Exploitation of Redox-active 1,4-Dicyanobenzene and 9,10-Dicyanoanthracene as the Organic Electrode Materials in Rechargeable Lithium Battery

Qijiu Deng,^a Shou-Jie He,^c Jingfang Pei,^a Cong Fan,^{*a} Chao Li,^a Bei Cao,^{*b} Zheng-Hong Lu,^{*c,d} and Jingze Li^{*a}

^a State Key Laboratory of Electronic Thin Films and Integrated Devices, School of Microelectronics and Solid-state Electronics, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, P. R. China

^b State Key Laboratory of Synthetic Chemistry, Institute of Molecular Functional Materials, Department of Chemistry, The University of Hong Kong, Hong Kong, P. R. China

^c Department of Physics, Yunnan University, Yunnan 650091, P. R. China

^d Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario M5S 3E4, Canada

*Corresponding Author

fancong@uestc.edu.cn; lijingze@uestc.edu.cn; bcao@hku.hk; zhenghong.lu@utoronto.ca

Abstract: A new redox-active family of aromatic dicyanides was developed as organic electrodes in rechargeable batteries. The detailed electronic properties of two primary representatives of 1,4-dicyanobenzene (DCB) and 9,10-dicyanoanthracene (DCA) were studied. It is discovered that, as compared with DCB, the large aromatic π conjugation in DCA leads to better electron conductivity and more stable reduced states of DCA^- and DCA^{2-} . The Li-ion batteries with DCA electrode are shown to have highly reversible operations.

Keywords: aromatic dicyanides; organic electrode; Li-ion battery

1. Introduction

To meet the increasing need for sustainable development in energy storage, it is desirable to exploit more efficient and cleaner electronic energy-storage system [1]. The commercial electrochemical batteries hardly meet the rapidly growing need for electronic devices, particularly in Li-ion batteries with the conventional inorganic electrodes (*e.g.*, LiCoO_2 and LiFePO_4) [2]. Alternatively, organic electroactive compounds are becoming very attractive as alternatives for the next-generation batteries [3]. Compared to the inorganic counterparts, organic materials are structure contrivable, abundant on earth and almost without concern for production cost. Moreover, high gravimetric energy density and cycling stability can be realized within organic batteries [4, 5]. Although many progresses have been made recently, the development of organic electrode materials is still at an early stage. Performance limitations like poor electronic conductivity must be resolved for organic electrodes to be alternatives of inorganic electrodes.

To be usable as an electrode material, an organic compound should possess redox couple. And the redox couple should be thermodynamically reversible or at least exhibit kinetic reversibility, which means that the oxidized and reduced states, along with the possible intermediate(s) formed during the oxidation or reduction process, should be stable enough in battery environment. Otherwise

electrochemical decomposition will gradually happen during battery operations. However, only a few kinds of organic electrode materials have been currently reported, mainly including organo-disulfides/-thioethers [6], nitroxyl radicals [7, 8], aromatic carbonyl compounds [9, 10], conjugated dicarboxylates and the related anhydrides/imides [11, 12], aromatic amines/diimines [13, 14], and tetracyanoquinodimethane (TCNQ) [15, 16] *etc.*. Considering the richness of organic structures, however, there should be many opportunities to develop new organic redox-active compounds.

Herein, we reported a new redox-active family of aromatic dicyanides was used as organic electrode materials in rechargeable batteries. Two primary representatives of 1,4-dicyanobenzene (DCB) and 9,10-dicyanoanthracene (DCA) were fully studied and compared. Tested as the electrode material in Li-ion batteries, DCA is shown to exhibit highly reversible two-electron discharge/charge potentials around 1.8 and 1.4 V (vs. Li/Li⁺), respectively.

