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1 **Impact of the microstructure on electrochemical**
2 **performances of dilithium benzoquinone dioximate as**
3 **positive material for Li-ion battery**

4 Roberto Russo^[a,b,c,f], Carine Davoisne*^[a,c,f], Adolfo Urrutia^[a,c,f], Yann Danten^[d], Carlo
5 Gatti^[e], Gwenaëlle Toussaint^[b,c], Philippe Stevens,^[b,c] Christine Frayret^[a,c,f], Matthieu
6 Becuwe*^[a,c,f]

7
8 ^[a] *Laboratoire de Réactivité et Chimie des Solides (LRCS), UMR CNRS 7314, Université de*
9 *Picardie Jules Verne, 15 rue Baudelocque, 80000 Amiens, France.*

10 ^{[b]Yann} *Department Electric Equipment Laboratory (LME), EDF R&D, Avenue des*
11 *Renardières, 77818 Morêt-sur-Loing Cedex, France*

12 ^[c] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, Amiens,*
13 *France.*

14 ^[d] *Institut des Sciences Moléculaires, UMR CNRS 5255, 351 Cours de la Libération, 33405*
15 *Talence, France*

16 ^[e] *CNR SCITEC, CNR Istituto di Scienze e Tecnologia Chimiche "Giulio Natta", Sede Via C.*
17 *Golgi, 19, 20133 Milano, Italy*

18 ^[f] *Institut de Chimie de Picardie (ICP), FR CNRS 3085, 80039 Amiens, France*

19
20 **Corresponding authors**

21 Matthieu Becuwe, matthieu.becuwe@u-picardie.fr

22 Carine Davoisne, carine.davoisne@u-picardie.fr

23 **Orcid**

1 **Roberto Russo** : [0000-0003-4439-2520](#) ; **Carine davoisne**: [0000-0001-8660-9367](#) ; Yann
2 Danten : 0000-0002-1994-2503; Carlo Gatti : 0000-0002-0047-1596; Gwenaelle Toussaint :
3 [0000-0003-0964-143X](#) ; Philippe Stevens : [0000-0003-2344-2699](#) ; Christine Frayret : 0000-
4 0003-1732-1591 ; Matthieu Becuwe : [0000-0002-1949-3955](#)

5 **Keywords**

6 Organic batteries, positive electrode, dioximate, self-polymerization, Transmission Electron
7 Microscopy,

8 **Abstract**

9 Herein we would like to highlight the impact of the material microstructure on
10 electrochemical performances of dilithium benzoquinone dioximate (Li₂-BQDO) and its
11 oxidized and self-polymerized version (PNND), a promising electroactive material for energy
12 storage application. Li₂-BQDO showed a reversible exchange of two lithium ions at high
13 redox potential (3.0 V vs. Li⁺/Li), acting as a lithiated organic positive electrode for lithium-
14 ions batteries. After a preliminary computational study, electrochemical performance of the
15 oxidized form of Li₂-BQDO, which polymerize inside the cell, were also investigated. Thanks
16 to TEM analysis coupled with XRD experiment the role of microstructure and crystal
17 structure in the energy storage process was highlighted.

18 **Keywords:** Benzoquinone dioxime, lithium-ion battery, organic electrode, Transmission
19 Electron Microscopy

20 **1. INTRODUCTION**

21 In the last decade, the development of different chemistries for lithium-ion battery
22 (LIB) technology have led to a considerable increase in the energy storage performance.^{1,2}
23 Nowadays, researchers are continuously improving the performance of various
24 electrochemical aspects. However, the huge increase in the lithium batteries-manufacturing,
25 mainly driven by the automotive sector, is showing limits in terms of costs and impact on

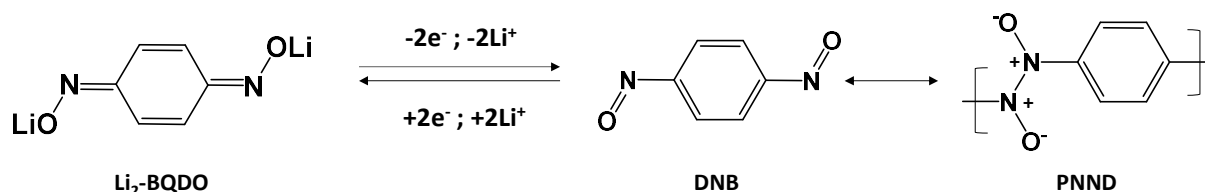
1 natural resources. In fact, traditional lithium-ion batteries are based on inorganic-based
2 materials³, composed mainly of Ni, Co, V,... which are characterized by high extraction and
3 processing costs, as well as poor and unfavorable geolocation. Finally, these materials are
4 toxic and hardly recyclable, which leads to a relatively high environmental impact of
5 production⁴. Therefore, in order not to nullify the advantages deriving from electric energy
6 using storage materials with possible element shortage and price hike, it is essential to find
7 alternative materials characterized by low costs and easy supply, as well as sustainable
8 production with low environmental impact, but with adequate electrochemical properties to
9 allow the development of technologies for mobility and electronics application.

10 In this context, organic materials made up of elements such as carbon, nitrogen and
11 oxygen, extremely abundant on the earth's crust, easily available (some of them may be
12 obtained directly from bio-sources) and low processing cost gained a huge success in the last
13 few years.⁵⁻⁷ Considering the enormous potential in energy storage applications, over the
14 decades many organic materials have been developed, based on wide span of chemistry and
15 redox-active groups. In particular, among the most studied it is possible to list the molecules
16 that incorporate carbonyl groups, such as quinones, those based on nitrogen, such as imides
17 and azo compounds, as well as derivatives of carboxylates⁸⁻¹¹.

18 Quinones are undoubtedly one of the most studied classes of organic compounds. The
19 simplest structure among them is p-benzoquinone (p-BQ), composed of an aromatic ring with
20 two oxygens substituents in para position. During the redox reaction, benzoquinone can be
21 reduced by the insertion of two metal ions to form a hydroxyquinone salt. Following the
22 reduction, the ring recovers its aromaticity, which leads to a significant lowering of the energy
23 of the system. Furthermore, benzoquinones have shown an incredible versatility as they can
24 be used for vast type of metal ions (Li^+ , Na^+ , K^+ ,...), structure can be easily modified through
25 the facile addition of substituent on the aromatic ring to tune the (electro-)chemical properties

1 and can be obtained from bio-sources, making them advantageous from an economic and
 2 environmental point of view.¹² A final advantage of quinones is that they can serve as
 3 precursors for the creation of electroactive motifs. One example is TCNQ (7,7,8,8-tétracyano-
 4 p-quinodiméthane), which can be obtained from simple benzoquinone by condensation of
 5 Knoevenagel using malonitrile. This transformation leads to enhanced redox properties
 6 resulting from the electroactivity of the nitrile groups (3V vs Li).

7 Very recently, an electroactive molecule, easily synthesized by the action of hydroxyl
 8 amine on p-benzoquinone, was revealed as solid-state positive electrode for Li-ion batteries.¹³
 9 In this work, five lithiated dioxime (lithium dioximate) have been investigated and exhibited
 10 interesting electrochemical performance with redox around 2.5-3.2 V vs. Li⁺/Li and capacity
 11 in the range of 210-360 mAh g⁻¹. In addition to the electrochemistry investigation, this work
 12 elucidated the redox mechanism of this class of compounds thanks to an *Ex-situ* infrared
 13 study and by using the diffraction technique to understand the role of the crystalline structure.
 14 It was proposed that the redox mechanism of the benzoquinone dioximate/poly-
 15 dinitrosobenzene (subsequently 1,4-Phenyleneazine-N,N-Dioxide) couple involves
 16 polymerization of the oxidized form while such aspect does not seem to affect the
 17 reversibility of the lithium ion de-/intercalation mechanism (Scheme 1).



