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Nonaqueous arylated quinone catholytes for lithium-organic flow batteries⁺

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+ Electronic Supplementary Information (ESI) available.

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Abstract

Chemically modified organic redox couples have the advantages of tunable redox properties, high solubility, environmental benignity, and cost effectiveness. Inspired from nature, a series of quinone derivatives bearing electron-donating methoxy or electron-withdrawing trifluoromethyl groups are synthesized in moderate to high yields by the Pd-catalyzed Suzuki cross-coupling reactions. This study utilizes the synthetic quinones as redox-active organic molecules for nonaqueous lithium-organic flow batteries. The aryl moiety incorporated quinone scaffolds show the enhanced electrochemical stability and rate capability. The nonaqueous catholyte, 2-phenyl-1,4-naphthoquinone, reaches a cell voltage of ~2.6 V, specific capacity of 196 mA h g⁻¹, while the discharge capacity is retained at ~92% for 150 cycles. Moreover, the tubular lithium-organic flow battery system features stable cycle performance under a continuous circulation without clogging-associated intermittency flow.

Introduction

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The stringent regulation of greenhouse gas emission accelerates the exploitation of renewable energy for the progressive replacement of combustion turbines, gasoline vehicles, or coal power plants.^{1–5} However, the intermittency, geographical restriction, and output fluctuation of sustainable energy sources such as wind or solar power impede their stable power supply.^{1,3,4} Hence, there is increasing demand for large-scale electrochemical energy storage systems that can be combined with renewable energy sources. In particular, redox flow batteries (RFBs) have been regarded as attractive candidates owing to their cost effectiveness, modularity, and design flexibility.^{6–11} However, the conventional aqueous RFB systems including all–vanadium, iron–chromium, and zinc–bromine redox couples operate under strong acidic and corrosive conditions, which is likely to cause environmental

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problems. The metal-based redox couples are also involved in the issues related to scarcity and price rise.

Redox-active organic molecules have attracted significant attention as alternative active materials to replace inorganic compounds for greener and more sustainable RFBs.^{6–16} Classical or modern organic synthetic methods have provided tools to access a wide range of redox-active organic scaffolds. And they also have enabled the structure-dependent tunable (electro)chemical properties.^{5,15,17–23} In particular, quinone-based molecules have several advantages such as fast kinetics, sustainability of natural resources, and cost-effective synthetic protocols.^{24–28} According to the Deuchert and Hünig classification, quinone is categorized into the Wurster-type compound undergoing a two-electron transfer process to furnish hydroquinone skeleton.²⁹ Previously, we unveiled the prototype tubular lithium– organic batteries by utilizing 5,12-naphthacenequinone (NAQ) and 1,2-benzanthraquinone (BAQ) as the 1st generation organic catholytes (Fig. 1a).²⁸ Although they showed high power density, their low solubility in organic electrolytes limited the electrolyte circulation, only allowing an intermittent flow mode.

Herein, we report that synthetic approach coupled with lithium battery technology can provide three-fold advances for lithium-organic flow batteries: (i) enhanced electrochemical stability toward lithium metal, (ii) tunable electrochemical properties, and (iii) conformity and enhanced solubility to the flexible-tube type design. The π -extended quinone derivatives bearing electron-donating or electron-withdrawing substituents are synthesized by the palladium-catalyzed Suzuki cross-coupling reactions. Aryl moiety incorporation significantly affects the electrochemical behavior and cycle stability of molecular engineered catholytes.

Experimental section

General synthesis of arylated quinones

To a dried Schlenk tube were added 2-bromo-1,4-naphthoquinone (Br-NQ, 100 mg, 0.42 mmol, 1.0 equiv.), arylboronic acid (0.63 mmol, 1.5 equiv.), potassium carbonate (1.26 mmol, 3.0 equiv.), Pd(OAc)₂ (3 mol%), and PPh₃ (12 mol%). The reaction mixture in tetrahydrofuran (THF)/water solution (5 mL, 10:1, v/v) was stirred at 80 °C for 8 h under an argon atmosphere. The residue was filtered through a Celite pad, then repeatedly rinsed with dichloromethane (DCM). The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography.

