Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
Materials Chemistry A

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COMMUNICATION

Hyper-conjugated lithium carboxylate based on perylene unit for high-rate organic lithium-ion batteries

L. Fédèle,[a-c] F. Sauvage, [a-c] and M. Becuwe*[a-c]

A high-rate cycling lithium carboxylate-based organic anode material using perylen core as stabilization platform is described. The hyper-conjugated core unit of perylene associated with lithium carboxylate confers to the electrode an outstanding rate capability without any electrode formulation engineering, maintaining over 120 mAh.g^{-1} after one hundred cycles at 5 Li$^+$/1h rate.

The current energetic context prompts research and development of new alternative electrode materials, firstly to cut electrochemical storage cost, but also to anticipate the ever strengthening environmental regulations aiming at lowering ecological footprint, toxicity and ease waste recyclability.[1] One approach, led for the last few years, envisions the integration of organic electrodes, some of which can be issued from biomass resources from the cradle to the grave.[2,3] More favorable, organic-based electrode materials have gained much interest as an alternative to the benchmarked inorganic class of insertion materials, although their electrochemical performances in terms of gravimetric and volumetric energy density still lag behind.[4,5] The richness of organic chemistry paves the way to a broad variety of chemical and crystallographic structures affording "easier" control of the HOMO/LUMO energetics, electronic distribution within the molecular framework or new molecular brick assembly for smarter electrochemical storage systems (*e.g.* metal-organic framework,[6,7] hybrid materials[8-10]). Inspired from the Metal-Organic Framework (MOF), Tarascon *et al.* proposed a new family of organic electrodes based on two redox-active lithium carboxylate functions separated by a π-conjugated aromatic phenyl ring (di-lithium terephthalate). The properties of lithium carboxylates are particularly appealing because of their favorable ratio between number of electron exchange (Δ_x) vs. molecular weight (M_w), their high structural robustness upon successive charge/discharge sequences and their electrochemical reactivity lying below 1 V (vs. Li$^+$/Li) making them attractive as a negative electrode for lithium-ion batteries.[11-13] This first work has initiated both fundamental and applied researches. Keeping the same phenyl ring core unit, it has been shown high energy amplitude between the dilithium terephthalate and the closely related quinone

derivatives which attains close to 2 eV.[14] By contrast to redox active function, the subtle role played by the central unit remains not completely understood, beside its influence on radical anion stabilization by mesomerism. For instance, substitution on the phenyl ring by introducing electron donor or electron acceptor moieties can modify by a few hundreds of meV the energy at which the lithium inserts/de-inserts into/from the carboxylate, but in turn strongly hampers the reversibility of the lithium insertion.[15,16] To our current understanding, we postulate that uniform electronic distribution in the π-spacer is required. On a second aspect, we recently intuited that π-aromatic conjugation enhancement through naphthyl core unit has little effect on the redox potential but offers greater rate capability to the carboxylate function.[17] We achieved on di-lithium 2,6-naphtalene di-carboxylate a gravimetric capacity of around 115 mAh.g^{-1} at 2 Li$^+$/1h rate over 50 cycles.

Confirming this first intuition, we highlight in this work the achievement of an unprecedented rate capability on lithium carboxylate-based electrode by means of molecular engineering of the π-spacer through a suitable introduction of a hyper-conjugated perylene core unit which on the one hand extends further the intramolecular π-aromatic conjugation between the lithium carboxylates, conferring at once a centro-symmetric crystal structure and high stability of the radical anion. More precisely, Tetralithium perylen-3,4,9,10-tetracarboxylate (Li$_4$-PTC) was successfully synthesized through a one-pot hydrolysis/lithiation reaction of the corresponding dianhydride (PTCDA) counterpart (Fig. 1a). The obtention of the tetralithium salt was confirmed by ^{1}H liquid NMR in deuterated water (†ESI Fig. S1) consistently data reported in the literature for alkaline derivative.[18,19,25]