18
 19 **Scheme 1 - Electrochemical mechanism of lithium insertion/de-insertion involving di-**
 20 **lithium benzoquinone dioximate (Li₂-BQDO) (Left) and the poly *p*-dinitrosobenzene**
 21 **(PNND) (Right) /redox moieties.**

22 Owing to the interesting discovery of this player in the field of redox active organic electrode
 23 material (OEM), it is of crucial interest to understand the nature of structure-activity

1 characterizing such backbone/redox center combination. This requires to proceed in several
2 steps to disentangle distinct aspects that might influence electrochemical features. This is due
3 in particular to the fact that such “C-nitroso compounds” (*i.e.* molecules having the nitroso
4 group (R–N=O) attached to a carbon atom) present fascinating chemical features, which have
5 drawn the attention of scientist’s community. This system represents a molecular OFF-ON
6 switch of the chemical bond between two nitrogen atoms, with an involvement of monomer-
7 dimer equilibrium. Indeed, reactions of aromatic C-nitroso compounds can give rise to dimers
8 in *Z* and *E* configurations thanks to photothermal “chemical switch”, by which it is possible to
9 break the chemical bond between two nitrogen atoms and bind them again. The possibility of
10 occurrence of oligomerization and the above-mentioned polymerization of 1,4-
11 dinitrosobenzene, with potential creation of shorter or longer chains, in which, depending on
12 the conditions, the azodioxide group can appear either in its *E*- or in *Z*-form, leads to a very
13 specific and complex situation in the context of electrochemistry, which is not the one of
14 conventional OEMs. Prior to elucidating very precisely the structure-property relationships
15 encompassing all these aspects, it is necessary to provide a first glimpse of how the monomers
16 behave in the context of using such materials for their electrochemical properties. This will
17 leave the opportunity, in a further study, to see the departure that can eventually occur from
18 this simplest situation among distinct possible situations. In the present investigation, a
19 quantum chemistry computation has thus been undertaken to first address the chemical
20 reaction involving *p*-dinitrosobenzene (DNB) and di-lithium benzoquinone dioxime (Li₂-
21 BQDO) monomers. From the experimental point of view, both Li₂BQD and its oxidized
22 polymerized counterpart, (PNND), were synthesized and electrochemically characterized. The
23 crystal structure of both compounds was then investigated using X-ray diffraction technique,
24 while the microstructure of the crystals was observed with the TEM microscope, leaving the
25 opportunity to understand its role in the lithium insertion/de-insertion process.

1 2. MATERIAL AND METHODS

2 **2.1 Materials.** p-Benzoquinone dioxime (95%) was supplied by Alfa-Aesar. LiOH.H₂O
3 (98%), FeCl₃·6H₂O (97%) and HCl solution (36%) were purchased by Sigma-Aldrich. All
4 solvents were purchased dry from Sigma-Aldrich.

5 **2.2 Synthesis.** All the starting materials, intermediates and final products of Li₂-BQDO and
6 PNND were characterized by ¹H NMR and FTIR spectroscopy. The infrared spectra, recorded
7 in transmission mode and NMR spectra are reported in the supporting info (Fig. S3-S6).

8 **2.3 Analytical and Electrochemical characterizations.** The infrared spectra (FTIR) were
9 acquired in transmission mode in the range 400-4000 cm⁻¹, using a Nicolet Avatar 370DTGS
10 spectrometer, with a resolution of 2 cm⁻¹. The spectra were recorded by analyzing IR pellets,
11 which were prepared by mixing active material and potassium bromide KBr (Sigma Aldrich,
12 spectroscopic grade) in a ratio of 1:100. The powder mixture was pressed with a 13 mm
13 evacuable die set (Specac Ltd, UK), resulting in an IR pellet. ¹H and ¹³C NMR spectra were
14 recorder with 400 MHz Avance III HD spectrometer (Bruker Co., US), equipped with a
15 cryosonde. All the spectra reported in the present work have a chemical shift (δ) in ppm
16 relative to tetramethylsilane (TMS). All the solvents employed for NMR analysis were
17 purchased from Sigma Aldrich (99.9% D atom). The powder measured used to measure X-ray
18 powder diffraction was cycled electrochemically, recovered, washed, ground and placed into
19 a zero-background sample holder. The X-ray powder diffraction patterns were collected on a
20 Bruker D8 Advance diffractometer with a Cu Kα₁ and Kα₂ radiation and equipped with a
21 Lynkeye detector operating at 40 kV and 40 mA in between 2θ = 10-60° with a 2θ step size of
22 0.019° in reflection geometry. Although a zero-background sample holder was used, the
23 inhomogeneous background is a result of residual amorphous material from the composite
24 electrode and was included in the Pseudo-Voigt profile function refinement.

1 Thermogravimetric analyses (TGA) were performed on a Netzsch thermal analyzer STA
2 449C Jupiter equipped with a differential analysis microbalance coupled with a mass
3 spectrometer QMS 403 Aeolos (heating rate: 5 °C min⁻¹ under argon flow). The lithium
4 content in the salts was determined by atomic absorption spectroscopy (AAS). The
5 measurement was carried out using the AAnalyst 300 spectrometer (Perkin-Elmer, USA),
6 equipped with a lithium hollow cathode lamp (wavelength: 670.8 nm), using a mixture of
7 air/acetylene as oxidant/fuel with 5.8/1 ratio. The morphological and chemical analyses were
8 performed using a Quanta 200 scanning electron microscope (FEI, Thermo-Fisher, USA)
9 equipped with a X-ray energy dispersive spectroscope (X-Max 80, Oxford Instruments Co.,
10 UK). A few milligrams of active material powder were deposited on double-sided carbon
11 tape, adhered to the SEM sample holder. The microstructural and chemical investigations at
12 different charging state were performed using a transmission electron microscope TECNAI
13 F20 STWIN working at 200kV and equipped with an X-ray energy dispersive spectroscope
14 (X-Flash 6 TI 60, Bruker) and a GIF Tridiem (GATAN) for electron energy loss spectroscopy
15 (EELS). The cycled sample were transferred from the glovebox to the TEM without air
16 exposure according the procedure detailed by Dupont *et al.*¹⁴ The cristallographic information
17 were obtained through selected area electron diffraction. The EELS was performed with 1–1.2
18 eV energy resolution, a dispersion of 0.2 eV/channel, a conversion and a collection angle of
19 5.8 and 21.7 mrad, respectively. The energy loss near edge structure (ELNES) acquisitions
20 were performed in STEM mode in defocus to limit the electron beam interaction. All the
21 energy losses presented an error of ±0.2 eV. The electrochemical activity of the active
22 materials was investigated in half-cell vs lithium metal through galvanostatic tests, performed
23 with Swagelok-type cell. The cells were assembled under an inert atmosphere, inside a
24 glovebox filled with argon, with controlled content of H₂O and O₂ (less than 0.1 ppm). The
25 electrodes were prepared mixing 7-11 mg of active material (70% wt% of the composite

1 electrode) with 30% wt% of conductive carbon type Ketjenblack EC-600JD (AkzoNobel,
2 Netherlands). The two components were mixed through 30 minutes of ball-milling. The
3 negative electrode was made with a lithium metal disc, punched from a commercial lithium
4 metal sheet (99.9% based on trace metals, Sigma-Aldrich). The positive electrode and the
5 lithium disk were separated with a glass fiber separator (Whatman®), soaked with 150 ml of
6 1 M LiPF₆ solution in ethylene carbonate:dimethyl carbonate 1:1 wt% (electrolyte LP30 ,
7 certified battery purity, Merck), as electrolyte. All cells were galvanostatic tested using a
8 biological VMP-3 (Biologic SAS, France).

9 **3. RESULTS AND DISCUSSION**

10 **3.1 Preliminary theoretical investigations.** Density Functional Theory (DFT)
11 calculations have become very common in the field of OEMs for batteries to complement the
12 characterization of experimental works or even to take part in elucidating the mechanisms. As
13 a first insight focused on the monomers DNB and Li₂-BQDO (Scheme 1), a molecular DFT
14 modelling complemented by a thorough electronic structure analysis was undertaken to
15 provide an initial glimpse of the redox phenomena in this class of materials. At the molecular
16 state, for a redox system containing two active centers as it is the case here and by considering
17 two successive steps each involving one electron/one Li⁺, the redox mechanism can be
18 envisioned similarly to the suggestion of Rathore *et al.*¹⁵, or alternatively, instead of two
19 successive one-electron/one Li⁺ steps, one can suspect that the reaction may involve either
20 only a single reduction or a direct double reduction. In such context, the description of the
21 electrochemical features can be reached by focusing on three species: the “initial” (oxidized)
22 form fully devoid of neighboring Li⁺, an “intermediate” (singly reduced) form and a “final”
23 (doubly reduced) form exhibiting an environment of two Li⁺, each of them being located in
24 the vicinity of each of the redox centers. Within the electrochemical process, the molecular

1 species presented in scheme 1 may evolve from the oxidized state , *i.e.* DNB, containing two
2 N=O redox centres, towards the fully reduced state, *i.e.* Li₂-BQDO, characterized by an uptake
3 of two electrons and involving a complex structure with two Li⁺, which are supposed to be
4 located in the neighborhood of each of the oxygen atoms, if one considers a direct double
5 reduction. The present computational approach considers the two options of reaching either
6 an uptake of one electron (single reduction) or directly two electrons (double reduction)
7 starting from the oxidized specie. Within these electrochemical processes, the two following
8 molecular species presented in scheme 1 are involved: the oxidized state , *i.e.* DNB,
9 containing two N=O redox centres, and the fully reduced state, *i.e.* Li₂-BQDO, characterized
10 by an uptake of two electrons and involving a complex structure with two Li⁺, which are
11 supposed to be located in the neighborhood of each of the oxygen atoms, if one considers a
12 direct double reduction.

