

Article

# Long-Life, High-Rate Lithium-Organic Batteries Based on Naphthoquinone Derivatives

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### Abstract

We report the facile synthesis of new naphthoquinone (NQ)-derivatives for use in lithium-organic batteries to improve performance. The rational design of these NQderivatives is based on theoretical calculations. Our lithium-organic batteries demonstrate remarkable charge-discharge properties, for example, a high discharge capacity of 250 mAh  $g^{-1}$  (363 mAh  $cm^{-3}$ ), discharge potential plateaus in the range of 2.3–2.5 V, and 99% capacity retention after 500 cycles at 0.2 C. In particular, the batteries had excellent rate performance up to 50 C with reversible redox behavior, unlike most other organic cathode materials. The key to success was a simple molecular substitution, addition amino groups at the 2- and 3- positions of the NQ ring, yielding 2,3-diamino-1,4-naphthoquinone (DANQ). DANQ has an exceptionally low band-gap of 2.7 eV and greater than 20-fold enhancement in the lithium diffusion rate compared to unmodified NQ. The fundamental shortcoming of the organic molecules, i.e., their solubility in the electrolyte, was resolved by covalent linking of the amino groups to the surfaces of the cathode framework. The cyclization of amino groups in **DANQ** yielded 1*H*-naphtho[2,3-d]imidazole-4,9-dione (**IMNQ**), enabled us to achieve a 0.15 V enhancement in the redox potential owing to the delocalized electron distribution in the hetero-aromatic ring. Our work suggests that NQ-derivatives with modulated charge/ion transport properties are a viable alternative to the more widely studied lithium metal oxides.

## Introduction

Advances in lithium ion batteries (LIBs) have played a transformative role in the area of portable electronics and automotive technologies.<sup>1-3</sup> There is an increasing demand to develop high-energy and inexpensive LIBs for more widespread use for diverse applications, including large-scale energy storage systems.<sup>4,5</sup> Currently commercialized LIBs based on graphite anodes materials and lithium metal oxides cathode materials have several limitations because of their low specific energies (100–265 Wh kg<sup>-1</sup>) and high prices.<sup>1,6,7</sup> Consequently, this has directed LIB research toward new, state-of-the-art electrode materials that have higher energy densities yet are lightweight and inexpensive.<sup>5,8</sup>

LiCoO<sub>2</sub> is the most commonly used cathode material for LIBs by taking advantage of its high discharge voltage.<sup>9</sup> Research has shown that LiCoO<sub>2</sub> has a considerably low capacity  $< 170 \text{ mAh} \cdot \text{g}^{-1}$ , compared to the theoretical capacity of 274 mAh $\cdot \text{g}^{-1}$ . This discrepancy is ascribed to the inherently limited lithium-diffusion kinetics and structural/chemical instability.<sup>9,10</sup> In light of this, over the last few decades, a variety of new cathode materials have been investigated;<sup>11-15</sup> these include organic compounds, which have unique features that conventional inorganic materials do not possess such as high theoretical gravimetric capacities, low-temperature synthesis (therefore relatively inexpensive), and flexibility.<sup>13-15</sup>

Various organic compounds have been synthesized as cathode active materials for LIBs. For example, quinones,<sup>16-21</sup> ketones,<sup>22,23</sup> aromatic imides,<sup>24,25</sup> polyacetylene,<sup>26,27</sup> and polymerized carbonyl compounds,<sup>28-31</sup> where their redox properties can be tailored straightforwardly by modifying their chemical structures. In particular, quinones have long been considered the most promising candidates for organic cathode materials owing to their high capacities and excellent electrochemical stabilities.<sup>13,15</sup>

Nevertheless, over the last few decades, in the development of lithium-organic batteries, several major drawbacks concerning the use of quinones have been found; for example, they are highly soluble in liquid electrolytes,<sup>14</sup> have poor electrical conductivities,<sup>32</sup> and show slow redox kinetics.<sup>33</sup> For these reasons, most quinone-based organic electrodes have lower capacities than their theoretical values,<sup>34,35</sup> much like conventional lithium transition metal oxides. In addition, quinone-based electrodes suffer from rapid capacity fade with cycling.<sup>33</sup> Finally, because large amounts of conductive additives (carbon, > 50% in most cases) must be added to achieve reasonable rate performances, loading of active materials in the electrode is reduced, which reduces the energy density of the battery.<sup>35</sup>

