



A two-compartment cell for using soluble benzoquinone derivatives as active materials in lithium secondary batteries

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ARTICLE INFO

Article history:

Received 13 June 2011

Received in revised form 31 August 2011

Accepted 31 August 2011

Available online 9 September 2011

Keywords:

Lithium secondary battery

Positive electrode

Soluble active materials

Benzoquinone derivatives

Solid electrolyte diaphragm

ABSTRACT

In this study, soluble redox couples were used as active materials for an electrode using a newly designed two-compartment cell. In this cell, liquid electrolyte was separated by a solid electrolyte diaphragm, which prevents dissolved active materials from reaching the counter electrode. To balance the apparent current density and the apparent energy density, a porous sheet made of carbon paper as a current collector was set on the side of the positive electrode with an active material impregnated into it, and Li foil was set on the side of the negative electrode. Some soluble benzoquinone derivatives were examined by charge/discharge cycling for use as active materials of the positive electrode in lithium secondary batteries. Some of them showed specific capacities close to the theoretical values, assuming two-electron reduction. Among them, 2,5-dipropoxy-1,4-benzoquinone (DPBQ) could be cycled regardless of whether the amount used exceeded the solubility (with precipitate in the electrolyte) or not (all is dissolved). This implies that the active material reacts at the surface of the current collector in the dissolved state, and the precipitated fraction also participates by dissolution into the electrolyte. The results also suggest that a good cycle performance using our two-compartment cell requires an active material with relatively high solubility.

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1. Introduction

Lithium secondary batteries are widely used because of their high-energy characteristics. To improve battery performance, various active materials have been investigated. In addition, low-polluting materials are becoming more desirable due to considerations of environmental effects. To date, organic materials without any heavy metals have been proposed as promising active materials for use as a positive electrode [1–3].

Among the organic materials tested, 1,4-benzoquinone (BQ) generally gives reversible redox reactions at relatively high potential [4]. If we could use the two-electron redox reaction of BQ, a high capacity of nearly 500 mAh g^{−1} should be expected. However, the use of BQ is practically difficult due to sublimation and dissolution into an electrolyte solution. Several studies have tried to apply this redox reaction to battery system through the immobilization onto solid nano particles [5], the synthesis of various polymers [6–10], the introduction of substituents groups [3,4,11,12], and so on.

Recently, we investigated the electrochemical characteristics of 2,5-dialkoxy-1,4-benzoquinone derivatives (DABQs, A = M: methoxy, E: ethoxy, and P: propoxy) for their use in lithium

secondary batteries [13,14], and found that the two-electron redox reaction induced by the benzoquinone skeleton leads to high capacities. While DMBQ shows relatively good cycle performance, DEBQ and DPBQ show fast capacity-decay during cycling. One of the main reasons for the decrease in capacity is the dissolution of DEBQ and DPBQ into the electrolyte solution.

Generally, dissolution of the active material leads not only to a loss of utilization but also to self-discharge (chemical short-circuit) if the dissolved species reach the counter electrode. The insertion of a barrier made of solid electrolyte (SE), such as coating of the electrode, has been proposed to prevent self-discharge when the active materials are soluble [15,16]. Based on this concept, we designed a two-compartment cell to improve the cycle performance of soluble benzoquinone derivatives. In this cell, the active material (a benzoquinone derivative) is put into the positive electrolyte solution, and a diaphragm made of a lithium ion-conducting glass–ceramic plate is placed between the positive and negative electrolyte solutions, which prevent the active material from reaching the negative electrode. Electrochemical reaction of the active material is designed to proceed at the surface of the current collector under a dissolved state. This implies that the active material no longer needs to be electronically conductive. However, if the active material is stored in the cell in the dissolved state, the energy density would not be very high. On the other hand, if the active materials in the precipitated state in the electrolyte solution could react after dissolution,