13 In view of gaining a preliminary insight on the way Lithium may locate in the vicinity
14 of the DNB to form a complex entity upon reduction (*i.e.* Li₂-BQDO) for a reaction simply
15 involving monomers, the Electrostatic Surface Potential (ESP) maps have proven to constitute
16 a precious tool.¹⁶ The minima are more specifically meaningful since they constitute areas
17 that are characterized by an accumulation of electron, where Li⁺ ions may lie. The ESP maps
18 of the three species that are involved during the electrochemical process of reduction of DNB
19 are gathered in Figure 1, which concomitantly presents the representation of the three relaxed
20 systems along with the corresponding bond lengths. Especially, focusing on the ESP map of
21 DNB, it is straightforward to identify two minima, both located nearby each redox center, at ~
22 -22.3 and ~ -26.7 kcal/mol, within the red area exhibiting an electron-rich area. Among these
23 two minima, the highest absolute value is situated in the vicinity of oxygen atom while the
24 other one is nearer to the nitrogen atom. Each minimum is situated at a roughly equivalent
25 distance from either the oxygen or nitrogen atom although the distance from the minimum at

1 ~ -22.3 kcal/mol is slightly farther from nitrogen compared to the distance between oxygen
2 and the minimum at ~ -26.7 kcal/mol. Upon either one/two electron(s) uptake, the molecular
3 entity evolves towards a complex involving one/two Li^+ interacting with the oxygen(s)
4 atom(s) of the mono-/di-anion through electrostatic interaction, which is clearly reflected in
5 the ESP landscape. This latter is indeed modified accordingly, ending up with the doubly
6 reduced state $\text{Li}_2\text{-BQDO}$ which is characterized by a large red area covering the anion. The
7 “intermediate” state corresponding more precisely to the singly reduced complex exhibits on
8 the unreduced redox center a single minimum at ~ -55.6 kcal/mol nearby the oxygen atom. It
9 is straightforward to identify that the Li^+ positioning effectively takes place within this area
10 forming an almost linear arrangement with the C-N chemical bond (Figure 1) and thus
11 constituting a kind of double chelation with Li^+ interacting preferentially with Oxygen but
12 also with Nitrogen located however a bit farther (and presumably being less charged than
13 Oxygen). The DFT modelling confirms and quantifies the geometrical structures of the two
14 Li^+ complexes hypothesized through the ESP maps of DNB (Figure 1). Beyond these aspects,
15 further characterization on the mechanism was gained thanks to an accurate electronic
16 structure analysis based on the approaches developed in prior works **REFERENCES** (see ESI for
17 full details).

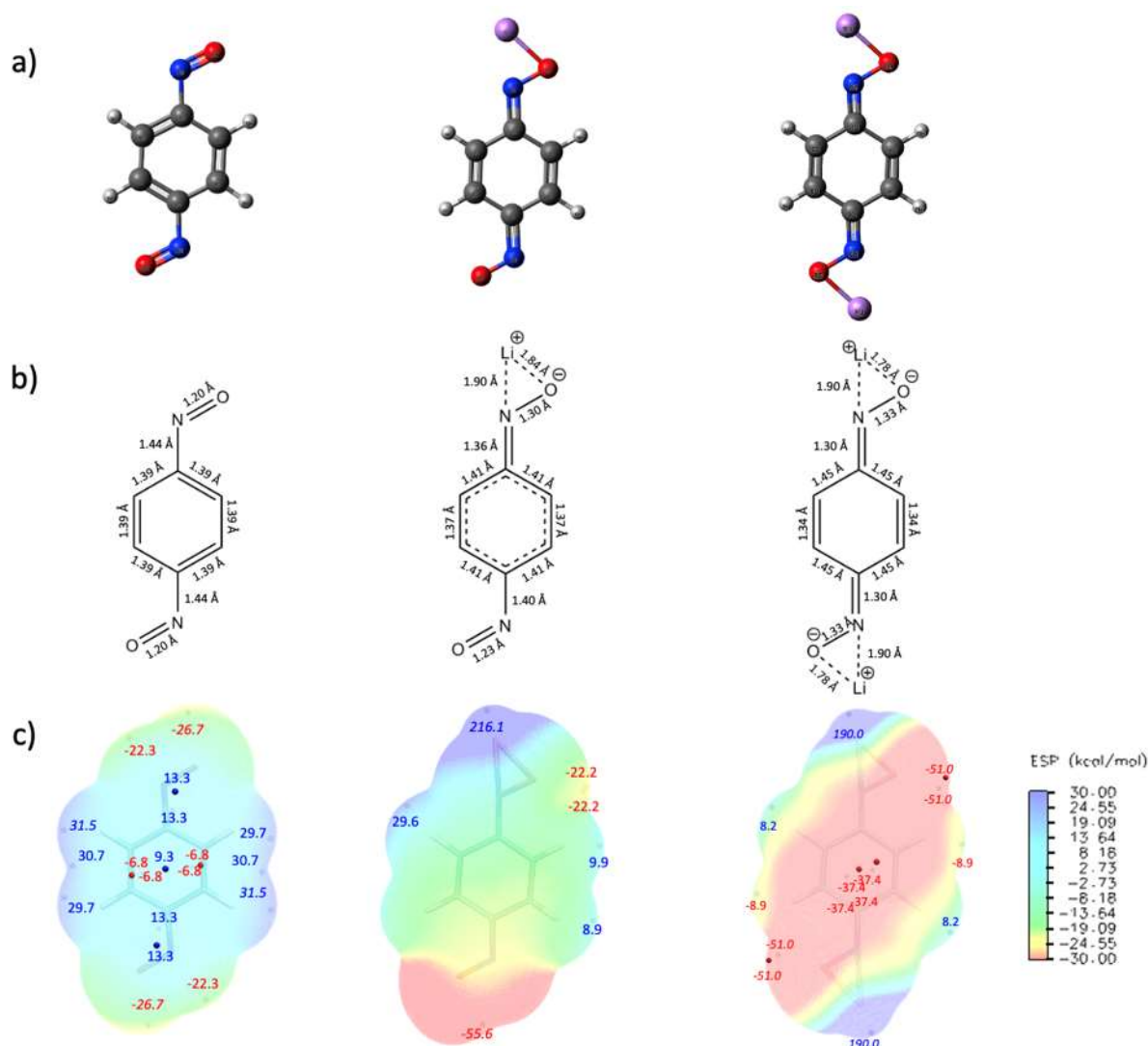
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26 Sustainable Energy. *Physical Chemistry Chemical Physics*, 2020, *22*, 20212–20226.

27

1 The main learnings accessible through this methodology correspond to the following
2 observations: i) the simple representation of the redox process proposed in Scheme 1 (for the
3 part indicating the sole consideration of monomer entities) is in fact slightly oversimplified in
4 case of redox reactions considered between Li₂-BQDO and DNB; a slightly revised model for
5 this mechanism has been proposed in which the Nitrogen atom is involved for the charge
6 transfer effects and chelation of Li⁺, which is consistent with the location of Li⁺ in between
7 the two ESP minima nearby the NO group ; ii) the redox potential estimated for the double
8 reduction is consistent with a classification of this moiety within the positive OEMs; iii) the
9 analysis of various indices gives an explanation of this classification, by highlighting the
10 stabilization induced thanks to the redox center moiety upon lithiation of DNB, which
11 counterbalance and even overcome the lack of aromaticity within the ring; iv) the DNB is
12 characterized by a lower HOMO-LUMO gap than *p*-benzoquinone.