Many strategies have been proposed to overcome these flaws. For example, polymerization of organic active materials,<sup>28-31</sup> physical/chemical fixation of active materials to the cathode framework,<sup>17,21,36</sup> and the use of solid-state electrolytes to mitigate dissolution of the active material into the electrolyte.<sup>19,21</sup> In particular, the rational design of quinone derivatives via ring modification is an encouraging approach to improve electrical conductivity and reduce solubility.<sup>13,18,37,38</sup> Although such approaches have shown promise, the achievement of long-life and rate performance from lithium-organic batteries remains a challenge. To date, there are few reports detailing better performances of batteries containing organic electrode materials as compared to those of commercial lithium metal oxide.<sup>30,31</sup>

Herein, we present a facile synthesis of new naphthoquinone (NQ)-derivatives prepared through simple organic reactions. In particular, substitution of the 2- and 3positions of the NQ ring with amino functional groups led to an exceptionally low band-gap (2.74 eV), and a remarkably enhanced lithium diffusion rate was achieved, enabling the construction of high-rate (> 20C) lithium-organic batteries. The problem of the dissolution of active materials into the electrolyte was resolved using a carboxylated cathode framework so that the NQ-derivatives can be tethered to the framework via the formation of peptide bonds.

Our lithium-organic batteries had excellent electrochemical stability, high discharge potential plateaus over 2.3 V with high initial capacities of 250 mAh·g<sup>-1</sup> (363 mAh·cm<sup>-3</sup>), and 99 % capacity retention after 500 cycles at 0.2 C. The present work opens a new platform in designing organic electrode materials for the future LIBs.

### Experimental

Synthesis of 2,3-diamino-1,4-naphthoquinone (DANQ). 10 g of 2,3-dichloro-1,4naphthoquinone (DCNQ) (44 mmol, 98 %, Alfa Aesar) was dissolved in 200 mL of acetonitrile (ACN, HPLC grade, J.T. Baker) and 16.5 g of potassium phthalimide (89.1 mmol, 98 %, Sigma-Aldrich) was added to the mixture. The reaction mixture was refluxed with stirring for 12 h under nitrogen atmosphere. After cooling to room temperature, yellow solid was collected using suction filtration and further dried under vacuum. The dried yellow solid was transferred to round bottom flask containing distilled water. 10 mL of hydrazine hydrate (90%, Alfa Aesar) was added into the flask and the mixture was stirred for 12h at 60 °C. Upon cooling to room temperature, the dark blue power was obtained as a final product (DANQ) after filtration, which was further purified by recrystallization from ethanol. The yield of reaction was 7.46 g (90%). The completion of the reaction was confirmed by <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, Bruker AVB-300) spectroscopy (DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  (ppm) 5.46 (s, 4H), 7.57-7.61 (m, 2H), 7.74-7.78 (m, 2H).  $\delta_{\rm C}$  (ppm) 124.5, 127.6, 131.1, 132.6, 178.4.

**Synthesis of 1***H***-naphtho[2,3-d]imidazole-4,9-dione (IMNQ).** A mixture of 15g of **DANQ** (79.7 mmol) and 25 mL of formic acid (97 %, Alfa Asear) in distilled water (100 mL) was refluxed with stirring for 5 h. After cooling to room temperature, the pH of the solution was

adjusted to 9 with the addition of 30 % ammonium hydroxide (ACS reagent grade, Sigma-Aldrich). The dark yellow powder (**IMNQ**) was obtained in yield of 13.1 g (83%) after repeated filtration and washing with distilled water. The product was recrystallized from DMSO for further purification and characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR (Bruker AVB-300) spectroscopy (DMSO- $d_6$ ):  $\delta$  (ppm) 7.83-7.88 (m, 2H), 8.07-8.12 (m, 2H), 8.31 (s, 1H), 14.12 (s, 1H).  $\delta$  (ppm) 126.3, 132.7, 133.8, 142.9, 176.3, 178.7.

**Molecular and structural characterization**. The powder XRD data of **DANQ** and **IMNQ** were collected in a 2D beamline at the Pohang Accelerator Laboratory (PAL) using synchrotron radiation. The molecular characterization was carried out by combining attenuated total reflectance/Fourier transform infrared spectroscopy (ATR/FT-IR, Spectrum Two<sup>TM</sup>, PerkinElmer) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250, VG SCIENTIFIC, a monochromatic Al K $\alpha$  source of 1486.6 eV). The use of KBr pellet was avoided for FT-IR experiments because of significant interference with the peaks from absorbed water. Morphologies of **DANQ** and **IMNQ** crytals and surfaces of battery separator were examined by field emission scanning electron microscope (FE-SEM, XL30S FEG) with a 5 keV accelerating voltage.