Preparation of organic catholytes

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All chemicals were handled inside an Ar-filled glove box filled. Tetraethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich) was dehydrated by anhydrous CaH₂ (Sigma-Aldrich) before use. Quinone powder was dissolved in 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)- TEGDME electrolyte.

Lithium metal half-cell test

Synthetic quinone (0.05 M) dissolved in LiTFSI (1.0 M)-TEGDME was used as the catholyte. Electrochemical performance was measured using 2016 coin cells. Carbon paper with a thickness of 280 μ m (TGP-H 090, Toray) was used as a positive electrode, and microporous polyethylene (PE) film was used as a separator. A coin cell was assembled in the argon-filled glove box using lithium metal as a counter electrode. 40 μ L of the catholyte was injected into a coin cell. During the measurement, temperature was maintained at 25 °C, and precyclings were carried out for the system stabilization, then the following galvanic tests were recorded.

Results and discussion

Our synthetic approach and redox chemistry are based on the naturally occurring molecules such as ubiquinone and vitamin K derived from 1,4-naphthoquinone (NQ), and they involve the biological redox processes using protons as charge carriers (Fig. 1b).^{25,26,30,31} Inspired from nature, we designed the 2nd generation organic molecules from Br-NQ and phenylboronic acid. Fig. 1c shows the Suzuki cross-coupling reactions to provide arylated quinones bearing electron-donating group (EDG) or electron-withdrawing group (EWG), e.g., OCH₃ or CF₃ moieties. Subsequently, we apply the synthetic compounds in the tubular flow batteries using lithium-ions as charge carriers (Fig. 1d), which will be discussed *vide infra*.

Table 1 shows the standard reaction conditions to afford 2-phenyl-1,4-naphthoquinone (PNQ-1). In this reaction, the active Pd⁰ species is *in situ* generated from Pd(OAc)₂ precatalyst in the presence of triphenylphosphine (PPh₃) ligand, while producing the corresponding phosphine oxide.^{32–35} The optimized reaction conditions (entry 1) showed 86% yield of PNQ-1 by forming C–C bond (see its ¹H NMR spectrum presented in Fig. S1, ESI[†]). The change in solvent decreased the yields (entries 2 and 3) owing to the reduced solubility of an inorganic compound K₂CO₃. When the reactions were performed at room temperature (entry 4) or in air (entry 5), the reaction yields significantly decreased to 51% or 37%, respectively. Low reactivity at room temperature and the deactivation problem of the Pd⁰ species under air exposure can impede the catalytic reactions. We used NQ as a negative control sample for the following electrochemical tests, which does not possess an aryl moiety.

The electrochemical properties of NQ and PNQ-1 were investigated by the galvanostatic charge and discharge processes, where a lithium metal was used in a half-cell without any surface modification. Carbon paper as a positive electrode was utilized to infiltrate the