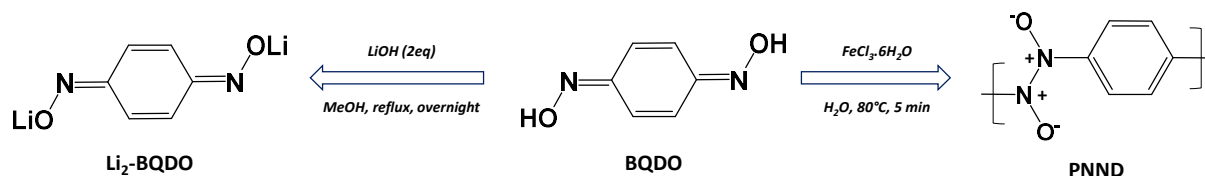
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1
2 **Figure 1: Evolution of systems from DNB towards Li₂-BQDO upon Lithium reduction**
3 **according to the electrochemical mechanism proposed in Scheme 1: “Initial” or oxidized**
4 **state (left), “intermediate” or singly reduced state (middle, Li-BQDO) and “final” or**
5 **doubly reduced state (right, Li₂BQDO). a) DFT-computed structures b) interatomic**
6 **distances indicated on the optimized geometry and c) Electrostatic surface potential**
7 **(ESP) maps. Color code: blue (red) to visualize electron depletion (electron**
8 **accumulation) within the range of 30.0 (deep blue)/-30.0 (deep red) kcal/mol. Surface**
9 **local minima and maxima are represented along with corresponding values. See also**
10 **Figure S1-2 for additional calculations.**

11

1 **3.2 Synthesis of dilithium benzoquinone dioximate and its oxidized version.** In
 2 parallel with this modelling investigation, dilithium 1,4-benzoquinone dioximate (**Li₂-BQDO**)
 3 were synthesized *via* salt formation reaction. To do so, benzoquinone dioxime (**BQD**) was
 4 reacted with LiOH.H₂O in methanol (Scheme 2), using the same procedure reported for the
 5 lithiation of dihydroxybenzene.



7 **Scheme 2 - Synthetic routes of Dilithium benzoquinone dioximate (Li₂-BQDO) and**
 8 **Polydinitrosobenzene (PNND) from Benzoquinone dioxime.**

9 The synthesis of Li₂-BQDO was confirmed by FTIR and NMR analysis. NMR spectrum
 10 (Supporting info, Figure S3-4) after the lithiation showed the disappearance of O-H peaks
 11 located at 12.10 ppm (s, 2H), observed in the pristine material (Supporting info, Figure S3).
 12 Furthermore, the aromatic hydrogen located were shifted at upfield (7.00-6.58 ppm) due to
 13 the presence of lithium ions, compared to the peaks in the BQD spectrum, located in the 7.85-
 14 6.44 ppm range (Figure S4). FTIR spectra (Figure S5a) corroborate the complete lithiation of
 15 benzoquinone dioxime. Disappearance of the O-H stretching band (around 3500 cm⁻¹) after
 16 lithiation and the shifting of C-N stretching peak from 991 cm⁻¹ in BQD to 970 cm⁻¹ in Li₂-
 17 BQDO, due to the presence of lithium ions is observed. Lithium content was measured using
 18 atomic absorption spectroscopy (AAS) analysis, giving a complete chemical formula of
 19 Li_{2.03±0.05}-BQDO. Finally, a thermogravimetric analysis (TGA, Figure S5b) was employed to
 20 determine the thermal stability and the degree of solvation. The analysis showed a no weight
 21 loss to 200 °C, where then its loss of the total mass. Moreover, we can deduce that the
 22 synthesized molecule is not in a solvated state and so can be used for electrochemical tests.
 23 The oxidized counterpart of dioxime (**PNND**) was synthesized using the procedure reported

1 by Muller and coworkers.¹⁷ FTIR spectrum show the shifting to 1306 cm^{-1} of C-N band
2 (Figure S6a). An important piece of information derived from the FTIR spectra is the
3 appearance of a band at 1251 cm^{-1} attributed to the trans O-N=N-O isomer resulting from the
4 self-polymerization of dinitrosobenzene (named **PNND**) at room temperature. This crucial
5 feature is of great interest because most of the time, the oxidized version of the quinone, for
6 example, is generally soluble and leads to a loss of capacity. The presence of a polymer in the
7 oxidised state should make it possible to avoid such phenomena.¹⁸ NMR spectrum of **PNND**
8 showed the disappearance of hydroxide peak at 12.10 ppm. Moreover, all the other peaks
9 were shifted to upfield, from 7.85-6.44 ppm to 7.23-6.65 ppm, for the presence of O-N=N-O
10 group (Figure S5). Furthermore, TGA carried out under air atmosphere reveals that there is no
11 trace of solvent trapped in the material structure and that **PNND** is thermally stable up to
12 200°C (Figure S6b).

13 **3.3 Material characterization using PXRD and SEM.** The crystallinity of both
14 materials was investigated by powder X-ray diffraction (PXRD) performed with a Bruker D8
15 Advance diffractometer with a Cu $K\alpha_1$ and $K\alpha_2$ radiation. No diffraction peaks were detected
16 in the powder pattern of the $\text{Li}_2\text{-BQDO}$ (Figure S7). It is possible to conclude that this
17 molecular material has no crystalline structure and is characterized by an amorphous
18 structure. XRD analysis was also performed on 1,4-phenyleneazine-N, N-dioxide (**PNND**),
19 resulting also from the polymerization of dinitrosobenzene (**DNB**). This polymer, unlike
20 Li_2BQD , showed a well-defined crystalline structure. ~~The powder pattern collected for **PNND**~~
21 ~~was included in the Pseudo-Voigt profile function refinement~~ (Figure S8). The refined unit
22 cell was monoclinic $P2_1/n$ with cell parameters $a = 6.3913(3)\text{ \AA}$, $b = 11.29544(11)\text{ \AA}$, $c =$
23 $3.71269(5)\text{ \AA}$, $\beta = 92.523(4)^{\circ}$, and $V = 267.770(14)$ with Bragg R -Factor = 0.146, $R_p = 1.30$,
24 $R_{wp} = 1.79$ and $R_{exp} = 0.72$ reliability factors. ~~All refined parameters, except a , were outside~~
25 ~~the standard deviation of those reported in Gallo and collaborators~~ (Table S1).¹⁹ Due to the

1 elemental nature of the composition of **PNND** and the presence of light elements such as H
2 and Li, further investigation with synchrotron and/or neutron measurements are recommended
3 for full structural refinement.

4 Scanning electron microscopy characterization of dioxime lithium salt and its oxidized
5 counterpart (**PNND**) revealed a clear distinction between their shape and size. **Li₂-BQDO**
6 appeared as irregular granules and varied in size from ~1 to 5 μm (Figure S9a). Similarly, but
7 with a different particle shape, **PNND** showed consisted of clusters of slender parallelepipeds
8 with a thickness around 1 μm and lengths ranging from 2 to 5 microns (Figure S9b).

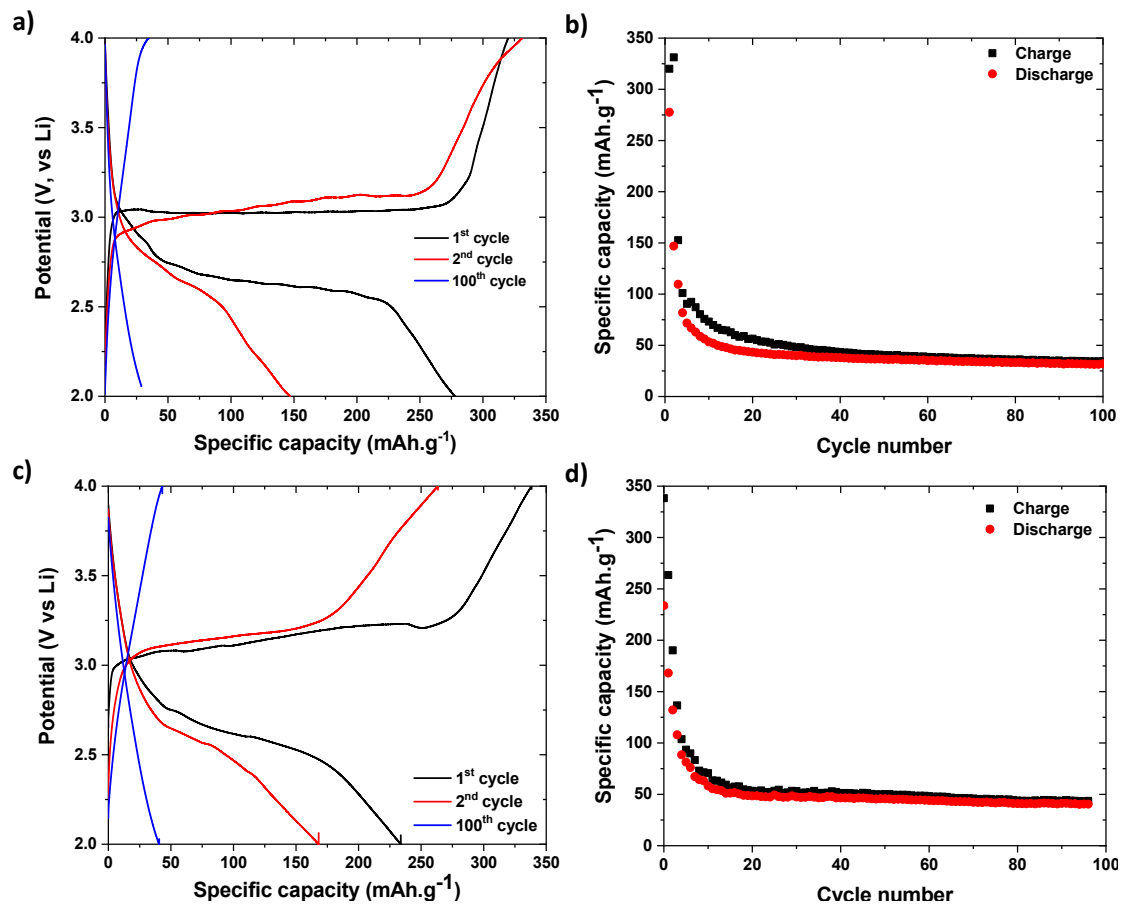
9 **3.4 Electrochemical activity of synthesized materials in half-cell configuration.** As
10 a preliminary study, the electrochemical performance of **Li₂-BQDO** were estimated using a
11 Swagelok-type[®] half-cells vs lithium metal disk, using LiPF_6 in EC/DMC (50:50) electrolyte
12 (commercially named LP30, battery grade purity). The galvanostatic profiles have been
13 measured at C/20 (1 e⁻/5 h) in 4.0-2.0 V potential window. All the electrodes were prepared
14 using an active material/conductive carbon (KJ600) ratio of 70:30. The mixing was carried
15 out through ball-milling for 30 minutes.