2. Experimental Section

DCB and DCA are commercially available. Electrochemical measurements were performed by using two-electrode half cells. The working electrodes were prepared by casting the slurry onto a clean copper foil with 5 MPa compression [17], where the electrode (~2 mg cm⁻²) contained the active materials (50 wt%), acetylene carbon black (40 wt%) and poly(tetrafluoroethylene) binder (10 wt%). The electrolyte (50 μ l) is 1 M bis(trifluoromethane)sulfonimide lithium in the solvents of 1,2-dimethoxyethane and 1,3-dioxolane with the volume ratio of 1:1. These cells (CR2032) were assembled in Ar-filled glove box with high purity of 99.999 %. The galvanostatic cycling test was carried on a CT2001A instrument [18]. Cyclic voltammograms (CVs) were tested on a CHI electrochemical workstation. The theoretical specific capacities of DCB and DCA are 418 and 235 mAh g⁻¹.

Scheme 1. (a) The proposed electrochemical mechanism for DCB and DCA in Li-ion battery; (b) The modified synthetic route for DCA.

3. Results and discussions

The electrochemical mechanism of DCB and DCA was proposed in **Scheme 1a**. Although DCA is structurally simple, its synthesis and purification were complicated due to the usage of toxic reagents

and its relatively poor solubility [19]. As depicted in **Scheme 1b**, we developed a modified one-pot synthetic route to **prepare** DCA with satisfactory yield above 50 % [20]. The ultraviolet-visible absorption spectra of DCB and DCA in dichloromethane solution were measured at room temperature. DCB shows two characteristic peaks at 283 and 291 nm while DCA **exhibits the bathochromic and multiple peaks** in the range of 350-450 nm. Meanwhile, DCA displays strong blue fluorescence in common organic solvents under UV light. Accordingly, the optical energy-band gaps (E_g) calculated from the onsets of absorption spectra for DCB (298 nm) and DCA (448 nm) were 4.16 and 2.77 eV [21].

Fig. 1. (a) CV curves for DCB and DCA in solution; (b) **Electrical characteristics of the thin-film devices for DCA, TPBi and Liq with ITO and Al as the electrodes and current collectors.**

The electrochemical behaviors of DCB and DCA were examined by CV in deaerated *N,N*-dimethylformamide solution [22]. As shown in **Fig. 1a**, both DCB and DCA displayed reversible **reduction potentials**, and the half-wave reduction potentials ($E_{1/2}$) were estimated to be -1.99 and -1.24 V relative to ferrocene/ferrocenium (Fc/Fc⁺) couple. Consequently, their lowest unoccupied molecular orbital (LUMO) levels determined from the reduction potentials were -2.81 eV for DCB and -3.56 eV for DCA, respectively [22]. On the other hand, their highest occupied molecular orbital (HOMO) levels, deduced from the LUMO and E_g , were -6.97 and -6.33 eV for DCB and DCA [23]. Due to the larger aromatic π skeleton, DCA exhibits lower LUMO than DCB and could lead to its better **electron conductivity**. To confirm the better electron-transporting **property** of DCA, **the thin-film device structure widely-used to test electron transport in organic light-emitting diodes was used to test its thin-film conductivity for electrons** [24]. For comparison, the control devices based on 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBi) and 8-hydroxyquinolinolato lithium (Liq) were constructed under the same conditions, where TPBi (LUMO = -2.7 eV) [25] is widely used as the electron-transporting material and Liq frequently serves as the electron-injecting material for its deep LUMO of -3.15 eV [26]. The **thin-film** devices were constructed by the following configuration: ITO [indium titanium oxide, **120 nm, anode**]/LiF (1 nm)/TmPyPB [1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene] (10 nm)/DCA (device A) or TPBi (device B) or Liq (device C) (30 nm)/TmPyPB (10 nm)/LiF (1 nm)/Al (**100 nm, cathode**). The obtained electron current-voltage curves were shown in **Fig. 1b**. Apparently, the device A based on DCA displayed significantly lower start-up voltage (6 V) for initiating the electron current than TPBi (12 V) as well as the distinctively larger electron current than Liq, which proves that low LUMO of organic material is benefited for electron injection and simultaneously the large π -conjugation system is advantageous to inter-molecular charge transportation [27]. **On the other hand, the neat film of DCB cannot be prepared through vacuum evaporation, likely for its too small molecular weight.**