quinone catholytes. The organic catholytes were prepared based on the TEGDME solution containing 0.05 M quinone as an active material and 1.0 M LiTFSI as a lithium salt. Fig. 2a shows the reversible redox processes of NQ and PNQ-1 involving two-electrons and twolithium ions. Through these consecutive two-electron transfer reactions, PNQ-1 is reduced into a lithiated hydroquinone species, redPNQ-1.^{26,29,30,36} Fig. 2b shows the voltage profiles of PNQ-1 at a current density of 100 mA g^{-1} corresponding to ca. 0.5 C-rate in a potential range of 1.8–3.0 V vs. Li/Li⁺. PNQ-1 presented two distinctive discharge plateaus at ca. 2.4 and 2.6 V, delivering a specific capacity of 196 mA h g^{-1} , which was comparable to a theoretical capacity of 229 mA h g^{-1} . These redox plateaus are consistent with the values evaluated from cyclic voltammograms (Fig. S2 in the ESI⁺). PNQ-1 also shows good rate capability delivering 161 mA h g^{-1} even at a rate of 2000 mA g^{-1} that corresponds to ca. 10 Crate (Fig. 2c; see also Fig. S3 for the concentration-dependent rate capability test). In terms of long-term cycle stability, PNQ-1 catholyte revealed good capacity retention (92%) over 150 cycles at ca. 0.5 C-rate with the high Coulombic efficiency of near 100% (Fig. 2d). The open-circuit voltage (OCV) of the PNQ-1 catholyte was moderately maintained in a voltage range of 2.56–2.71 V upon the prolonged storage time of ~50 h (Fig. S4). The intimate contact between the redox-active species and carbonaceous materials through π - π interaction and/or infiltration can suppress the crossover issue. In contrast, the specific capacity of NQ only reached 115 mA h g^{-1} with significant capacity fading after 150 cycles.

To investigate the capacity fading mechanism, the cycled half-cell was disassembled, and the surface of the lithium metal was examined by scanning electron microscopy (SEM) analysis. The surface of the lithium anode in the NQ cell was severely damaged, showing cracks and an inhomogeneous morphology after 150 cycles (Fig. 2e). In contrast, the PNQ-1 cell showed a clean lithium surface (Fig. 2f). This result is associated with the enhanced

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chemical stability of the synthetic quinone backbone toward a highly reactive lithium metal.^{37–44} The Suzuki cross-coupling reaction generates extended π -conjugated structure, causing the delocalization effect along with increased steric hindrance. Concurrently, the olefinic (more localized π -electrons) character of non-arylated NQ could be reduced.⁴⁵ In addition, electrochemical impedance spectroscopy (EIS) analyses were carried out to investigate the changes of internal resistance upon cycling (Fig. S5 in the ESI⁺). Compared to the PNQ-1 catholyte, the significant increasement of charge transfer resistance (R_{ct}) of the NQ catholyte was observed upon cycling, implying the poor electron-transfer kinetics of the NQ catholyte. To unambiguously demonstrate the chemical stability of PNQ-1 upon cycling, the ¹H NMR spectra were recorded (Fig. S6 in the ESI⁺). Whereas the decomposition of NQ was confirmed after cycling implying the unstable redox reaction with lithium metal, PNQ-1 showed relatived well-maintained NMR peaks. It indicates that the Suzuki cross-coupling chemistry can provide enhanced π -extension and chemical stability toward the quinone scaffold guiding the rational molecular design.

To evaluate the substituent-dependent electrochemical performances, we further synthesized a family of arylated quinones bearing methoxy (OCH₃) and trifluoromethyl (CF₃) moieties as EDG and EWG (Table 2). The arylboronic acids bearing *ortho/meta/para*-methoxy substituents were coupled in high yields of 86%, 80%, and 91% to furnish PNQ-2, 3, and 4 samples, respectively. In contrast, the yields of quinone derivatives bearing CF₃ groups were lower compared to those of methoxy functionalized quinones, showing the values of 67%, 54%, and 69% in PNQ-5, 6, and 7 samples, respectively (for the NMR spectra of the prepared compounds, see ESI⁺, Fig. S7–S14).

Subsequently, we prepared the organic catholytes from the synthetic quinones (PNQ-2 to PNQ-7), where the same electrochemical conditions were applied as used for the PNQ-1 test.

