 ml of aqueous HCl solution (1M) then the precipitate was filtered and washed several times with water. The solid was dried under reduced pressure to afford (5), as a brown solid (6.8 g, 78%) which was used without further purification.

¹H NMR (400 MHz, DMSO-*d*₆), δ in ppm: 7.94 (s, 2H), 7.81 (d J=7.6 Hz, 2H), 7.47 (d, J=7.82 2H), 4.08 (s, 2H), 3.86 (s, 3H). ¹³C NMR (100.62 MHz, DMSO-*d*₆), δ in ppm: 166.20, 142.00, 136.53, 127.94, 127.62, 127.16, 52.00, 39.73, 35.18. IR (KBr): 3021, 2947, 1713, 1669, 1434, 1317, 1247, 1086921, 752

Dimethyl-2,6-anthracenedicarboxylate (6):

A mixture of Dimethyl-9,10-dihydro-2,6-anthracenedicarboxylate (5), (6 g, 20.25 mmol), 2,3dichloro-5,6-dicyano-1,4-benzoquinone (12.73 g, 56.09 mmol) in toluene (125 mL) was stirred at 115°C for 3h. The mixture was cooled at room temperature and filtered under vacuum. The precipitate was washed several times with toluene and then methanol until complete discoloration. The solid was dried under reduced pressure to give dimethyl anthracene-2,6dicarboxylate (6), (4.2 g, 70 %) as a brown solid.

¹H NMR (400 MHz, CDCl₃), δ in ppm: 8.82 (s, 2H), 8.59 (s, 2H), 8.20–7.93 (m, 4H), 4.02 (s, 6H). ¹³C NMR (100.62 MHz, CDCl₃), δ in ppm: 167.01, 132.98, 132.10, 131.82, 128.76, 128.58, 127.98, 124.60, 77.00, 52.38. IR (KBr): 3013, 2956, 1713, 1665, 1430, 1313, 1082, 921, 873, 756.

2,6-Anthracene-dicarboxylic acid (7):

To a suspension of 4 g of dimethyl-2,6-anthracenedicarboxylate (6) (13.59 mmol) in 70 mL of ethanol was added 7.62 g of KOH (135.91 mmol). The mixture was heated at reflux under stirring overnight. The mixture was cooled at room temperature and poured to 1M aqueous HCl solution (200 mL) then the dark brown precipitate was collected by vacuum filtration. The dark brown solid was washed several times with water dried under reduced pressure to afford anthracene-2,6-dicarboxylic acid (ADC, **7**) (3.2 g; 88 % yield).

¹H NMR (400 MHz, DMSO-*d*₆) δ in ppm: 8.89 (s, 2H), 8.83 (d, J = 1.5 Hz, 2H), 8.21 (d, J = 8.9 Hz, 2H), 7.98 (dd, J = 8.9, 1.6 Hz, 2H). ¹³C NMR (300MHz, DMSO-*d*₆), δ in ppm: 167.25,

132.40, 131.67, 131.52, 131.36, 128.80, 128.53, 124.57. IR (KBr): 3352, 1934, 1678, 1621, 1473, 1408, 1273, 921, 747

Dilithium 2,6-Anthracene dicarboxylate (Li2-ADC) :

To a suspension of 0.5 g of 2,6-anthracene dicarboxylic acid (ADC) in 20 mL of ethanol was added 3 equivalents of LiOH. The mixture was then heated under stirring at reflux overnight to yield to the crystallization of the di-lithium salt as a brow powder (yield 89 %). The solid was collected by centrifugation and washed successively with pure ethanol, acetone and diethyl ether. The powder was finally dried under vacuum at 80°C and transferred into an argon-filled glovebox for storage.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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