



Short communication

Application of quinonic cathode compounds for quasi-solid lithium batteries

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H I G H L I G H T S

- ▶ Three high energy-density quinonic cathode compounds were incorporated in solid-state organic cathode batteries.
- ▶ The cycleabilities of organic cathode cells were improved by nearly two orders of magnitude compared to conventional cells.
- ▶ The general applicability of organic cathode solid-state cells was demonstrated.
- ▶ Compounds that have been regarded “unusable” became “usable” under novel cell design and construction.

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Solid-state cells are one of the strongest candidate designs for utilisation of renewable high-capacity organic cathode materials. Following our previous work on tetracyanoquinodimethane, further high-capacity quinonic compounds, namely dichlorodicyanobenzoquinone, tetrahydroxybenzoquinone and dihydroxybenzoquinone were investigated. Cell cycling experiments indicated that these compounds undergo reversible redox reaction with significantly less cyclic capacity decay. 3.4 V of cell voltage was attainable from DDQ cells and capacities exceeding 250 mAh g⁻¹ were obtained from THBQ and DHBQ. These results reassure that by adopting an appropriate battery design, cycleability of organic cathodes can be drastically improved and they can be exploited as low-cost environmentally friendly high energy-density cathode materials.

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1. Introduction

Recent surge in demands for large-scale batteries in electric vehicles and “smart grid” applications require development of battery materials that are low-cost, free of resource restrictions and environmentally friendly. The Ni–Co–Mn oxide cathodes on the market today falls short for this purpose because they require “rare metals” such as Co and preparation involves energy-intensive processes [1]. On the contrary, organic compounds present promising possibilities because they are high energy density, free of metallic species, raw materials are renewable and processing is less energy intense [2,3]. However, practical application has been unsuccessful due to low cycleability, primarily owing to low conductivity, side reactions and dissolution into electrolyte. The side reaction and low conductivity can be mitigated by careful selection of compounds and appropriate use of conductive

additives, but cathode dissolution remains as an obstacle. There have been attempts such as polymerisation [4–8], immobilisation by covalent bonding [9,10], physisorption [11,12], the use of radical polymers [13], to suppress the capacity loss, but important performance parameters such as energy density, rate performance or safety often had to be compromised one way or another. Adopting an all-solid design is one of the obvious strategies, but examples have been very limited to specific compounds [14].

We recently developed a general strategy to accommodate soluble quinonic cathode materials in quasi-solid cells, which electrolyte consisted of silica nanoparticles and room temperature ionic liquid (RTIL) [15]. It is anticipated that adoption of solid-state design provides more fundamental solution to the dissolution issue and enables the effective use of many monomeric compounds reported to date [3,16–18]. In addition to the previously reported tetracyanoquinodimethane (TCNQ), further candidate cathode compounds, namely 2,3,5,6-tetrahydroxybenzoquinone (THBQ), 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) and 2,5-dihydroxy benzoquinone (DHBQ) were integrated in test cells to characterise their battery performance. Quinones are well-known compounds

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and their cathode applications have been reported several times, but unmodified quinone tends to suffer low utilisation or rapid dissolution. DDQ has high electron affinity and redox potential due to aromaticity gain and charge delocalisation over electron-withdrawing substituents [19]. THBQ, which is a biomass-based material, has been studied in the past using conventional organic electrolyte such as propylene carbonate, vinylene carbonate etc [20]. The theoretical capacity of DHBQ is large, but due to its low molecular mass and high solubility, only its polymerised entity has been considered [21].

In this report, high energy-density solid-state cells of DDQ, THBQ and DHBQ were constructed to establish the methodology of using monomeric compounds for a cathode. Also, the rate and temperature dependence of cell performance was investigated to further pursue higher energy and power densities.

2. Experimental

2.1. Materials

DDQ, THBQ and DHBQ were purchased from TCI (Tokyo Kasei Corp.) and used without further purification. EC/DEC (1:1 mixture of ethylene carbonate and diethyl carbonate) 1 M LiClO₄ was purchased from Kishida Chemicals and stored under Ar atmosphere. 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (“[EMIm][Tf₂N]”, Iolitec) was vacuum desiccated at 483 K for 3 h and stored under Ar until use.

2.2. Quasi-solid electrolyte

The detailed procedure for preparation of silica-RTIL composite quasi-solid electrolyte is described elsewhere [22]. The mean diameter of fumed silica nanoparticles was ~6 nm and silica-RTIL ratio was 1:3 by volume. The thickness and conductivity of solid electrolyte was typically around 400 μm and ~1 × 10⁻³ S cm⁻¹ at room temperature (RT). Polyethylene oxide (PEO) membranes were prepared by dissolving PEG (MW = 6000), PEO (Mw = 4,000,000), and Li[Tf₂N] at 8:1:1 ratio in acetonitrile and vacuum drying at 343 K. The PEO residue was compressed at 2000 N at 333 K to form a film with a typical thickness of 20–30 μm. The cathode current collector was prepared by grinding a 4:1 mixture of acetylene black carbon (AB) and PTFE in pestle and mortar and drying under vacuum at 433 K.