**Electronic structures calculations.** The initial configurations of quinone-based compounds were generated using a program ChemBio3D Ultra 12.0 (Cambridge Soft) and were optimized with MM2 force field. The energies of molecular conformations were minimized by adopting B3PW91 hybrid GGA functional and 6-31G(d,p) basis set, without considering solvation effects. The analysis on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) diagrams of quinone-based compounds was undertaken at the final geometries. All density functional theory (DFT) calculations and their analyses were conducted by using the program package Gaussian 09.

**Carboxylation of gas diffusion layer (GDL).** The vacuum dried GDL (TGP-H-120, Toray) was heated to 70 °C for 2.5 h with constant agitation in a mixture of nitric acid/sulfonic acid (1:3 in volume). The resultant carboxylated GDL (GDL–COOH) was washed with distilled water until water becomes neutral and dried under vacuum for a week at 60 °C. The absence of residual acids in GDL–COOH and in GDL-DANQ was confirmed by combining energy-dispersive X-ray spectroscopy (EDS) analysis using SEM and XPS.

**Preparation of organic cathodes.** Two different types of organic cathodes were prepared. First, the organic cathodes were prepared with **DANQ** (or **IMNQ**), Super P carbon (Alfa Aesar), and PVdF binder (Solef) in a weight ratio of 60:30:10. The mixture was welldispersed in NMP (Sigma Aldrich) by ball milling (MillMM400) under an argon atmosphere and casted onto an Al-foil current collector by a doctor-blade method. Second, 20 mg mL<sup>-1</sup> of **DANQ** (in THF) or **IMNQ** (in DMSO) was infiltrated into porous GDL–COOH current collector. After soaking overnight, the **DANQ** (or **IMNQ**)-loaded GDL–COOH was heated to 60 °C. **NQ** (97%, Sigma-Aldrich) cathode was also prepared in the same way as a control. All fabricated cathodes were dried at room temperature for 24 h under argon blanket, followed by vacuum drying for another 24 h. The dried electrodes were cut by a disc cutter (MTI, 15mm diameter). The cathode loading of the fabricated organic cathodes was in range of 1.8-2.5 mg cm<sup>-2</sup>.

**Electrochemical characterization.** Coin type (CR2032, MTI) cells were fabricated by assembling a Li-metal anode, a porous polypropylene separator (Celgard 2400) and the organic cathode in a high-purity argon-filled glove box to avoid any possible contamination by moisture and oxygen. The liquid electrolyte was prepared by dissolving 1M lithium bis(trifluoromethane) sulfonimide (LiTFSI, 98.0%, TCI) in a mixture of dimethoxy ethane (DME, 99.5 % Sigma-Aldrich) and 1,3-dioxolane (DIOX, 99.8 %, Sigma-Aldrich) in volume

ratio of 1:2. Galvanostatic discharge/charge tests and cyclic voltammetry analysis of the Li– organic cells were performed in voltage window of 1.8–3.0V using battery cycler (WBCS3000, Wonatech).

### **Results and Discussion**

In the present study, two **NQ** derivatives were prepared and used as new organic cathode materials. Firstly, as shown in Figure 1a, 2,3-diamino-1,4-naphthoquinone was synthesized from 2,3-dichloro-1,4-naphthoquinone by Gabriel synthesis with the use of potassium phthalimide,<sup>39</sup> enabling large scale synthesis and yielding tens of grams of product. The obtained 2,3-diamino-1,4-naphthoquinone is referred to as **DANQ**. A one-pot procedure for the conversion of two amino groups into cyclic imidazole was then carried out to yield hetero-aromatic 1*H*-naphtho[2,3-d]imidazole-4,9-dione (hereafter, **IMNQ**), as shown in Figure 1b. The successful syntheses of **DANQ** and **IMNQ** with high yields were confirmed by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and FT-IR experiments, as described in Figure S1, S2 and Figure S3 of Supporting Information. Note that **DANQ** has been synthesized<sup>39</sup> and utilized for anion sensing<sup>39-41</sup> and ligand preparation,<sup>42,43</sup> but has not been used for batteries. The preparation of **IMNQ** through different synthetic protocol was reported in the 1950s;<sup>44</sup> however, no further research on **IMNQ** has been conducted.