To get more insights about the electronic structures of DCB, DCA and their possible charged states, the density function theory calculations were performed. And BP86 functional **was chosen** to calculate the **redox potentials** of DCB/DCB⁻ and DCA/DCA⁻ couples. The obtained data of -1.78 (DCB/DCB⁻ vs. Fc/Fc⁺) and -1.15 V (DCA/DCA⁻ vs. Fc/Fc⁺) were in good agreement with the experimental values (-1.99 and -1.24 V). The calculated C≡N bond lengths in DCB and DCA are both 1.17 Å. As the reduction proceeds, the C≡N bond is broken and gradually elongated. For DCB⁻ and DCB²⁻, the C≡N bond length becomes *cal.* 1.19 and 1.21 Å. And the situation is the same for DCA⁻ and DCA²⁻, with the C≡N bond length being 1.18 and 1.19 Å. It is well known that the injected electron occupies the LUMO of DCB or DCA, so the weaker elongation of C≡N bond in DCA⁻ and DCA²⁻ is expected because the larger π aromatic system could delocalize charge more efficiently. The calculated frontier orbitals and their corresponding energy levels were depicted in **Fig. 2**. All the DCA-related **LUMOs** are expectantly stabilized compared to the DCB analogues. Meanwhile, the electron spin density and the single occupied molecular orbital (SOMO) for the radical intermediate of DCB⁻ or DCA⁻ are not localized but evenly distributed throughout the whole molecule, which should be advantageous for their chemical stability.

Fig. 2. Molecular orbitals and the related energy levels calculated for DCB, DCA and their charged states.

Fig. 3. The CV curves of (a) DCB and (d) DCA; The initial 5 galvanostatic discharge-charge curves of (b) DCB and (e) DCA; and the cycling profiles of (c) DCB and (f) DCA, respectively.

Subsequently, the electrochemical performance of DCB in Li-ion batteries was initially tested. The CV experiment with the scan rate of 0.1 mV s⁻¹ was firstly performed to examine its electrochemical behavior. Unexpectedly, DCB displayed unclear reduction potentials in the voltage window of 1-3 V (Fig. 3a) or 0.3-2 V (vs. Li⁺/Li) (not shown here) during multiple scans, and the redox potentials around 1 V was from the carbon black (inset of Fig. 3a). These observations were contrary to its reversible electrochemical behavior in solution. Next, the galvanostatic discharge-charge performance for DCB was tested, and the initial 5 discharge-charge curves were depicted in Fig. 3b. DCB exhibited unclear discharge or charge potential (1-3 V) along with the negligible capacity (<50 mAh g⁻¹) (Fig. 3c). Therefore, the possible reasons for the battery inefficiency of DCB could be ascribed as follows: i) DCB with small molecular weight exhibits catastrophic dissolution problem in liquid electrolyte [28]; ii) DCB could display apparent kinetic redox reversibility in solution but its reduced product (DCB⁻ or DCB²⁻) may not be stable enough in real battery environment [29].

On the other hand, unlike the case of DCB, DCA exhibited the step-by-step reduction potentials in the same voltage window of 1-3 V (Fig. 3d). The first reduction potential occurred at 1.79 V and the second one appeared at 1.33 V. More importantly, the reduction behaviors of DCA were reversible, as confirmed by the oxidation peaks (1.67 and 2.12 V) observed during the back anode scans. Noticeably, it seemed there was a third reversible redox behavior of DCA appearing at 1.55/1.71 V, but the intensity of the redox potentials was smaller than the other two. The similar phenomena were reported for the carbonyl-based derivatives and were possibly resulted from the interaction between DCA and cell matrix (e.g., carbon additive, cell electrolyte) [30]. Therefore, DCA should exhibit two electron redox processes. The first redox process (1.79/2.12 V) can be assigned to the DCA/DCA⁻ couple while the second redox one (1.33/1.67 V) is deduced to the DCA⁻/DCA²⁻ couple. Obviously, the electrochemical reversibility is benefited from the stability of its reduced products structurally supported by the large π conjugation, which simultaneously makes DCA more suitable as cathode