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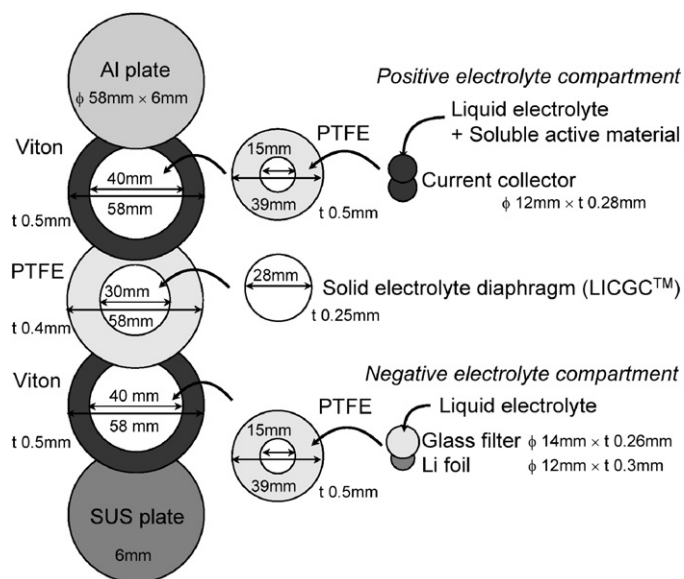


Fig. 1. Schematic representation of the two-compartment cell for a soluble active material.

the energy density should be increased. Therefore, we also examined whether the active material that exceeded the solubility could be cycled.

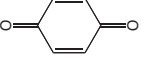
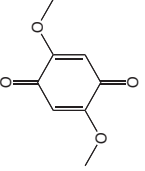
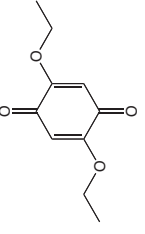
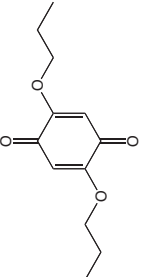
2. Experimental

BQ and DMBQ were purchased (98% for both, Tokyo Kasei Corporation) and used without further purification. DEBQ and DPBQ were synthesized, as described in the literature [17]. γ -butyrolactone containing 1 mol L⁻¹ of lithium perchlorate (LiClO₄/GBL, Kishida Chemical) was used for the electrolyte solution. The chemical structures and theoretical capacities of the organic active materials used in this study are listed in Table 1. Solubility of each material into the electrolyte solution was roughly estimated by visual observation during stepwise dissolving. The average and standard deviation for each material derived by three or more trial was also listed in Table 1.

Cyclic voltammetries (CVs) of the BQ and DABQs dissolved in the electrolyte solution were conducted using an electrochemical analyzer (ALS760, BAS). About 2 mL of each solution was placed in a Pyrex® glass cell. A glassy carbon electrode sealed in PEEK (ϕ 3 mm, BAS) was used as the working electrode (WE). Prior to the measurement, the surface of GC was polished with 6 μ m diamond powder and buffed with 0.05 μ m alumina powder. Pt mesh (100 mesh, 10 mm $\times$ 20 mm) was used as the counter electrode (CE). As the reference electrode (RE), a piece of Li foil (Honjo Metal) was set in a glass tube with a Vycor® glass plug at the end. Initial direction of each CV was cathodic, from the open circuit potential.

A schematic representation of the two-compartment cell for a soluble active material is shown in Fig. 1. In this cell, the LiClO₄/GBL was used for both the anode and cathode electrolyte solutions. The positive and negative electrodes were in contact with the positive and negative electrolyte solutions, respectively. A plate of lithium ion-conducting glass–ceramic (LICGC™, OHARA) is placed between the positive and negative electrolyte solutions. For the positive electrode (current collector), a material with a high porosity to increase the apparent energy density and with a proper pore size to reduce the diffusion length of the dissolved active material is desirable. According to these criteria, we used two circular pieces of carbon paper (TGP-H-090, Toray) in layers as the positive electrode. A circular piece of Li foil (Honjo Metal) was used as the negative

Table 1
Chemical structures, formula weights, density, theoretical capacities, and solubilities in the electrolyte of BQ, DMBQ, DEBQ, and DPBQ.

Chemical structure	1,4-Benzoquinone (BQ)	2,5-Dimethoxy-1,4-benzoquinone (DMBQ)	2,5-Diethoxy-1,4-benzoquinone (DEBQ)	2,5-Dipropoxy-1,4-benzoquinone (DPBQ)
				
Formula weight	108.1	168.2	196.2	224.3
Density ^a [g cm ⁻³]	1.318	1.50	1.223	1.273
Theoretical capacity ^b [mAh g ⁻¹]	496	319	273	239
Theoretical capacity ^b [mAh cm ⁻³]	654	478	334	304
Solubility ^c [mol L ⁻¹]	2.6(2)	0.006(3)	0.3(1)	0.06(2)

^a Calculated from the crystallographic data [13,17].

^b Assuming a two-electron redox reaction.

^c Measured using 1 mol L⁻¹ LiClO₄/GBL at room temperature.

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