Both **DANQ** and **IMNQ** were highly crystalline, as shown by representative power X-ray diffraction (XRD) profiles in a 2 $\theta$  scan range of 5–30° in Figure 2. **DANQ** was found to have crystallized in the orthorhombic space group  $P2_12_12_1$ , while **IMNQ** crystallized in the monoclinic space group P2. The refined unit cell parameters obtained from DASH program<sup>45</sup> are a = 27.25 Å, b = 23.96 Å, c = 3.35 Å for **DANQ**; and a = 28.21 Å, b = 10.95 Å, c = 10.81

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Å,  $\alpha = \gamma = 90.00^{\circ}$ , and  $\beta = 104.30^{\circ}$  for IMNQ. Note that NQ represented monoclinic  $P2_1/c$  space group, having the unit cell parameters a = 8.27 Å, b = 7.76 Å, c = 11.71 Å,  $\alpha = \gamma = 90.00^{\circ}$ , and  $\beta = 99.30^{\circ}$ .<sup>46</sup> This indicates that the modification of ring structure of NQ leads to a significant change in molecular packing. Scanning electron microscopy (SEM) images are shown in Figure 2, and these further show the dissimilar crystal morphologies of DANQ and IMNQ.



**Figure 1.** Synthetic procedures for (a) 2,3-diamino-1,4-naphthoquinone (**DANQ**) and (b) 1*H*-naphtho[2,3-d]imidazole-4,9-dione (**IMNQ**).





**Figure 2.** Powder XRD profiles of (a) **DANQ** and (b) **IMNQ** samples. Miller indices of the reflection planes (*hkl*) are given in each figure. SEM images in (a) and (b) show the dissimilar crystal morphologies.

To examine the electrochemical properties of **DANQ** and **IMNQ**, organic cathodes were fabricated by integrating DANQ (or IMNQ), Super P carbon, and polyvinylidene (PVdF) binder in a weight ratio of 60:30:10. Lithium foil was used as the counter electrode. Figures 3a and 3b show representative galvanostatic discharge/charge voltage profiles of the Li-organic cells at room temperature, cycled between 1.8 and 3.0 V (vs Li/Li<sup>+</sup>) at 0.2 C (50 mA g<sup>-1</sup>). Overall, the redox behaviors of **DANQ** and **IMNQ** are analogous, i.e., two stable plateaus were seen, ascribed to the two-step reduction of the carbonyl groups into enolates followed by re-oxidation of the enolate groups. The Li-DANO and Li-IMNO cells displayed discharge capacities of 250 mAh $\cdot$ g<sup>-1</sup> (363 mAh $\cdot$ cm<sup>-3</sup>) and 229 mAh $\cdot$ g<sup>-1</sup> (348 mAh $\cdot$ cm<sup>-3</sup>), respectively, corresponding to 89% (DANQ) and 85% (IMNQ) of the theoretical capacities. This suggests that the presence of strong electron-donating groups in **DANO** lowered the reduction potential (Figure 3a), which can be noticeably enhanced by cyclization (Figure 3b) (IMNO) owing to electron delocalization in the hetero-aromatic ring. The redox potentials of DANQ and IMNQ cathodes were determined by differential capacity (dQ/dV) analysis (inset plots of Figures 3a and 3b); 2.33 and 2.17 V (lithiation) / 2.41 and 2.27 V (delithiation) for DANQ; 2.48 and 2.40 V (lithiation) / 2.57 and 2.38 V (delithiation) for IMNQ. This suggests that the modification of ring structure of NO is a simple vet powerful means to modulate the electrochemical properties of Li-organic batteries.



**Figure 3.** The two-electron electrochemical lithiation and delithiation of the (a) **DANQ** and b) **IMNQ** in voltage window of 1.8-3.0V at 50 mA g<sup>-1</sup>. Inset graphs represent the differential capacities, analyzed by numerical differentiation of the galvanostatic curves. All the specific capacities are calculated based on the mass of active materials.

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Furthermore, modulation of molecular structures of NQ-derivatives has led to dissimilar Li<sup>+</sup>-ion diffusion properties in the organic cathodes. Cyclic voltammetry analysis of the **DANQ** and **IMNQ** cathodes was carried out to evaluate the Li<sup>+</sup>-ion diffusion coefficients ( $D_{Li}$ ) of the cathodes using the Randles-Sevcik equation,<sup>47</sup> as described in Equation (1).

$$I_{\rm p} = 2.69 \times 10^5 n^{1.5} A D_{Li}^{0.5} v^{0.5} C_{Li} \tag{1}$$

where  $I_p$  is the peak current, *n* is the number electrons in the reaction, *A* is the electrode area, *v* is the scanning rate, and  $C_{Li}$  is the lithium-ion concentration in the electrolyte. Representative voltammograms obtained with the **DANQ** cathode are shown in Figure 4a.