Solid-state NMR ^{13}C experiments, using CP-MAS sequence, were carried out to show the carbon structure evolution between the pristine PTCDA and the material retrieved after the one pot hydrolysis/lithiation process (Fig. 1b). This comparison highlights that the initial peak at 157 ppm, ascribed to the carbonyl dianhydride unit, has entirely vanished after the reaction. In parallel, for the product retrieved, a new peak appears at 179 ppm for which the chemical shift is characteristic of a lithium carboxylate group.[20] The

aromatic peaks at 132, 124/122 and 114 ppm are corresponding to the aromatic carbon in position #2, #3 and #4.[21] These positions are also noticeably affected by the opening reaction of the two di-anhydride ending groups.
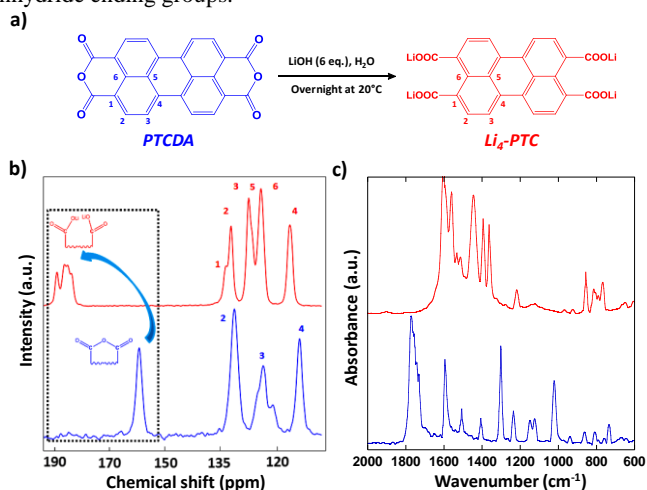
a)

Fig. 1 (a) Synthesis of Tetralithium Perylen-3,4,9,10-Tetracarboxylate (Li₄-PTC). Comparison between pristine PTCDA (blue curve) and precipitated Li₄-PTC solid (red curve) by (b) Solid-state NMR ^{13}C using CP-MAS sequence (full spectra available in †ESI Fig S2) and (c) FT-IR in transmission mode zoomed on important region (full spectra available in †ESI Fig S3).

They shift respectively towards deshielding to 136, 131, 128 and 120 ppm as a result from the lithium salt formation. The complete opening of the di-anhydride to form the lithium carboxylate was also confirmed by FT-IR (Fig. 1c). Similarly, the intense band at 1772 cm^{-1} attributed to the di-anhydride C=O function totally disappears to the benefit of a new band at 1598 cm^{-1} ascribed to the lithium carboxylate.[22] However, one could notice that this wavenumber is comparatively low for a lithium carboxylate function. This reflects the strong electronic coupling between the lithium carboxylate bonds and the hyper-conjugated perylene core,[23] a feature already spotted in delocalized lithium carboxylate.[7-9,11] Beside the carboxylate, we also noticed significant modifications of other IR bands in the core unit for which we have tabulated the wavenumber and the corresponding bond attribution († ESI Table S1).[24,25] Again, such modifications give the evidence of the significant impact of the dianhydride opening on the inner electronic/bond structure of the perylene unit which we remind also falls in good agreement with the color modification of the material which turns from red to orange as a result from an energy gap enhancement between the respective HOMO and LUMO levels in the molecule. The lithium stoichiometry of the material has been determined by atomic absorption spectrometry leading to a lithium content of 4.08 (+/- 0.02) per formula unit. The thermal stability of the two materials has been determined by TGA analysis in air showing on the one hand its robustness until 450 °C and on the other hand its hydrophobicity since no noticeable mass loss attributed to water has been experienced († ESI Fig. S4) and confirmed using Karl-Fischer titration († ESI experimental section). The electrochemical properties of Li₄-PTC vs. lithium have been investigated in composite powder using 40 % wt. of Super P carbon as conductive filler. The figure 2 reports the evolution of lithium

insertion/deinsertion at different cycling rates ranging from 2 to 10 Li$^+$ per hour. Note that lower rates have also been examined and are in good agreement with literature.[26] Lithium insertion in Li₄-PTC involves the reduction of the four lithium carboxylate units inducing a lithium uptake on each carboxylate as showed in scheme 1.

Scheme 1. Expected mechanism for lithium insertion in Li₄-PTC.