We found the electronic effect of the substituents including OCH_3 and CF_3 on Published on 03 July 2018. Downloaded by University of Sussex on 7/4/2018 2:41:59 PM

electrochemical performances. The effect of the ortho/meta/para-substituent positions were investigated through galvanic tests (Fig. 3). We observed that $para-OCH_3$ (PNQ-4) and $para-CF_3$ (PNQ-7) arylated guinones have low charge overpotentials, and stable discharge voltage properties. Thus, PNQ-4 and PNQ-7 were selected as representative electron-rich and electron-deficient redox molecules, and their rate capability and cycle stability were compared (Fig. 4). The para-OCH₃ bearing PNQ-4 showed two distinct plateaus at 2.37 and 2.61 V with an initial discharge capacity of 187 mA h g^{-1} at a current rate of 100 mA g^{-1} (Fig. 4a). As the current density increased, the discharge capacity gradually decreased, and the capacity retention at 2000 mA g^{-1} corresponding to ca. 10 C-rate was 81% of the initial specific capacity at 100 mA g^{-1} . The electron-deficient PNQ-7 also showed two distinct discharge plateaus at 2.45 and 2.68 V. However, its initial specific capacity was 93 mA h g⁻¹ at a current rate of 100 mA g^{-1} , which was much lower than that in PNQ-4 because of its higher molecular weight along with potential electronic effect (Fig. 4b). Nevertheless, it showed good rate capability, with 70% of the initial specific capacity at a current rate of 2000 mA g^{-1} . Remarkably, both PNQ-4 and PNQ-7 showed superior cyclability for 95 cycles at a current rate of 100 mA g⁻¹ with the Coulombic efficiency of ca. 100%. Morphological characteristics of metallic lithium surface were also investigated by SEM analyses, and the interfacial structures of the cycled lithium anode with PNQ-4 and PNQ-7 were remarkably intact without showing serious crack or dendritic lithium growth (ESI⁺, Fig. S15). With the respect to molecular structure, the arylation by the Pd-catalyzed Suzuki coupling can provide improved electrochemical stability from the enhanced delocalization of PNQ derivatives.

For practical applications of the organic catholyte, we fabricated a tubular lithium-organic redox battery architecture based on a spiral lithium foil anode, fully soluble PNQ-1 catholyte,

and carbon cloth electrode (see also Fig. S16 and S17 in the ESI⁺). To prevent a direct contact between the lithium foil and carbon cloth, a porous separator was used. Then, we performed the galvanostatic charge and discharge tests using 0.1 M of PNQ-1 catholyte at a current density of 0.25 mA cm⁻² in a voltage range from 1.8 to 3.0 V (Fig. 5a). The voltage profile showed a distinct two-electron transfer reaction, which agrees with the half-cell tests. The initial volumetric capacity of PNQ-1 was 1.6 A h L⁻¹, and it retained 75% of the initial capacity after 30 cycles corresponding to 140 h (Fig. 5b). We increased the concentration of the PNQ-1 catholyte from 50 to 150 mM to improve its energy density, and these values were compared to those of the BAQ catholyte that our group reported previously.²⁸ The energy density was proportional to the concentration of catholyte, and the 150 mM of PNQ-1 reached up to the value of 6.0 W h L⁻¹ (Fig. 5c).

The solubility of PNQ-1 was then quantitatively determined by UV/Vis spectroscopy (Table S1 and Fig. S18 in the ESI⁺). Based on the Beer–Lambert law, the maximum solubility of PNQ-1 in the TEGDME electrolyte was 0.31 M, which was 16 times higher than that of the BAQ catholyte. This highly improved concentration allows for the continuous electrolyte circulation. The tubular lithium-organic flow battery was connected with an external electrolyte tank to provide the catholyte upon cycling (Fig. S17). The PNQ-1 catholyte from an external reservoir was circulated using a peristaltic pump (a flow rate of 25 mL min⁻¹) that was purged with nitrogen gas to maintain the inert conditions and to avoid air exposure. Fig. S19 shows the charge–discharge behavior of the tubular flow battery with 0.1 M of fully soluble PNQ-1 catholyte. Remarkably, no abrupt capacity drop occurred for 20 h that can be caused by the flow channel clogging. These enhanced circulation and performance are associated with the high solubility and chemical stability of PNQ-1. The charge–discharge capacity of PNQ-1 in the tubular flow battery was moderately stable while showing an

average energy efficiency of ~70% (Fig. 5d). Further, as a proof-of-concept demonstration, the tubular lithium-organic flow battery was connected to a silicon photovoltaic (PV) module^{46,47} (see also the photocurrent–voltage curve presented in Fig. S20). The tubular battery was photocharged by the PV module with a current of 20 mA (Fig. 5e), and was electrochemically discharged with a current of 10 mA. To demonstrate the module operation under practical conditions, the tubular battery integrated with a solar cell panel was connected to a fan (Fig. 5f). The discharged tubular battery was readily charged by the solar cell, and allowed to operate a fan.