From the linear relationship between  $I_p$  and  $v^{0.5}$ , four  $D_{Li}$  values for each cathode were obtained, corresponding to two individual peaks of oxidation and reduction (Representative linear regressions obtained from **DANQ** are shown in Figure S4 of Supporting Information). An **NQ** cathode was also examined as a control. As plotted in Figure 4b, the lowest  $D_{Li}$  values were found for the **NQ** cathode, clearly showing that modification of the **NQ** ring structure raised the Li<sup>+</sup>-ion transfer rate. In particular, the **DANQ** cathode has high  $D_{Li}$  values of  $2.28 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> and  $6.41 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup> for oxidation and  $1.30 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> and  $4.74 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup> for reduction. These values were up to 22 times greater than those of **NQ** cathode  $(1.00 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \text{ and } 2.43 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  for oxidation and  $2.15 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup> and  $3.15 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup> for reduction). Expeditious Li<sup>+</sup>-ion migration in **IMNQ** seemed to be impaired as 2- to 3-times lower  $D_{Li}$  values than **DANQ** were estimated  $(1.02 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ and } 2.40 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  for oxidation and  $2.10 \times 10^{-8} \text{ cm}^2$ s<sup>-1</sup> and  $2.94 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  for reduction). The large discrepancies in Li<sup>+</sup>-ion diffusion rates for **DANQ**, **IMNQ**, and **NQ** should be closely associated with the dissimilar molecular packing, where the corresponding crystal structures were orthorhombic, monoclinic, and monoclinic, respectively (Figure 2).

In order to further underpin the mechanisms underlying the dissimilar Li<sup>+</sup>-ion diffusion properties of **DANQ**, **IMNQ**, and **NQ**, we have investigated the electronic structures of various **NQ**-derivatives. Figure 4c depicts the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) diagrams of **DANQ** and **IMNQ** in comparison to various quinone-based compounds, calculated using density functional theory using the B3PW91 exchange-correlation functional and 6-31G\*\* basis set. Remarkably, while most of quinones have wide band gaps, around 4.0 eV, **DANQ** has much smaller band gap of 2.7 eV, similarly sized band gaps are found in semiconductors. We attributed this to the strong electron-donating amino groups to 2- and 3- position of **NQ**, which significantly destabilize the HOMO energy, thereby decreasing the HOMO-LUMO gap. The high  $D_{Li}$  values of DANQ can be attributed to the low band gap, facilitating fast electron/Li<sup>+</sup> transfer in the cathode. Cyclization of amino groups into imidazole enhanced the HOMO energy of **IMNQ** to yield similar HOMO-LUMO band gap to most of the quinone-based materials.

A comparison of the HOMOs and LUMOs of **DANQ** and **IMNQ** to those of **NQ** is shown in Figure 4d. The increased electron density in the  $\pi$ -conjugated aromatic ring of **DANQ** is clearly seen.



**Figure 4.** (a) Representative voltammograms of the **DANQ** cathode obtained at different scan rates and (b) Li<sup>+</sup>-ion diffusion coefficients of the **DANQ**, **IMNQ**, and **NQ** cathodes, calculated using the Randles-Sevcik equation. (c), (d) The HOMO/LUMO energy diagrams and morphologies of the **DANQ** and **IMNQ**, compared to those of various **NQ**-derivatives. The HOMO-LUMO gap is indicated.

 We now investigate the long-term battery performances of the Li-organic cells. To improve the established strengths of the synthesized **NQ**-derivatives, organic cathodes were fabricated without polymeric binder, using a porous gas diffusion layer (GDL) as the current collector. The porous GDL allows high loading of active material (in the range of 1.8 to 2.5 mg cm<sup>-2</sup> in the present study) and allows easy access of liquid electrolytes by providing a large surface area. To remedy the dissolution of active materials into liquid electrolytes during battery cycling, the GDL surfaces were chemically modified with carboxylic acid groups (GDL–COOH) to induce the formation of peptide bonds with the amino groups of **DANQ** by heat treatment. The absence of residual acids in GDL–COOH and in GDL-**DANQ** was confirmed by combining EDS analysis and XPS, as provided in Figure S5 of Supporting Information. Note in passing that amide bond formation is not expected for **NQ** and **IMNQ** with GDL–COOH, but physisorption of **IMNQ** onto the surfaces of GDL–COOH may take place via acid-base interactions.

