Electrochemistry Communications 72 (2016) 64–68

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

A dual–ion battery using diamino–rubicene as anion–inserting positive electrode material

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ARTICLE INFO

Article history:
Received 4 August 2016
Received in revised form 1 September 2016
Accepted 2 September 2016
Available online 06 September 2016

Keywords:
Organic batteries
Anion insertion
Diamino-rubicene
Redox-active amine
Dual-ion cell

ABSTRACT

A novel and non-polymeric anion-inserting electrode material has been designed and prepared for promoting research on molecular ion rechargeable batteries: 5,12-diaminorubicene (DARb). The apolar core structure of a rubicene molecule has been coupled to two amino-groups for producing an original conjugated primary diamine exhibiting low affinity for polar solvents such as common carbonate-based battery electrolytes. The electrochemical reactivity of this organic molecule has been probed in a dual-ion cell configuration (vs. Li) using six different electrolyte formulations in terms of solvent (PC, EC-DMC) and lithium salt ($LiPF_6$, $LiClO_4$, LiTFSI). This diamino-rubicene material systematically showed a reversible electroactivity and promising performances when using 1 M $LiPF_6$ in EC:DMC (1:1 vol.%) as the electrolyte, such as an average potential of ~3.4 V vs. Li^+/Li^0, an initial capacity of 115 $mAh \cdot g^{-1}$ and a good capacity retention over 60 cycles without any optimization.

1. Introduction

Owing to the depletion of fossil fuels and the impacts of the subsequent global warming, the concept of sustainability is rapidly expanding to our technology-oriented society. While clean energy conversion and storage systems are being aggressively pursued, current rechargeable systems such as secondary (rechargeable) batteries are facing possible environmental concerns due to the large-scale production, the use of non-renewable resources (ores) and high-temperature synthesis routes in elaborating active electrode materials [1–4]. Consequently, we can easily perceive the interest in promoting new generations of low-polluting electrochemical storage devices. One possible alternative could be nestled in the development of redox-active organic compounds because the latter are based on more abundant chemical elements and possess some versatile electrochemical properties. For instance, beyond the redox potential tuning by designing the structure arrangement (see for example Refs. 5–7), organics can interestingly operate according to two types of electrochemical mechanisms (both n- and p-type[1]) and in various cell configurations, as reported by Novák et al. many years ago [9]. Over the last ten years, significant progress was achieved in the field attracting much interest from the energy storage community as highlighted in several recent reviews on the topic [10–12]. In particular, long-term cycling stability curves (>1000 cycles) have been reported by Zhou's group and Yao's group [13–15] for Li-organic batteries using carbonyl-based polymers as the positive electrode. However, elaborated in their charged state, such n-type organic electrode materials reversibly accommodate lithium at a relatively low operating potential (<2.4 V vs. Li^+/Li^0). Alternatively, p-type redox-active organic compounds which involve an anion-inserting process upon charging may react at higher potentials [8,9] bringing to us another playground in designing organic electrochemical storage systems including the development, in principle, of molecular ion batteries [9] as recalled by Yao and co-workers in a visionary study [16]. Although existing p-type electrode materials consist in organic polymers and oligomers (see for instance, refs 9, 17–23), we have recently reported that crystallized host organic structures based on aromatic secondary amines can electrochemically accommodate anions at potentials higher than 3.2 V vs. Li^+/Li^0 [24,25].

In light of its stunning electrochemical and chemical properties, we decided to dig further on the potentiality of low-weight aromatic amines as intercalation electrode material. We are proposing in this study a novel organic electrode molecule belonging this time to the primary amine family and built on a condensed aromatic rubicene system. Also known as a molecular fragment of C70, this organic backbone is a stiff polycyclic aromatic hydrocarbon with planar π-orbital surfaces potentially providing good intermolecular electronic coupling [26,27]. Although poorly investigated in the literature, rubicene possesses a large

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[1] n-type structures involve upon oxidation an ionic compensation with cation release whereas p-type structures imply an anion uptake. Note that p- and n-type structures are also named System A and B, respectively, according to Hünig's classification [8].

http://dx.doi.org/10.1016/j.elecom.2016.09.002
1388-2481/

apolar moiety that may intrinsically limit its affinity and tendency to be solvated by polar solvents such as common carbonate-based battery electrolytes. In addition, the extended aromatic core of rubicene is suitable to stabilize positive charges and unpaired electrons by delocalization, thus favoring the reversibility of p-type redox reactions by avoiding side reactions. We therefore coupled the rubicene core with the redox properties of amino groups to design a diamino-rubicene (denoted DARb) as a first prototype of non-polymeric active electrode material based on a conjugated primary diamine. In this communication, we report the preparation of the DARb compound and its preliminary anion-inserting properties measured in a lithium half cell.

2. Material and methods

2.1. Chemicals

Fluorenone (98%, Alfa Aesar), magnesium turnings (99.8%, Alfa Aesar), sodium sulfide hydrate (>60%, Aldrich), acetic acid (>99%, Aldrich), nitric acid (69.5%, Carlo Erba) and toluene (Carlo Erba) were used as received. Supporting salts such as $LiClO_4$ (Aldrich, battery grade), $LiPF_6$ (Novolyte) and LiTFSI (Novolyte) were also used without further purification. Propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC) were of battery grade and purchased from Novolyte.

2.2. Analytical techniques

Infrared spectra were recorded on a FT-IR Bruker Vertex 70. Electrospray ionization high-resolution mass spectrometry (ESI-HRMS) data were obtained in the negative ion mode with a Q-TOF Ultima Global instrument (Waters-Micromass) equipped with a pneumatically assisted electrospray ion source (*Z*-spray) and an additional sprayer for the reference compound (LockSpray). ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz. Chemical shifts (δ) are given in ppm relative to TMS.