These galvanostatic measurements scrutinized at elevated cycling rates emphasize clearly on the power performance of this new electrode molecule. It is noteworthy that these results have been obtained without calling for any engineering of electrode formulation and therefore can be further improved. Although perylene di-anhydride (PTCDA) and di-imides counterpart inserts lithium at higher potentials, in a range of *ca.* 2.4 V,[27] the tetra-lithiated version exhibits an electrochemical activity at a much lower potential, namely 1.1 V vs Li$^+$/Li. Note that the redox potential of Li₄-PTC is superior to the first proposed di-lithium terephthalate (0.90 V vs Li$^+$/Li) and di-lithium 2,6-naphthalene di-carboxylate (0.85 V vs. Li$^+$/Li).[6,9] This difference is theoretically not very surprising since the enhancement of π-conjugation in the core unit affords n-π* orbital energy stabilization moving from phenylene to perylene-based spacer.
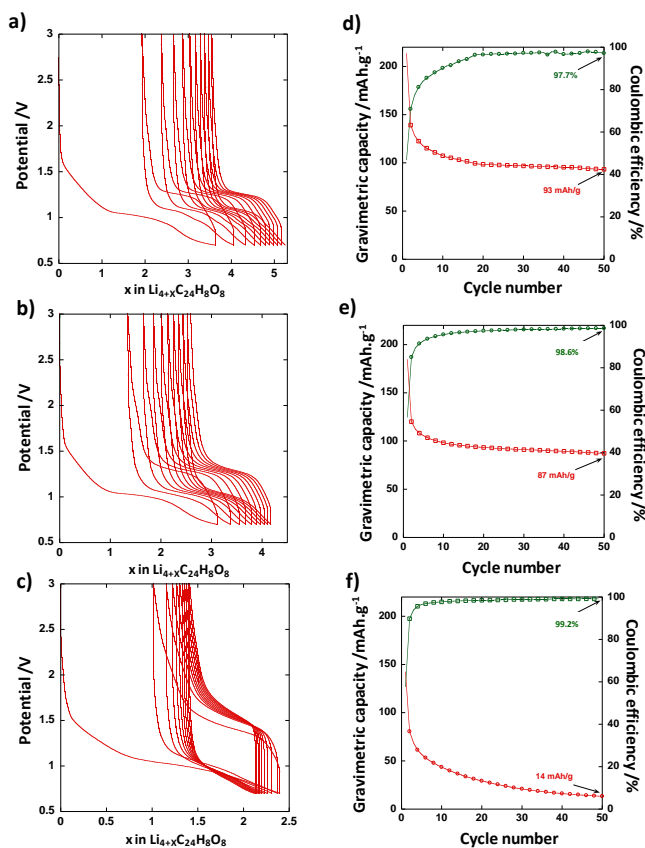

Fig. 2 Galvanostatic curves of the first ten cycles between 0.7 to 3 V vs. Li$^+$/Li and corresponding gravimetric capacity retention curve over 50 cycles in discharge (red line) and coulombic efficiency (green line) of Li₄-PTC cycled at 2 Li$^+$/1h (a,d), 5 Li$^+$/1h (b,e) and 10 Li$^+$/1h rate (c,f).

This is also in good consistency with pure theoretical DFT calculations showing systematically the conjugation extension in the

core unit increases the redox potential of the carboxylate.[28] Secondly, by contrast to the aforementioned molecules for which the carboxylate were in *para* position or at two extreme ending positions, in Li_4-PTC there is also closer interactions between the lateral carboxylates which are respectively in β-position. This vicinity induces a slight twist of the carboxylate with respect to the perylene backbone to minimize electrostatic interactions which in turn would also influence the carboxylate orbitals energy and thus its redox potential. Lithium insertion in Li_4-PTC sustains a reversible insertion capacity of *ca.* 1.8 Li^+ (105 $mAh.g^{-1}$) until 5 $Li^+/1h$. This capacity is slightly decreasing to 1.4 Li^+ (82 $mAh.g^{-1}$) when a more drastic cycling condition of 10 $Li^+/1h$ is applied. The gravimetric capacity of the electrode starts fading upon cycling at this stringent regime; stressing the requirement to optimize the electrode formulation for power capability, *i.e.* integrating a better suited separator, enhance electronic and ionic percolation in the electrode to withstand high current density. Until 5 $Li^+/1h$ rate, a very stable capacity close to 90 $mAh.g^{-1}$ is maintained over 50 cycles with coulombic efficiency nearing 99.0 %. The superior discharge/charge rate capability demonstrated in Li_4-PTC stems from the hyper-conjugated perylene π backbone giving one additional evidence for the role exercised by the carboxylate core unit. A comparison between phenylene (Li_2-BDC), naphtalene (Li_2-NDC) and perylene (Li_4-PTC) core unit using rigorously same electrode configuration and cycling rate supports the statement that π-conjugation enhancement offers greater rate capability to the carboxylate unit († ESI Fig. S5)