A schematic illustration of organic cathode fabrication is shown in Figure 5a. SEM images in the figure confirm successful pore-filling of GDL by loaded **DANQ**. Based on elemental analysis of GDL-COOH, the maximum amount of **DANQ** that can form peptide bonds (assuming that only one amino group of **DANQ** makes the bond) is expected to be 2.7 mg cm<sup>-2</sup>. Therefore, our loadings are well positioned within the limit, leading to the smooth surface morphology of GDL-**DANQ** with uniformly covered **DANQ**, as confirmed by SEM image taken under high magnification (Figure 5b).

The peptide bond formation of **DANQ** with GDL-COOH was confirmed by FT-IR spectra and XPS analysis. As shown in Figure 5c, for GDL-**DANQ**, the IR peak intensities corresponding to characteristic peaks of C=O and C=C (from quinone) were found to be significantly shifted and two amide peaks appeared. The direct comparison of XPS spectra of

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**DANQ** and GDL-**DANQ** in the C 1s, N 1s, and O 1s binding energy regions, Figure 5d, further indicated the peptide bond formation. The appearance of new peak at 289.7 eV in C 1s region and shifts of N 1s peak associated with primary amine (–NH<sub>2</sub>) and of O 1s peak corresponding to C=O were evident.

Figure 6a shows the discharge/charge capacities of the Li-organic cells, cycled in the potential range of 1.8-3.0 V (vs Li/Li<sup>+</sup>) at 0.2 C and 25 °C for 100 cycles. The Li-DANO cell shows a first discharge capacity of 250 mAh·g<sup>-1</sup> (363 mAh·cm<sup>-3</sup>) and a high capacity of 244  $mAh \cdot g^{-1}$  (354 mAh  $\cdot cm^{-3}$ ) was maintained after 100 cycles, corresponding to 98% capacity retention compared to the first discharge capacity and a high coulombic efficiency of > 99%throughout. These results contrast sharply with the low initial discharge capacity of 190 mAh  $g^{-1}$  (270 mAh·cm<sup>-3</sup>, 57% of the theoretical capacity) and poor capacity retention seen in the Li-NO cell (86 mAh $\cdot$ g<sup>-1</sup>, 122 mAh $\cdot$ cm<sup>-3</sup>, 45%) under the same cycling conditions. Obviously, the capacity of a battery based on unmodified **NO** is considerably lower than its theoretical capacity, which could be associated with the poor electrical conductivity of NQ. The IMNQ cathode had better cycling performance than the NQ cathode, with a first discharge capacity of 240 mAh·g<sup>-1</sup> (364 mAh·cm<sup>-3</sup>) that stabilized at around 234 mAh·g<sup>-1</sup> (356 mAh·cm<sup>-3</sup>) after 15 cycles. However, after 15 cycles, rapid fade accompanied by poor coulombic efficiency was observed for the Li-IMNQ cell. As a result, the Li-IMNQ cell can deliver only 152 mAh  $g^{-1}$  (231 mAh  $cm^{-3}$ ) after 100 cycles with 64% capacity retention. It should be noted here that negligible contribution of GDL-COOH to discharge capacity was confirmed in the same potential window (Figure S6).



**Figure 5.** (a) Schematics showing the fabrication of organic cathodes using a porous GDL as the current collector; functionalization of the surfaces of GDL by carboxylic acid groups and impregnation of **DANQ** into porous GDL frameworks, followed by heat-treatment to link

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**DANQ** with GDL surfaces. SEM images were taken after completing each step, as provided in (a). (b) SEM image of GDL-**DANQ** taken at high magnification. (c) FT-IR spectra of **DANQ** before and after the formation of peptide bond with GDL-COOH. Relevant peaks in the wavenumber range 1800–1350 cm<sup>-1</sup> are assigned in the figure. (d) XPS spectra in the C 1s, N 1s, and O 1s binding energy regions for **DANQ** before and after the peptide bond formation with GDL–COOH.

This result prompted us to determine the extent of active mass loss for the three organic electrodes. In order that the surface of separator, positioned in the cathode side, was examined by SEM after disassembling the cells after 50 cycles. As shown in Figure 6b, the surface of separator for the Li-DANQ cell was smooth with insignificant amounts of DANQ (high magnification image in inset confirms the retained pores of the separator). In contrast, a large quantity of NQ crystals is deposited on the separator in the Li-NQ cell. This indicates that the capacity fade of the Li-NQ cell is mostly caused by a significant loss of active mass into the electrolyte. Although a small number of IMNQ aggregates were identified for Li-IMNQ cell after cycling, we found that IMNQ underwent a structural transition into imidazole anions under repeated cycling. This was confirmed by <sup>1</sup>H NMR spectra and a noticeably lowered lithiation plateau (Figure S7). Thus, we inferred that the imidazole anion impeded the interaction between Li<sup>+</sup> and carbonyl oxygen atoms of IMNQ, thereby lowering capacity.