2.3. Cathode preparation

The organic cathode pastes were prepared by blending quinonic compounds with Ketjen Black (KB, 1270 m² g⁻¹) and solution casting in THF. The quinone–KB mixture suspension in THF was dried at 363 K in air for 2 h and further by vacuum drying at 343 K. The residue was mixed with PTFE and manually ground using a pestle and mortar until paste formed. The typical thickness of such pastes was 200–300 μm.

2.4. Cell construction

The cathode–electrolyte combined disc was assembled by stacking solid electrolyte, PEO film, 3–4 mg of cathode paste (5–7 mm in diameter) and a carbon current collector disc in a die with the internal diameter of 10 mm. The entire stack was compressed in the die at ~100 MPa to form a pellet. 8 μl of [EMIm][Tf₂N] was dropped on the electrolyte side and the pellet was left in vacuum for ~15 min to remove any remaining bubbles. 5 μl of EC/DEC 1 M LiClO₄ was dropped on a freshly cut shiny lithium metal, left for ~15 min and the pellet was placed over. The cell was sealed in a CR2032 coin cell

under argon atmosphere. Charge–discharge (C/D, also known as constant current cyclic voltammogram) measurements were conducted with Hokuto Denko HJ1001SD8 potentiostat.

2.5. Liquid cell construction

A U-shaped electrochemical cell was filled with EC/DEC with 1 M LiClO₄. A metallic lithium anode, reference electrode (3–4 cm²) and cathode paste mounted on platinum mesh were immersed in the electrolyte. The C/D measurements were conducted using a Solartron 1400 Cell Test System.

3. Results and discussion

Cathode pastes containing ~75 wt.% of quinonic compounds, 20 wt.% conductive additive (Ketjen Black, “KB”) and 5 wt.% binder (polytetrafluoroethylene, “PTFE”) were prepared. Their theoretical capacities and estimated cell voltages are summarised in Table 1. Fig. 1 shows the SEM/EDX map of DDQ, THBQ and DHBQ cathode pastes. The typical dimension of DDQ and THBQ crystals were 3–5 μm and that of DHBQ were ~20 μm (Supplementary Fig. S1). The spatial distribution of DDQ, THBQ and DHBQ was determined by chlorine or oxygen signal distribution (Fig. 2). The DDQ showed highly homogeneous distribution of Cl signals. The THBQ showed generally homogeneous distribution, but crystal grains showing as “hotspots” of oxygen signals were also observed. DHBQ was also generally homogeneous and oxygen signal hotspots were rare. Upon SEM/EDX imaging, local charge accumulation did not occur even without gold deposition. This indicated that conductive additives provided sufficient electronic conductivity to cathode. This is a desirable or necessary property for a battery using insulating active materials.

3.1. Cell assembly and battery performance

Cells were assembled by stacking silica-composite quasi-solid electrolyte, PEO layer, cathode paste and carbon paste current collector and compressing together into a pellet at 100 MPa [15]. After wetting the pellet with RTIL, metallic lithium anode was mounted and a cell was assembled [15]. In the first sequence of cell characterisation, active compound fractions were set to ~50% and C/D measurements (constant current cyclic voltammogram) were carried out at RT and 0.2 C rate. Measurements were conducted both in liquid electrolyte cells and solid-state cells. The potential profiles and cycleability properties were then compared and analysed to verify reversible battery reactions (Fig. 3).

A cell using a DDQ paste (67.1 wt.% DDQ, 26.9 wt.% KB, 6.0 wt.% PTFE) was constructed and evaluated in a liquid cell. Two potential plateaus near 3.4 V and 3.2 V, which corresponded to the first and second redox potentials, appeared. However, the specific capacity was only 50 mAh g⁻¹–DDQ for the first cycle and the subsequent

Table 1

Theoretical capacity and cell voltages of DDQ, THBQ and DHBQ measured by liquid cell experiments. Theoretical energy densities were calculated accordingly.

| | DDQ | THBQ | DHBQ |
|----------------------|--------------------------|--------------------------|--------------------------|
| Molecular structure | | | |
| Theoretical capacity | 237 mAh g ⁻¹ | 311 mAh g ⁻¹ | 382 mAh g ⁻¹ |
| Cell voltage | 3.6–3.0 V | 3.0–1.6 V | 3.2–1.8 V |
| Energy density | ~750 Wh kg ⁻¹ | ~800 Wh kg ⁻¹ | ~950 Wh kg ⁻¹ |

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