material [11]. Afterwards, the galvanostatic discharge-charge performance for the DCA-based Li-ion batteries was tested, and the initial 5 discharge-charge curves were depicted in **Fig. 3e**. Remarkably, the obtained capacities were not exceeding the theoretical capacity of DCA (235 mAh g^{-1}) when considering its two-electron **mechanism**. Meanwhile, the phenomenon of step-by-step, two-electron process is seldom observed for other organic molecules [31, 32]. The cycling profile of the DCA-based battery was shown in **Fig. 3f**, which exhibited the discharge capacity of 330 mAh g^{-1} and the Coulombic efficiency (CE) of 56 % in the 1st cycle. The low CE value is mainly ascribed to the formation of surface electrolyte interface and other possible side reactions. And the capacity contribution from acetylene carbon black herein was lower than 10 mAh g^{-1} . However, the capacity of the DCA electrode was observed to decay in the initial 10 cycles but became stable afterward, with 96 mAh g^{-1} at the 30th cycle. Although many factors would account for the poor cyclability of organic cathodes (*e.g.*, crystal structure) [33, 34], the capacity loss of DCA herein was mainly attributed to its unacceptable dissolution in liquid electrolyte [30, 35], which can be easily checked by the color change of liquid electrolyte and/or blue fluorescence. To further improve the battery performance, the fabrication of all-solid-state battery and/or embedding DCA into polymer can be the effective technical modifications [16, 36, 37].

4. Conclusions

In conclusion, a new promising redox-active family of aromatic dicyanides **is developed and its application as the organic electrodes in Li-ion batteries is tested**. 1,4-Dicyanobenzene and 9,10-dicyanoanthracene in this family are fully studied. **Due to its larger π conjugation, 9,10-dicyanoanthracene exhibits better electrochemical stability and higher electron conductivity than does of 1,4-dicyanobenzene. This new redox-active family is shown to have controllable two-electron discharge/charge potentials and is expected to be usable as electrodes in other types of rechargeable batteries.**

Acknowledgement

This work is supported by the Startup Grant of UESTC (ZYGX2015KYQD058); the National Science Foundation of China (11234013, 21473022, 21673033, 51603028, **U1402273**); the Science and Technology Bureau of Sichuan Province of China (2015HH0033); the University Grants Committee of HKSAR Area of Excellence Scheme (AoE/P-03/08). This research uses the computing facilities offered by Information Technology Services, The University of Hong Kong.

References

- [1] M. Armand, J.M. Tarascon, Building better batteries, *Nature*, 451 (2008) 652-657.
- [2] X. Dai, A. Zhou, J. Xu, Y. Lu, L. Wang, C. Fan, J. Li, Extending the High-Voltage Capacity of LiCoO_2 Cathode by Direct Coating of the Composite Electrode with Li_2CO_3 via Magnetron Sputtering, *J. Phys. Chem. C*, 120 (2016) 422-430.
- [3] Y. Liang, Z. Tao, J. Chen, Organic Electrode Materials for Rechargeable Lithium Batteries, *Adv. Energy Mater.*, 2 (2012) 742-769.
- [4] E. Deunf, P. Moreau, E. Quarez, D. Guyomard, F. Dolhem, P. Poizot, Reversible anion intercalation in a layered aromatic amine: a high-voltage host structure for organic batteries, *J. Mater. Chem. A*, 4 (2016) 6131-6139.
- [5] H. Chen, M. Armand, M. Courty, M. Jiang, C.P. Grey, F. Dolhem, J.-M. Tarascon, P. Poizot, Lithium Salt of Tetrahydroxybenzoquinone: Toward the Development of a Sustainable Li-Ion Battery, *J. Am. Chem. Soc.*, 131

(2009) 8984-8988.