16 **Li₂-BQDO** molecule showed an average insertion potential of ca. 3.0 V (Figure 2a), higher
17 than what reported for various organic systems, such as quinones²⁰ and diimides²¹. A large
18 polarization (400 mV), possibly originated from conductivity issue, was also observed. This
19 indicates an energy-expensive structural rearrangement during the redox process. The charge
20 phase displayed a specific capacity of 320 mAh g^{-1} , close to the theoretical capacity of 393
21 mAh g^{-1} . 277 mAh g^{-1} of capacity was observed after the discharge, for 87% of reversibility
22 during the first cycle. Despite the promising electrochemical properties shown in the first
23 cycle, several drawbacks were observed along cycling. In the second cycle, despite no change
24 in the oxidation capacity (331 mAh g^{-1}), the discharge capacity drops to 146 mAh g^{-1} , for a
25 coulombic efficiency of only 44%. Moreover, a poor capacity retention was observed along

1 the first 10 cycles. The residual reversible capacity is only 52 mAh g⁻¹, which corresponds to
2 a capacity retention of 21% compared to first cycle. After that, the capacity remains constant,
3 reaching 31 mAh g⁻¹ of reversible capacity after 100 cycles (Figure 2b).

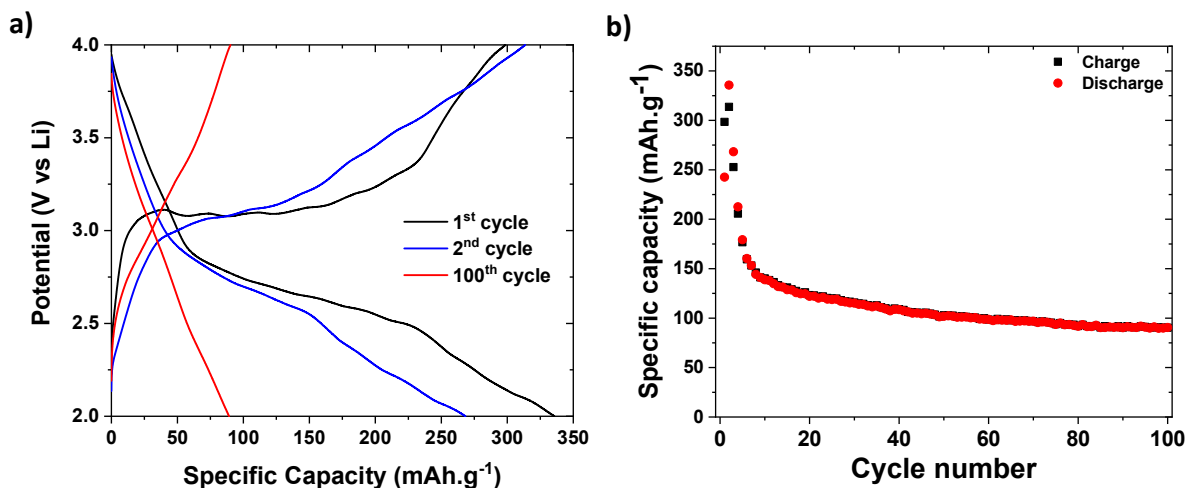
4 This capacity fading can be explained by several phenomena. Firstly, the dissolution of the
5 active material in the electrolyte, frequent phenomenon for small organic molecules. Another
6 cause may be the non-optimized electrode formulation. Indeed, for the preliminary test, a
7 simple formulation consisting in a hand-milled electrode with active material and conductive
8 carbon was employed. The addition of binder and another mixing process can significantly
9 improve the electrochemical properties. Lastly, the capacity fading can be addressed to side-
10 reactions that affect the redox process, hindering the reversibility of the lithium intercalation
11 process. About the dissolution of active material in the electrolyte, a visual analysis after 10
12 cycles showed no traces of active material in the separator. The dissolution of the active
13 material in the electrolyte causes the color of the separator in contact with the electrode. As
14 further confirmation, both benzoquinone dioxime and **PNND** were kept in a mixture of LP30
15 solution for one week, showing no dissolution (Figure S10). To investigate the effects of the
16 formulation on electrochemical properties, a different formulation was prepared, with the
17 addition of binder and changing the mixing method. In this formulation, 10w% of PVDF
18 (binder) was added in the electrode composite, for a final ration of 60/30/10
19 (AM/KJ600/PVDF) and the powder was ball-milled for 30 minutes. The results obtained with
20 this different formulation were illustrated in Figure 2c-d. Nevertheless, this formulation
21 showed electrochemical performances almost identical to the previous one. Despite the higher
22 specific capacity in the first charge (338 mAh g⁻¹ compared to 320 mAh g⁻¹ of the previous
23 case), the discharge phase showed a large irreversibility (31%), for a reversible capacity of
24 233 mAh g⁻¹. In second cycle, a marked capacity drop was observed (168 mAh g⁻¹ of
25 reversible capacity), just slightly better compared to non-formulated electrode. After 100

1 cycles, the reversible capacity was quantified in 40 mAh g^{-1} , for an overall capacity retention
 2 of 17%, which represent only a small improvement over what was seen in the first test. In the
 3 light of the data obtained with this formulation, it is evident that the problem of capacity
 4 fading was not due to electric or ionic bad conductivity, which can usually be improved with
 5 an optimized formulation, but seems to be linked to a problem of parasitic reactions that affect
 6 the electrochemical reaction, hindering the reversibility of the lithium intercalation reaction.



7
 8 **Figure 2 – (a) Galvanostatic profile of 1st, 2nd and 100th cycle and (b) corresponding**
 9 **capacity retention curve upon 100 cycles of Li₂BQD electrode (70:30 AM/KJ600) in half-**
 10 **cell vs Li, window range of 4.0-2.0 V with LP30 electrolyte. (c) Galvanostatic profile of**
 11 **1st, 2nd and 100th cycle and (d) corresponding capacity retention curve upon 100 cycles of**
 12 **Li₂BQD electrode (60:30:10 AM/KJ600/PVDF) in half-cell vs Li, window range of 4.0-**
 13 **2.0 V with LP30 electrolyte.**

1 The oxidized equivalent of benzoquinone dioxime, polymerized Dinitrosobenzene (PNND),
2 obtained *via* chemical synthesis, was also tested in a half-cell *vs.* Li, using the same set-up
3 described above (Figure 3). Contrary to dilithium benzoquinone dioximate, **PNND** has no
4 Lithium ions in its structure, so the first electrochemical step was the intercalation of lithium,
5 with relative reduction of the molecule. When the half-cell was connected to the potentiostat,
6 a voltage of 3.9 V *vs.* Li⁺/Li was measured. As reported recently, the **PNND** is above 3.0 V,
7 the threshold below which oxidation occurs due to oxygen, confirming the air-stability of the
8 molecule to exposure to air. The first discharge showed a specific capacity of 336 mAh g⁻¹, a
9 value identical to that observed for the charge of the lithiated dioxime (Figure 3a). In this
10 case, the reversible capacity was measured in 313 mAh g⁻¹, with an irreversibility of 7%, an
11 promising result for organic materials. The average redox potential measured was 3.0 V *vs.*
12 Li⁺/Li with the same polarization, in line with what was measured in the previous cases. The
13 second cycle showed a reduction in capacity to 268 and 293 mAh g⁻¹ for discharge and
14 charge, respectively. In the subsequent cycles, a constant loss of capacity was measured, with
15 a consequent low retention of capacity. However, after 10 cycles, the coulombic capacity
16 tends to become constant along cycling. After 100 charge/discharge cycles, it can be seen that
17 the capacity value remains constant, with a specific capacity of 90 mAh g⁻¹ and a coulombic
18 efficiency of 99.5% (Figure 3b). At this stage, the origin of this reactivity is not perfectly
19 identified, but we can assume that we have a partial dissolution of the compound which
20 saturates the electrolyte, thus make capacitance constant.