It should be also noted that the cycle performance of unbound **DANQ** prepared by embedding **DANQ** into unmodified GDL was markedly different from Figure 6a. Although the cell showed the high initial capacity of 250 mAh·g<sup>-1</sup> (363 mAh·cm<sup>-3</sup>), the value rapidly decreased to 85 mAh·g<sup>-1</sup> (123 mAh·cm<sup>-3</sup>) after 50 cycles yielding poor capacity retention of 34% (Figure S8). This indicates the importance of peptide bond formation in improving the cycle life.

The improved battery performance of the **DANO** cathode was also demonstrated at different C-rates. As shown in Figure 6c, the cell delivered a reversible capacity of 250  $mAh \cdot g^{-1}$  (363  $mAh \cdot cm^{-3}$ , 0.2 C), 235  $mAh \cdot g^{-1}$  (341  $mAh \cdot cm^{-3}$ , 0.5 C), 223  $mAh \cdot g^{-1}$  (323  $mAh \cdot cm^{-3}$ , 1 C), 204  $mAh \cdot g^{-1}$  (296  $mAh \cdot cm^{-3}$ , 2 C), 178  $mAh \cdot g^{-1}$  (258  $mAh \cdot cm^{-3}$ , 4 C),  $159 \text{ mAh} \cdot \text{g}^{-1}$  (231 mAh  $\cdot \text{cm}^{-3}$ , 5 C), 142 mAh  $\cdot \text{g}^{-1}$  (206 mAh  $\cdot \text{cm}^{-3}$ , 10 C), and 117 mAh  $\cdot \text{g}^{-1}$ (170 mAh·cm<sup>-3</sup>, 20 C). This indicates that the Li-DANQ cells can deliver 47% of discharge capacity even at 20 C, compared to that at 0.2 C. Although cycling at 50 C resulted in a low discharge capacity of 84 mAh $\cdot$ g<sup>-1</sup> (122 mAh $\cdot$ cm<sup>-3</sup>), further cycling at low rates (after cycling at various rates) brought the cell back to almost the same capacity of 222 mAh  $g^{-1}$  (342  $mAh \cdot cm^{-3}$ ) at 1 C, 235  $mAh \cdot g^{-1}$  (341  $mAh \cdot cm^{-3}$ ) at 0.5 C, and 250  $mAh \cdot g^{-1}$  (363 mAh·cm<sup>-3</sup>) at 0.2 C, corresponding to 100 % retention of initial capacity. The rate performance of our Li-DANQ cell is superior to other Li-organic batteries based on nonpolymerized quinone-derivatives reported to date. Control experiments using the NQ cathode are also shown in Figure 6c, and these show greatly decreased capacity values from 170  $mAh \cdot g^{-1}$  (241 mAh \cdot cm<sup>-3</sup>, 0.2 C) to 55 mAh \cdot g^{-1} (78 mAh \cm<sup>-3</sup>, 20 C) and 10 mAh \cm<sup>-1</sup> (14 mAh  $cm^{-3}$ , 50 C). Most importantly, the Li-NO cells did not show reversible behavior upon bringing the cells back to low C rates, analogous to most organic cathodes.

Besides its high discharge capacity and rate performance, the new Li-**DANQ** battery has a long cycle life. Currently, the Li-**DANQ** cell has been extended to 500 cycles and retains a significant capacity of 248 mAh $\cdot$ g<sup>-1</sup> (360 mAh $\cdot$ cm<sup>-3</sup>, capacity retention of 99%) with high coulombic efficiency of 99% throughout (Figure 6d).



**Figure 6.** (a) The discharge/charge capacities and coulombic efficiencies of the Li-DANQ and Li-IMNQ cells, compared to those of Li-NQ cell for 100 cycles at 0.2 C rates. (b) Surface morphologies of the separators of each cell taken after 50 cycles by SEM. (c) Rate performance of the Li-DANQ cell, compared to that of the Li-NQ cell. (d) Discharge/charge capacities and coulombic efficiencies of the Li-DANQ cell at 0.2 C with an extended life of 500 cycles.