- [6] P. Novák, K. Müller, K.S.V. Santhanam, O. Haas, Electrochemically Active Polymers for Rechargeable Batteries, *Chem. Rev.*, 97 (1997) 207-282.
- [7] K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, Rechargeable batteries with organic radical cathodes, *Chem. Phys. Lett.*, 359 (2002) 351-354.
- [8] K. Oyaizu, H. Nishide, Radical Polymers for Organic Electronic Devices: A Radical Departure from Conjugated Polymers?, *Adv. Mater.*, 21 (2009) 2339-2344.
- [9] A.J. Wain, G.G. Wildgoose, C.G.R. Heald, L. Jiang, T.G.J. Jones, R.G. Compton, Electrochemical ESR and Voltammetric Studies of Lithium Ion Pairing with Electrogenerated 9,10-Anthraquinone Radical Anions Either Free in Acetonitrile Solution or Covalently Bound to Multiwalled Carbon Nanotubes, *J. Phys. Chem. B*, 109 (2005) 3971-3978.
- [10] R.-h. Zeng, X.-p. Li, Y.-c. Qiu, W.-s. Li, J. Yi, D.-s. Lu, C.-l. Tan, M.-q. Xu, Synthesis and properties of a lithium-organic coordination compound as lithium-inserted material for lithium ion batteries, *Electrochem. Commun.*, 12 (2010) 1253-1256.
- [11] M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribiere, P. Poizot, J.M. Tarascon, Conjugated dicarboxylate anodes for Li-ion batteries, *Nat. Mater.*, 8 (2009) 120-125.
- [12] W. Deng, J. Qian, Y. Cao, X. Ai, H. Yang, Graphene-Wrapped Na₂C₁₂H₆O₄ Nanoflowers as High Performance Anodes for Sodium-Ion Batteries, *Small*, 12 (2016) 583-587.
- [13] K. Nishi, T. Nishiumi, M. Higuchi, K. Yamamoto, A High Energy Rechargeable Battery Based on a One-Step Successive Two-Electron Transfer Process, *Electrochem. Solid-State Lett.*, 8 (2005) A382-A384.
- [14] J.K. Feng, Y.L. Cao, X.P. Ai, H.X. Yang, Polytriphenylamine: A high power and high capacity cathode material for rechargeable lithium batteries, *J. Power Sources*, 177 (2008) 199-204.
- [15] S.i. Tobishima, J.i. Yamaki, A. Yamaji, Cathode Characteristics of Organic Electron Acceptors for Lithium Batteries, *J. Electrochem. Soc.*, 131 (1984) 57-63.
- [16] Y. Hanyu, I. Honma, Rechargeable quasi-solid state lithium battery with organic crystalline cathode, *Sci. Rep.*, 2 (2012) 453.
- [17] J. Xue, C. Fan, Q. Deng, M. Zhao, L. Wang, A. Zhou, J. Li, Silver Terephthalate (Ag₂C₈H₄O₄) Offering in-situ Formed Metal/Organic Nanocomposite as the Highly Efficient Organic Anode in Li-ion and Na-ion Batteries, *Electrochim. Acta*, 219 (2016) 418-424.
- [18] J. Xue, C. Fan, L. Wang, A. Zhou, J. Li, Silver-Mediated Calcium Terephthalate with Enhanced Electronic Conductivity as an Organic Anode for Efficient Li-ion Batteries, *RSC Adv.*, 6 (2016) 29404-29409.
- [19] F. Glöcklhofer, M. Lunzer, B. Stöger, J. Fröhlich, A Versatile One-Pot Access to Cyanoarenes from ortho- and para-Quinones: Paving the Way for Cyanated Functional Materials, *Chem.-Eur. J.*, 22 (2016) 5173-5180.
- [20] Z. Lu, F. Zhan, L. Xue, J. Zhu, Synthesis of 9,10-anthracenedicarbonitrile, *Jingxi Shiyong Huagong*, 23 (2006) 37-40.
- [21] C. Fan, C. Yang, Yellow/orange emissive heavy-metal complexes as phosphors in monochromatic and white organic light-emitting devices, *Chem. Soc. Rev.*, 43 (2014) 6439-6469.
- [22] T.P.I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker, J. Salbeck, Spiro Compounds for Organic Optoelectronics, *Chem. Rev.*, 107 (2007) 1011-1065.
- [23] C. Fan, F. Zhao, P. Gan, S. Yang, T. Liu, C. Zhong, D. Ma, J. Qin, C. Yang, Simple Bipolar Molecules Constructed from Biphenyl Moieties as Host Materials for Deep-Blue Phosphorescent Organic Light-Emitting Diodes, *Chem.-Eur. J.*, 18 (2012) 5510-5514.
- [24] C. Fan, L. Zhu, T. Liu, B. Jiang, D. Ma, J. Qin, C. Yang, Using an Organic Molecule with Low Triplet Energy as a Host in a Highly Efficient Blue Electrophosphorescent Device, *Angew. Chem. Int. Ed.*, 53 (2014) 2147-2151.