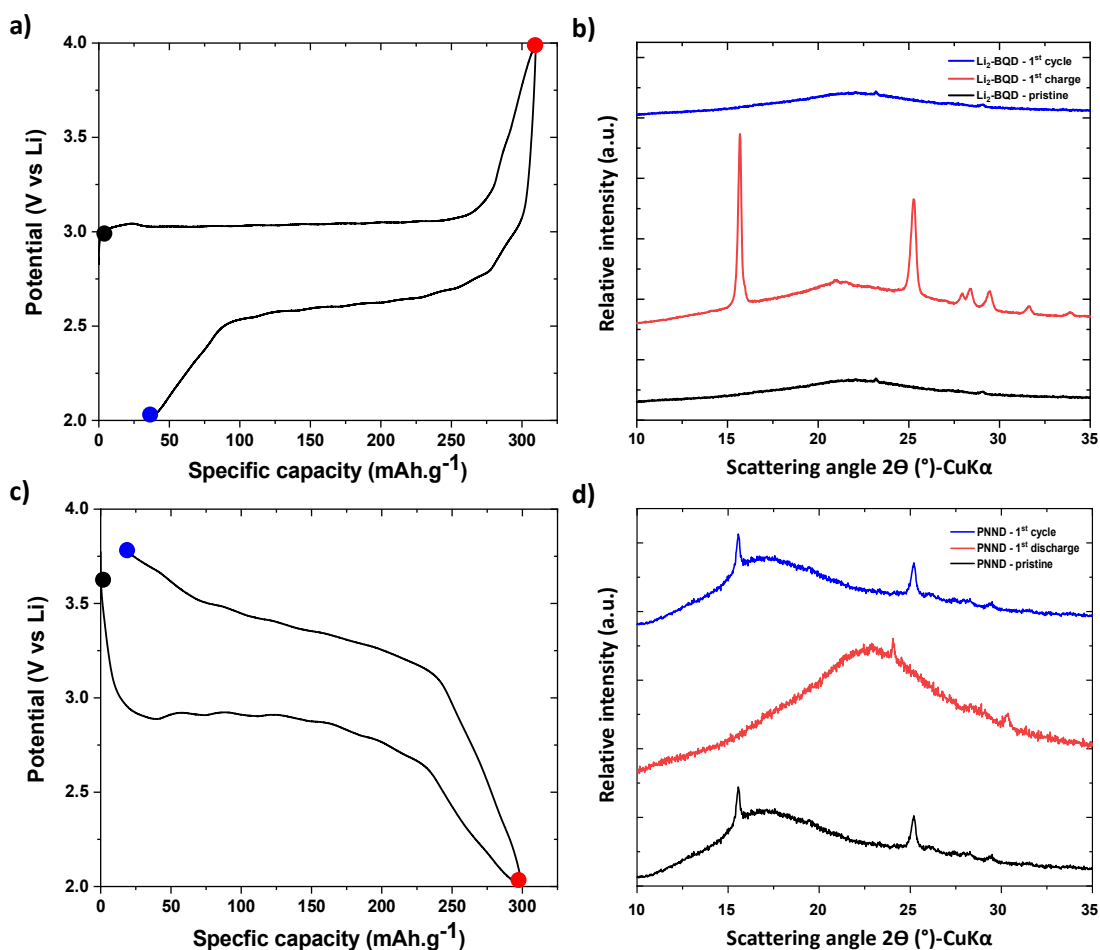


1
 2 **Figure 3 – (a) Galvanostatic profile of 1st, 2nd and 100th cycle and (b) corresponding**
 3 **capacity retention curve upon 100 cycles of PNND electrode (70:30 AM/KJ600) half-cell**
 4 **vs Li, window range of 4.0-2.0 V with LP30 electrolyte.**

5 3.5 Coupled XRD and TEM investigation of the redox activity and mechanism.

6 From the electrochemical tests performed on both the **Li₂-BQDO** and **PNND** electrodes, a
 7 marked difference emerged in terms of capacity retention along cycling. Although the redox
 8 mechanism is identical, **PNND** exhibited superior capacity stability over cycling. To
 9 investigate this important difference, *ex-situ* TEM/EELS analyses, coupled with *ex-situ* XRD
 10 diffraction, were performed on both materials, along the first complete cycle and after 20
 11 cycles. First, a complete cycle of dilithium benzoquinone dioximate was analyzed (Figure 4a).
 12 Before cycling, **Li₂-BQDO** displays in X-ray diffraction (Figure 4b) a broad contribution with
 13 no Bragg peaks, indicating an amorphous structure. After the charging stage, with the
 14 oxidation of benzoquinone dioxime, two main Bragg peaks appeared at $2\theta = 15.5^\circ$ (020
 15 reflection plane) and $2\theta = 25^\circ$ (011 reflection plane), indicating the appearance of crystalline
 16 phase attributed to the PNND reported structure (Figure 4b). After the discharge state (full
 17 cycle), the Bragg peaks nearly disappeared, faint peaks were visible at $2\theta = 15.5^\circ$ and $2\theta =$
 18 25° , indicating the remaining presence of a crystalline structure. Same type of observation is
 19 obtained from XRD pattern acquired for **PNND** material (Figure 4c and d). For **PNND**,

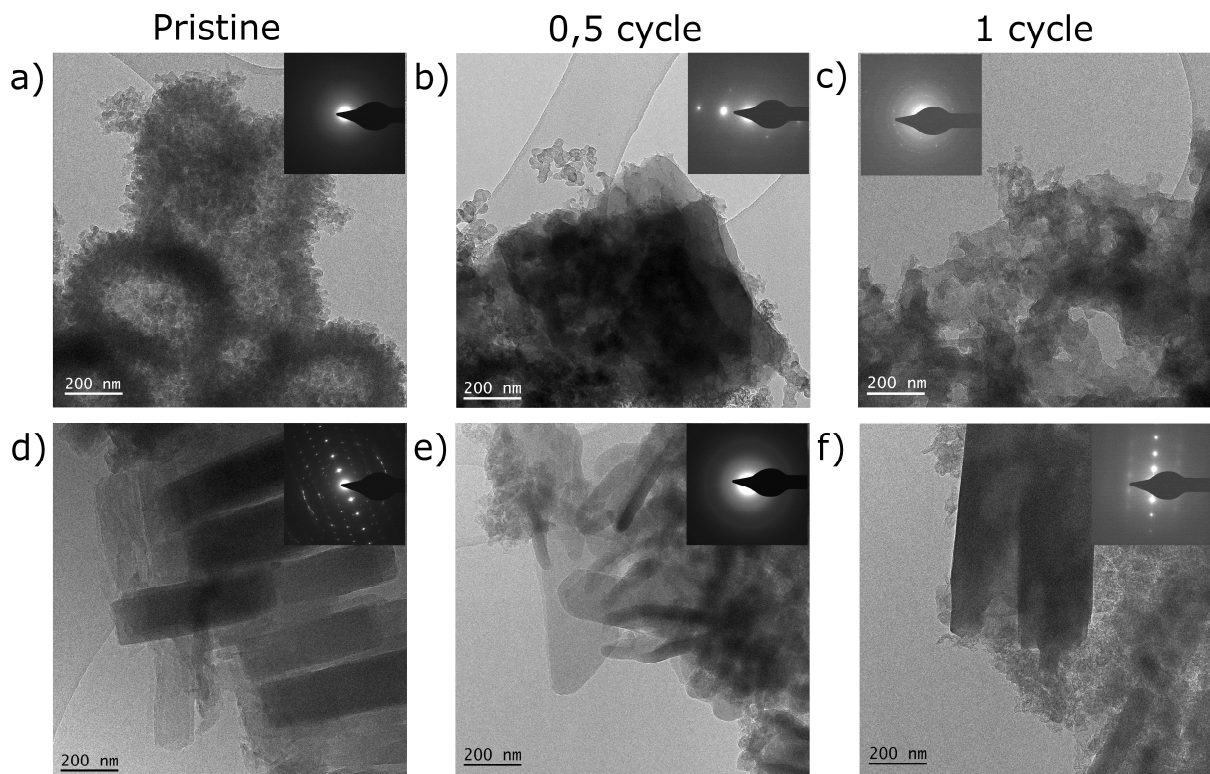
1 starting material shows two diffraction peaks at 15.5° and 25.3° which vanished upon
 2 discharge and reappearing after one full cycle. It should be noted that even if an amorphous
 3 signal is observed after discharge, two new peaks are distinguished at 24° and 30.5° , which
 4 are not attributed for the moment but not present previously for $\text{Li}_2\text{-BQDO}$. After one
 5 complete cycle, in the XRD powder pattern (Figure 4b, blue line) were observed the same
 6 Bragg peaks already found in the pristine material. This result confirmed the reversibility of
 7 the redox reaction, with the full recovery of the starting crystalline structure, which is also
 8 identical to what was obtained after the oxidation of $\text{Li}_2\text{-BQDO}$.