 Our results represent the best capacity retention and longest lifetimes of any reported non-polymerized organic cathodes. Figure 7a displays the capacity retention of our **DANQ** cathode against other organic cathodes based on quinone/carbon composites and quinones reported in the literatures, which clearly illustrates the impact of our results on the structure of widely studied quinone materials. Note that the literature values were collected over 20 independent references, published during the past ten years (The list of references is provided in Supplementary Information). Our results also disclose one of the highest energy density among any reported non-polymerized quinone-based organic cathode materials. We have shown Ragone curve for our Li-**DANQ** cell in Figure 7b, which marked significant progress from the previously reported results on quinone/carbon composites<sup>48,49</sup> and quinones.<sup>18,50,51</sup> The energy density of Li-**DANQ** cell edged up to 575 Wh kg<sup>-1</sup>, where the high value of 300 Wh kg<sup>-1</sup> was well-preserved at the high power density of 10000 W kg<sup>-1</sup>. This clearly shows the advantages of the rational molecular design of **NQ**-derivatives in enhancing the performance of the Li-organic cells by facilitating fast charge/ion transport and lower dissolution into the liquid electrolyte via covalent linking.

Our study demonstrates a new class of **NQ**-derivatives that are promising organic cathode materials for advanced lithium batteries. Further improvement of the specific capacity by optimizing the liquid electrolyte and type of polymeric binder is currently underway. Experiments on whether further modification of **DANQ** can improve the battery performance with enhance redox potentials will be a subject of our future studies.





**Figure 7.** (a) Capacity retention of our Li-**DANQ** cell, compared to other Li-organic cells reported in literatures. Most values were obtained at 0.2 C, except for a few measured at 0.1C. (b) Specific energy density vs. specific power density (Ragone curve) for various cathode materials; **DANQ** (solid star), quinone/carbon composites (solid symbols), and non-polymerized quinones (open symbols). KB: Ketjenblack, FGSs: functionalized graphene sheets, PAQ: 9,10-phenanthrenequinone, PYT: pyrene-4,5,9,10-tetraone, AQ: 9,10-anthraquinone, PAQS: poly(anthraquinonyl sulfide), PI: polyimide, BFFD: benzofuro[5,6-b]furan-4,8-dione, BDTD: benzo[1,2-b:4,5-b']dithiophene-4,8-dione, PID: pyrido[3,4-g]isoquinoline-5,10-dione, AQ: 9,10-anthraquinone, AQDS: 9,10-anthraquinone.

### Conclusions

We have designed new **NO**-based compounds that are promising cathode materials for advanced lithium-organic batteries. Two NQ-derivatives, DANQ and IMNQ, were prepared by large-scale synthesis, yielding tens of grams of product. Overall, the redox behaviors of **DANO** and **IMNO** were analogous to that of unmodified **NO**; that is, both twostep reduction of the carbonyl groups into enolates and subsequent re-oxidation of the enolate groups were observed. However, the modification of the ring structure of NQ was a powerful means of modulating the electrochemical properties of the resulting compounds. Compared to other **NO**-derivatives, Li-**DANO** had the highest initial discharge capacity of 250 mAh g<sup>-1</sup>  $(363 \text{ mAh} \cdot \text{cm}^{-3})$  and 99% capacity retention of its initial capacity after 500 cycles at 0.2 C. Even at 20 C, the Li-DANQ cell can deliver the 47 % discharge capacity (117 mAh g<sup>-1</sup>, 170 mAh cm<sup>-3</sup>) compared to that at 0.2 C. After cycling at various rates up to 50 C, further cycling at low rates demonstrated 100% retention of initial capacity. This is in sharp contrast to the results of the NQ cathode, which showed a significant reduction in capacity (55 mAh  $g^{-1}$ , 78 mAh·cm<sup>-3</sup>) at 20 C and non-reversible redox behavior. The excellent rate performance of Li-DANO cell was rationalized by the fast charge/ion transport in DANO due to the exceptionally low band gap of 2.74 eV and the higher lithium diffusion coefficient (by more than an order of magnitude) than that of NQ. It is also encouraging in that IMNQ, synthesized by one-pot cyclization of amino groups in **DANQ**, raised the reduction potential by  $\sim 0.15$  V; however, the electrochemical stability of the hetero-aromatic molecule with cycling remains problematic. The present work highlights the discovery of new organic compounds that offer high energy, long cycle lifetimes, and fast charging/discharging capability as future route to advanced lithium batteries.

**Supporting Information Available:** Synthesis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR of the **DANQ** and **IMNQ**, XPS, EDS, discharge/charge voltage profiles of GDL-COOH, <sup>1</sup>H NMR, discharge/charge voltage profiles of Li-**IMNQ** cell after battery cycles, and discharge/charge voltage profiles, capacities, coulombic efficiencies of Li-**DANQ** cell with the use of unmodified GDL. This material is available free of charge via the Internet at http://pubs.acs.org.

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## **Naphthoquinone Derivatives**

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