- [25] C. Fan, L. Zhu, B. Jiang, Y. Li, F. Zhao, D. Ma, J. Qin, C. Yang, High Power Efficiency Yellow Phosphorescent OLEDs by Using New Iridium Complexes with Halogen-Substituted 2-Phenylbenzo[d]thiazole Ligands, *J. Phys. Chem. C*, 117 (2013) 19134-19141.
- [26] C. Schmitz, H.-W. Schmidt, M. Thelakkat, Lithium–Quinolate Complexes as Emitter and Interface Materials in Organic Light-Emitting Diodes, *Chem. Mater.*, 12 (2000) 3012-3019.
- [27] Y. Qiao, Y. Guo, C. Yu, F. Zhang, W. Xu, Y. Liu, D. Zhu, Diketopyrrolopyrrole-Containing Quinoidal Small Molecules for High-Performance, Air-Stable, and Solution-Processable n-Channel Organic Field-Effect Transistors, *J. Am. Chem. Soc.*, 134 (2012) 4084-4087.
- [28] M. Yao, S.-i. Yamazaki, H. Senoh, T. Sakai, T. Kiyobayashi, Crystalline polycyclic quinone derivatives as organic positive-electrode materials for use in rechargeable lithium batteries, *Mater. Sci. Eng. B*, 177 (2012) 483-487.
- [29] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, (2001) Chapter 2.
- [30] Y. Liang, P. Zhang, S. Yang, Z. Tao, J. Chen, Fused Heteroaromatic Organic Compounds for High-Power Electrodes of Rechargeable Lithium Batteries, *Adv. Energy Mater.*, 3 (2013) 600-605.
- [31] Z. Song, H. Zhan, Y. Zhou, Anthraquinone based polymer as high performance cathode material for rechargeable lithium batteries, *Chem. Commun.*, (2009) 448-450.
- [32] X. Wu, S. Jin, Z. Zhang, L. Jiang, L. Mu, Y.-S. Hu, H. Li, X. Chen, M. Armand, L. Chen, X. Huang, Unraveling the storage mechanism in organic carbonyl electrodes for sodium-ion batteries, *Sci. Adv.*, 1 (2015) e1500330.
- [33] L. Wang, C. Mou, Y. Sun, W. Liu, Q. Deng, J. Li, Structure-Property of Metal Organic Frameworks Calcium Terephthalates Anodes for Lithium-ion Batteries, *Electrochim. Acta*, 173 (2015) 235-241.
- [34] Q. Deng, C. Fan, L. Wang, B. Cao, Y. Jin, C.-M. Che, J. Li, Organic Potassium Terephthalate ($K_2C_8H_4O_4$) with Stable Lattice Structure Exhibits Excellent Cyclic and Rate Capability in Li-ion Batteries, *Electrochim. Acta*, (2016) DOI: <http://dx.doi.org/10.1016/j.electacta.2016.1011.1079>.
- [35] A. Iordache, V. Maurel, J.-M. Mouesca, J. Pécaut, L. Dubois, T. Gutel, Monothioanthraquinone as an organic active material for greener lithium batteries, *J. Power Sources*, 267 (2014) 553-559.
- [36] Z. Song, Y. Qian, T. Zhang, M. Otani, H. Zhou, Poly(benzoquinonyl sulfide) as a High-Energy Organic Cathode for Rechargeable Li and Na Batteries, *Adv. Sci.*, 2 (2015) 1500124.
- [37] M. Lécuyer, J. Gaubicher, A.-L. Barrès, F. Dolhem, M. Deschamps, D. Guyomard, P. Poizot, A rechargeable lithium/quinone battery using a commercial polymer electrolyte, *Electrochem. Commun.*, 55 (2015) 22-25.

Graphical Abstract