9
 10 **Figure 4 –Galvanostatic profile of the 1st cycle and X-ray powder patterns for (a and b)**
 11 **$\text{Li}_2\text{-BQDO}$ and (c and d) PNND in pristine (black line), after half cycle (red line) and one**
 12 **full cycle (blue line).**

1 The TEM investigation of **Li₂-BQDO** showed a microstructure composed of particles either
2 round with a range diameter of 5-25 nm or needle-like with a width range of 5-25 nm and a
3 length higher than 100 nm arranged in hollow-like agglomerates (Figure 5a). The SAED
4 pattern (Figure 5a, inset) exhibited a diffuse ring indicating an amorphous contribution, in
5 agreement with the XRD data. In Figure 6 is showed the chemical characterization obtained
6 by EELS of the pristine sample about the lithium information and for the carbon and nitrogen
7 edge. The broad and asymmetric contribution with a maximum at ~ 62 eV corresponds to the
8 Li K-edge (Figure 6a, full black line). It will be used as reference spectrum for the lithiated
9 phase. The white line with a sharp peak at 285 eV followed by a broad contribution at 290 eV
10 is related to the C K-edge (Figure 6b, black full line) with respectively the π^* and σ^* state. A
11 sharp peak followed by a broader contribution is also visible at 400 eV and corresponds to N
12 K-edge (Figure 6b, black full line). The presence of the nitrogen contribution confirmed the
13 presence of active material in the investigated area. The microstructure of the
14 electrochemically oxidized Li₂-BQDO exhibits marked differences (Figure 5b) with large
15 particles of irregular shape and a size ranging from 500 nm and up to 2.5 μ m. They form
16 relatively large and homogeneous masses as highlighted by white area according the (00-1) in
17 the dark field image (red circle in Figure S10b and arrow in Figure S10c, ESI). By
18 investigating them closely, some small, rounded grains (~ 5-25 nm) can be distinguished and
19 seem to be “glued” to the big particles. These observations are consistent with a growth
20 process and most probably here with a progressive polymerization of small organic grains as
21 proposed by Wang *et al.*¹³ The SAED pattern obtained on the large particles present a dots
22 pattern (see inset in Figure 5b), which is characteristic of mono-crystalline sample and the
23 indexation of the direction can be in accord with (00l) interplanar distance from **PNND**
24 (Figure S11b).¹⁹ The chemical characterizations obtained by EELS showed the absence of
25 contribution in the Li K-edge (Figure 6a, black dot line) and the presence of white lines in the

1 C K-edge and N K-edge (Figure 6b, black dot line) confirming that the crystalline area was
2 the active material and the complete lithium de-insertion after the charge process. The
3 microstructure after discharged sample showed relatively large, separated and porous area.
4 The diffraction pattern collected in this area exhibited defined rings, indicating a
5 polycrystalline character. The dark field image obtained on the discharged sample highlighted
6 the presence of small white areas (red arrows in Figure S12f), which diffract according to the
7 red circles (Figure S12e) and were distributed randomly. The inter-reticular distances
8 determined from the diffraction pattern (see Figure S9c) are $d_1 = 4.2 \text{ \AA}$, $d_2 = 3.0 \text{ \AA}$ et $d_3 =$
9 2.52 \AA . The chemical characterizations of discharged sample obtained by EELS showed the
10 presence of a contribution in the Li K-edge (Figure 6a, black dot line) similar to the pristine
11 sample. Moreover, the presence of white lines in the C K-edge and N K-edge (Figure 6b,
12 black dot line) confirmed the lithium re-intercalation in the active material during the
13 discharged process. The analysis of small crystalline area showed a fast amorphization under
14 the electron beam, as well as the characterization *via* EELS was performed in an average way.



15

1 **Figure 5 - TEM bright field images of Li₂BQD (a) pristine, after (b) half cycle and (c)**
2 **one full cycle. TEM bright field images of PNND d) pristine, after e) half cycle and f) one**
3 **full cycle. The associated diffraction patterns are in inset (and in Figure S7 ESI).**

4 The TEM analysis of the first complete cycle was also performed starting from PNND (Figure
5 5d-f). The images showed significant differences compared to the PNND obtained *via* electro-
6 oxidation from **Li₂-BQDO**. The microstructure was formed of needle-like particles, which
7 were arranged to form rectangular parallelepipeds, with lateral dimensions between of 150-
8 200 nm and lengths ranging up to 1-2 microns. The SAED patterns recorded on **PNND**
9 parallelepiped particles showed similar pattern (Figure 5d, inset), with arranged dots
10 corresponding to a monocrystalline phase and their indexation in agreement with the **PNND**
11 in the zone axis [001] (Figure S9d), indicating a preferential orientation growth. The EELS
12 reference spectra (Figure 6a and 8b, dark blue full line) showed the absence of lithium,
13 consistent with the oxidized form that does not have lithium ions in the structure, and the
14 presence of carbon and nitrogen confirming the presence of the active material. However, the
15 π^* state at 285 eV in the C-K edge is less intense compared to what observed with Li₂-BQDO.
16 After discharging the sample, the complete amorphization of the crystalline structure was
17 confirmed by X-ray diffraction, where the disappearance of the Bragg peaks was observed in
18 the powder pattern (Figure 4d, red line). The microstructure at the discharged state was
19 evolved. The visible parallelepiped particles showed a smoother edge, but also other particles
20 with 30-65 nm thick wall were observed in the image. The latter can be connected or not by a
21 thinner area in the middle, as little like *trivia monacha* (Figure 5e). The associated diffraction
22 pattern is composed of diffuse rings indicating an amorphous structure which is coherent with
23 the X-ray diagram. The EELS investigation on the Li-K edge (Figure 6a, dark blue dot line)
24 highlighted the presence of lithium, for which the shape and position of the main peaks fit

1 with what observed for **Li₂-BQDO**. The presence of active material was confirmed by the
2 presence of carbon and nitrogen peaks (Figure 6b, dark blue dot line).

3 The microstructure did not change after the charge phase. The shape and size of active
4 material particles is similar to the discharged state, with particles with 30-65 nm thick wall
5 connected or not by a thinner area in the middle, as can be seen in Figure 5f. The associated
6 diffraction pattern (inset Figure 5f and Figure S11f) is composed of dots arranged in a motif
7 indicating a crystalline sample. This result is coherent with the XRD measurement, but the
8 signal is less intense compared to the pristine sample. The indexation of diffraction peaks is
9 compatible with **PNND** crystalline structure, but with the modification in the intensity
10 distribution can indicate a slight change in the orientation of the crystal structure particles.

11 Finally, the EELS analysis on the Li-K edge (Figure S13a, dark blue dash-dot line) showed
12 the absence of lithium, confirming the reversibility of the lithium de-/insertion redox process.

13 As in the previous case, the presence of the active material in the investigated zone was
14 confirmed by C-/N-K edges (Figure S14b, dark blue dash-dot line).