Conclusions

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We designed and synthesized an arylated quinone family for nonaqueous organic catholytes. The chemical modification of quinone catholytes leads to enhanced electrochemical stability, high solubility, and reversible redox processes. In addition, the substituent-dependent electrochemical performance of arylated quinones has been systemically investigated using OCH₃ and CF₃ functionalities. The excellent performance can be attributed to the lowered reactivity toward lithium metal, owing to the enhanced π -electron delocalization effect and reduced olefinic character. In the tubular battery system, the arylated quinone PNQ-1 provides an energy density of up to 6.0 W h L⁻¹ at a concentration of 150 mM. We anticipate that this single-flow lithium battery architecture assisted by the molecular design can pave the way to provide sustainable and reliable lithium battery systems.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

Authors acknowledge the financial supports from the National Research Foundation of Korea

(NRF-2016R1A2B4015497) and the UNIST Research Fund (1.170048.01).

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Fig. 1 (a) Organic redox-active molecules of NAQ and BAQ for the 1st generation lithium-organic batteries (Ref. 28). (b) Biochemical redox processes. (c) Synthesis of the 2nd generation quinone derivatives by the Suzuki cross-coupling reactions. (d) A schematic of tubular lithium-organic flow battery configuration.

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Fig. 2 (a) Two-electron electrochemical lithiation and delithiation. (b) Voltage profiles of PNQ-1 at a current rate of 100 mA g^{-1} . (c) Rate capability tests of the PNQ-1 catholyte at different current densities: 100, 200, 400, 1000, and 2000 mA g^{-1} . (d) Cyclabilities of NQ and PNQ-1 for 150 cycles at 100 mA g^{-1} . SEM images of lithium metal anodes for (e) NQ and (f) PNQ-1 after 150 cycles.



Fig. 3 Normalized voltage profiles of (a) PNQ-1, PNQ-2, PNQ-3, and PNQ-4 and (b) PNQ-1, PNQ-5, PNQ-6, and PNQ-7 at a current rate of 100 mA g^{-1} , and (c) their cyclability at 100 mA g^{-1} .



Fig. 4 (a,b) Rate capability tests of PNQ-4 and PNQ-7 catholytes at different current densities from 100 to 2000 mA g^{-1} . (c,d) The cycle performance and Coulombic efficiency of PNQ-4 and PNQ-7 catholytes for 95 cycles at a current density of 100 mA g^{-1} .



Fig. 5 (a) The charge–discharge cycle behavior and (b) the cycling performance of fully soluble PNQ-1 catholyte for 30 cycles at a current rate of 0.25 mA cm⁻² and voltage window from 1.8 to 3.0 V. (c) Volumetric energy densities of PNQ-1 and BAQ. (d) The charge–discharge capacity of 0.1 M PNQ-1 in a tubular flow battery with the energy efficiency. (e) The photocharge and electrochemical discharge behavior, and (f) its digital photograph of a tubular battery equipped with a photovoltaic module.









^{*a*} The standard conditions and isolated yields. ^{*b*} The changes from the standard conditions: $Pd(OAc)_2$ (5 mol%), PPh₃ (20 mol%), 1,4-dioxane instead of THF, 100 °C for 12 h.



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Nonaqueous arylated quinone catholytes for lithium-organic flow batteries



The chemically tailored quinone catholytes have been utilized for the tubular lithium-organic flow batteries under a continuous electrolyte flowing mode.