The minimum cutoff potential exerts a noticeable impact not only on the gravimetric capacity but also on the coulombic efficiency. We gather in Fig. 3 the evolution of galvanostatic discharge/charge profile at 5 $Li^+/1h$ for different inferior cutoff potentials ranging from 0.7 to 0.4 V vs. Li^+/Li.
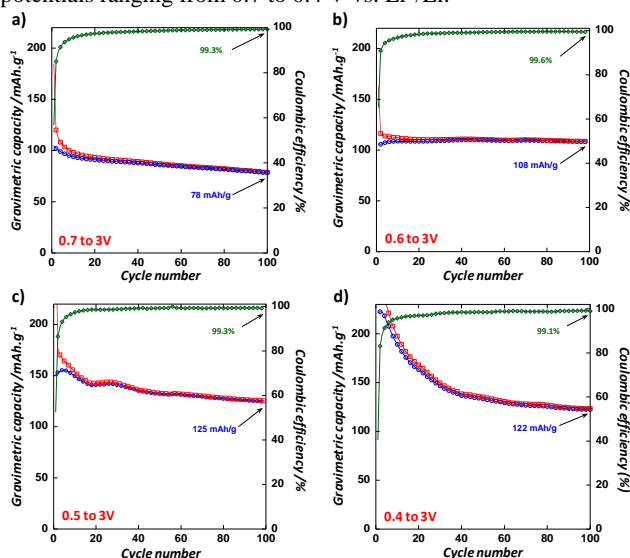

Fig 3. Evolution of gravimetric capacity in discharge (red line) and in charge (blue line) as a function of number of cycle, including the corresponding coulombic efficiency (green line) of Li_4-PTC cycled at 5 $Li^+/1h$ rate between (a) 0.7 to 3 V, (b) 0.6 to 3 V, (c) 0.5 to 3 V and (d) 0.4 to 3 V.

Compared to fig. 2, the lowering of the cutoff potential enables increasing the first cycle reversible gravimetric capacity from 105

$mAh.g^{-1}$ to 222 $mAh.g^{-1}$ for 0.4 V. Note that this capacity approaches the theoretical one of Li_4-PTC which is typically obtained at low cycling regime (*i.e.* Q = 234 $mAh.g^{-1}$), thus once again demonstrating its high power rate capability. From these results, the best coulombic efficiency is obtained at a cutoff potential of 0.6 V leading to a value of 99.6 % after 100 cycles. Nevertheless, the best compromise between coulombic efficiency and gravimetric capacity is obtained for a cutoff potential of 0.5 V. A coulombic efficiency of 99.3% is achieved whereas as high as 125 mAh/g gravimetric capacity is perfectly maintained at 5 $Li^+/1h$ rate.

Finally, although offering a higher capacity output for the first tenth of cycles, cutoff potentials lower than 0.5 V give no further benefits. The capacity retention starts to be harmed leading *in fine* to approximately a similar gravimetric capacity after 100 cycles.

Conclusions

In summary, we have explored successfully a new negative organic electrode material, namely the Tetralithium perylene-3,4,9,10-tetracarboxylate (Li_4-PTC). This work confirms previous intuition that extended π-aromatic conjugation backbone affords to boost the rate capability of carboxylate-based negative electrodes. Without any electrode formulation engineering, we reached more than 120 $mAh.g^{-1}$ gravimetric capacity for over one hundred cycles at 5 $Li^+/1h$ rate. Although electrode formulation optimization and nanostructuration are becoming preponderant to reach high power rate capability, the potentiality of Li_4-PTC in this context is clearly demonstrated since even at a more stringent regime of 10 $Li^+/1h$, this new material can still store reversibly about 80 $mAh.g^{-1}$ capacity. This work sheds the light on one role of the π-spacer in di-lithium carboxylate-based redox materials which will serve as a basis for future design of new organic materials not only for carboxylates but also for other redox active functions.

Acknowledgements

Notes and references

[a] *Laboratoire de Réactivité et Chimie des Solides (LRCS), UMR CNRS 7314, Université de Picardie Jules Verne (UPJV), Amiens, 33 rue Saint Leu, 80039 Amiens, France. E-mail: matthieu.becuwe@u-picardie.fr*
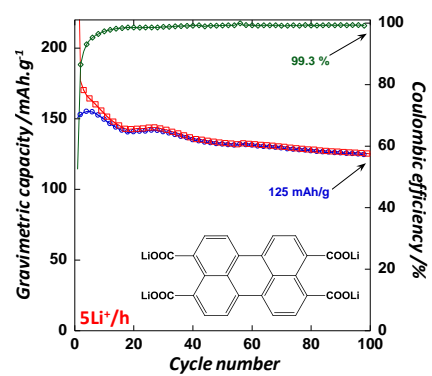[b] *Institut de Chimie de Picardie (ICP), FR CNRS 3085, Amiens, France.*
[c] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France.*
† Electronic Supplementary Information (ESI) available: experimental details, thermogravimetric analysis and scanning electron microscopy. See DOI: 10.1039/c000000x/

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