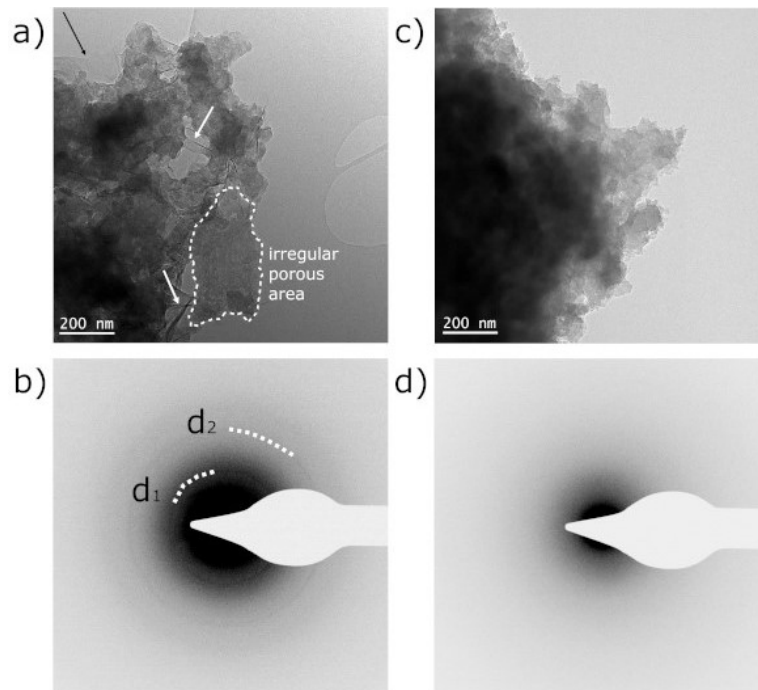
15 The results observed from the coupled TEM / XRD analysis over a full cycle, starting from
16 both **Li₂-BQDO** and **PNND**, may explain the differences, in terms of electrochemical
17 properties, between the two materials. Although the crystal structure remained unchanged for
18 all states involving dinitrosobenzene, as confirmed by TEM diffraction and *ex-situ* XRD
19 analysis, the microstructure was strongly different depending on the type of process (chemical
20 or electrochemical) used to obtain the polymeric equivalent (**PNND**). These differences in the
21 microstructures of **PNND**, both in the uncontaminated monomeric form and in the **PNND**
22 polymer form, can profoundly affect the lithium deactivation / insertion process during the
23 cycle. The radiation obtained through direct chemical synthesis is more orderly and oriented
24 than **PNND** obtained by electrochemistry, resulting in an improvement in the diffusion and
25 insertion of lithium ions in the active material, with a consequent improvement in

1 electrochemical performance, especially for regarding retention of capacity. Such finding is
2 interesting and should be investigate in more details in the future to maximize capacity.

3 In addition to studying the first complete redox cycle, TEM analysis was used to
4 investigate the differences between the two electrodes after 20 charge and discharge cycles, in
5 order to understand the observed differences in term of capacity retention (Figure 6). As
6 observed in the capacity vs. cycles profiles, most of the loss of capacity occurs, in both cases,
7 in the first 20 cycles, then it remains constant. The TEM images (Figure 6a) showed, in the
8 case of the benzoquinone dioxime electrode after 20 complete cycles, a microstructure
9 composed of irregularly shaped particles, characterized by marked porosity, since the color
10 scale in the particles is inhomogeneous (one of these areas is surrounded by the dashed line in
11 Figure 9a). Furthermore, the presence of thin sheets was also observed, as highlighted by the
12 white arrow in Figure 9a. The associated diffraction pattern in negative mode (Figure 6b) is
13 composed of a defined weak ring indicating the polycrystalline nature of this microstructure
14 (irregular particles + thin sheets). The inter-lattice distances d_1 and d_2 are respectively
15 approximately 4.4 Å and 2.6 Å, but the information was insufficient to obtain the adequate
16 indexation.

17 About the **PNND**-based electrode after 20 cycles (Figure 6c), it was also composed of
18 irregular shape particles which also was characterized by porous structure. In this case, the
19 presence of the thin sheets and their associated diffraction pattern was not observed. The
20 electron diffraction showed diffuse rings indicating the amorphous nature of the material. The
21 EELS analysis of $\text{Li}_2\text{-BQDO}$ after 20 cycles shows the presence of phosphorus, lithium,
22 carbon, oxygen and fluorine relative to the areas where the polycrystalline thin sheets are
23 present (Figure S14). These elements, deriving from the electrolytic salt, indicate the presence
24 of derivatives from the degradation of electrolyte. These polycrystalline structures and their

1 relative chemical composition were not detected in the dinitrosobenzene electrode indicating
2 in the latter case the degradation of the electrolyte is less marked.



3
4 **Figure 6 - a) TEM bright field images and b) associated diffraction patterns of Li_2 -**
5 **BQDO after 20 cycles; c) TEM bright field images and d) associated diffraction patterns**
6 **of PNND after 20 cycles.**

7 The phenomenon of electrolyte degradation can be used as an explanation for the greater loss
8 of capacitance on the part of the Li_2 -BQDO compared to the PNND. As further perspective, a
9 more in-depth analysis on the causes of this phenomenon will help to obtain a more
10 comprehensive understanding of the electrochemical properties of these materials, in order to
11 understand the possible chemical-physical modifications necessary to improve their
12 performance.

13

14 **4. Conclusions**

15 In the present work, a global approach in the study of benzoquinone dioxime derivatives as a
16 positive material for lithium-ion batteries was reported. By following a DFT molecular

1 modelling performed prior to any experiment and aimed at providing a first glimpse of the
2 redox mechanism characterizing DNB and Li₂-BQDO systems, the synthesis and
3 characterization of the dioxime derivatives were performed, both in the lithiated form and in
4 the delithiated polymerized (PNND) form. The materials were characterized through SEM
5 and XRD analyzes and showed an average redox potential of 3.0 V vs. Li⁺/Li, with a
6 promising specific capacity in the first cycle, measured in 277 and 313 mAh g⁻¹ for Li₂-
7 BQDO and PNND, respectively but exhibited low capacity retention low over long cycling,
8 with only 11% and 23% retention after 100 cycles. Thanks to a pool of techniques the redox
9 mechanism of insertion /desinsertion of lithium ions in the active material was investigated. It
10 was found that the difference of microstructure is the basis of the different electrochemical
11 performances observed in galvanostatic tests which is better in the case of the chemically
12 oxidized version. The marked formation of salts originating from the degradation of the
13 electrolyte was observed in the case of the Li₂-BQDO electrode, which allows to point to this
14 phenomenon the greater loss of capacity observed. This study allowed to understand in detail
15 the redox mechanism of benzoquinone dioxime, validating the proposed model both through
16 simulations and experimental tests. The exceptional electrochemical properties shown, such
17 as the insertion potential of 3.0 V vs. Li⁺/Li and the specific capacity greater than 300 mAh g⁻¹
18 ¹ observed in the first cycle open the way for future studies on derivatives of benzoquinone
19 dioxime as eco-sustainable positive materials for lithium batteries.

20 **Conflicts of interest**

21 There is no conflict of interest to declare.

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24 funding of this research work between LRCS and EDF (Convention CIFRE N° 2019/0926).

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2 analysis.

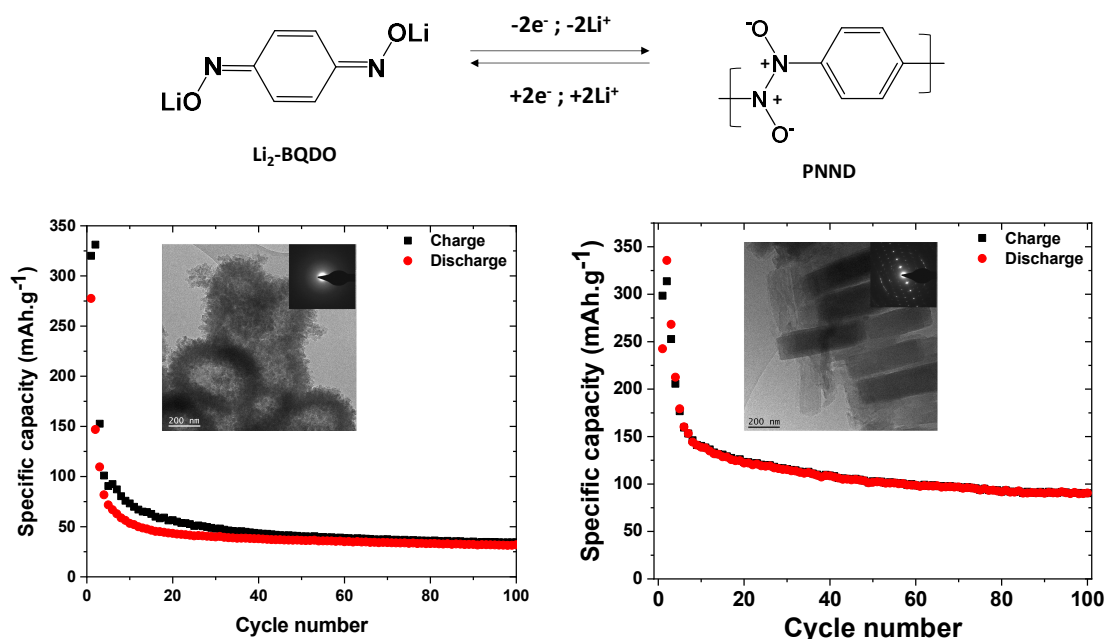
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21

22 **Graphic for manuscript**



23