2.3. Synthetic procedure

The synthesis of 5,12-diaminorubicene was inspired from a protocol published by Sachweh and Langhals [28]. Fluorenone (20.8 mmol, 3.75 g) is melted in a flask at 100 °C under argon then magnesium turnings are added (51.4 mmoles, 1.25 g). The reaction mixture is heated up to 300 °C. Once the exothermic reaction started boiling and the mixture turned dark red, the heating was switched off. The mixture is slowly cooled down and the product is purified overnight via simultaneous extraction–purification with boiling toluene in a homemade Soxhlet extractor. The solid product (rubicene) is recovered by filtration as a bright red powder. The 1.96 g (6 mmol, 56% yield) of recovered crude rubicene are then dispersed in 20 ml of acetic acid, to which 1.6 ml of concentrated nitric acid is added dropwise. After addition, the reaction is kept at 80 °C during 2 h. The reaction mixture is filtered and washed with water and ethanol, and the precipitate subsequently extracted twice with boiling toluene. The filtrated precipitate is a highly insoluble dark purple powder (5,12-dinitrorubicene). 0.75 g (1.8 mmol, 30% yield) of 5,12-dinitrorubicene and 23 g of hydrated sodium sulfide are dispersed in a mixture of 16 ml of water and 130 ml of ethanol. The reaction mixture is kept under reflux during 6 h and filtered while hot. The precipitate is washed thoroughly with ethanol and water. After recrystallization from a DMF:THF mixture and drying at 90 °C under vacuum 0.46 g (1.29 mmol, 71% yield; 12% total yield from starting fluorenone) of a dark blue powder are obtained, corresponding to pure 5,12-diaminorubicene (DARb): IR (KBr pellet) $\bar{\upsilon}_{max}$ 3390, 3050–2830, 1610, 1480, 1380, 1230, 820, 735, 660 cm^{-1}; ^1H NMR (400 MHz, d_6-DMSO): δ 8.56 (d, 2H, $J = 8.8$ Hz), 8.07 (d, 2H, $J = 8.4$ Hz), 8.02 (d, 2H, $J = 6.4$ Hz), 7.74 (t, 2H, $J = 8.0$ Hz), 7.31 (s, 2H), 6.68 (d, 2H, $J = 7.6$ Hz), 5.50 (s, 4H, NH_2); ^{13}C NMR (100 MHz, d_6-DMSO): δ 148.5, 140.2, 137.9, 131.7 (2C), 128.3, 127.6, 124.7, 124.2, 123.5, 119.9, 113.3, 108.1; ESI-HRMS *m*/*z* 357.1386 $[M + H]^+$ (calcd. for $C_{26}H_{17}N_2$, 357.1392).

2.4. Electrochemical study

The electrochemical performance of the material were tested vs. lithium in a Swagelok®-type cell using a Li metal disc as negative electrode and two fiberglass separators soaked with the desired electrolyte (six different formulations). The positive electrodes were prepared without binder in an argon-filled glove box by hand-milling powder of DARb with 33 wt.% of carbon black (Ketjenblack EC-600JD, AkzoNobel) with a typical loading of 4 $mgcm^2$ $mg \cdot cm^{-2}$ of active material. The cells were cycled in galvanostatic mode using a MPG-2 system (Bio-Logic S.A., Claix, France).

3. Results and discussion

The electrochemical behavior of aromatic amines has been widely investigated in liquid media [29–31] and one common application in molecular electrochemistry comes from the preparation of conducting polymers by electro-oxidation [32–34]. The oxidation reaction proceeds through the reversible formation of a radical cation, which is stabilized by electron delocalization on the aromatic-core structure giving usually rise to reversible faradaic peaks in cyclic voltammetry [29–31]. In solid state electrochemistry, the redox activity of amino groups involves a concomitant anion insertion process for maintaining charge neutrality within the electrode material. On the basis of the available literature till date, it seems however that the broad family of redox-active conjugated amines has been poorly investigated in battery applications except the particular case of polyaniline [9,35,36].

In principle, the electrochemical activity of the DARb material is expected to proceed through an initial radical cation formation (with simultaneous counter-ion uptake from the electrolyte) followed by a second oxidation step leading to the dication species with fully delocalized π-system (Scheme 1). The overall two-electron process gives an expected theoretical capacity of 150 $mAh \cdot g^{-1}$. Since the electrochemical reactivity of such an amino-compound should proceed through a reversible anion uptake process, we aimed at evaluating several guest anions characterized by different size and geometry: PF_6^-, ClO_4^- and $TFSI^-$ (Li^+ being the common counterion). Our recent studies on the interest of crystallized secondary amines have also pointed out that the anion-inserting process can be sensitive to the solvent nature as well [24,25]. Therefore we managed to explore different electrolyte solvents such as pure PC and the common EC:DMC (1:1 vol.%) mixture. The active material response was thus tested with a set of six electrolytes made of 1 M ionic salt solutions.

In a typical electrochemical procedure, the DARb electrode material was galvanostatically charged then discharged in a dual-ion cell configuration [9,37] at a cycling rate of 1 electron exchanged per diamino-rubicene unit in 5 h (Fig. 1). Interestingly, a reversible electrochemical activity can systematically be noted whereas common features can be observed such as the same stepwise process, an average potential located at ~3.4 V vs. Li^+/Li^0 or an initial charge capacity assigned to the uptake of 1.5–1.7 electrons per diamino-rubicene unit. These features do not seem influenced neither by the solvent nor the counterion nature. However, differences arise upon cycling and notably poor electrochemical stabilities for TFSI-based electrolytes. Such capacity fading could be interpreted by an extensive rearrangement (including Coulomb repulsions) that undergoes the p-type active molecule while incorporating the bulky $TFSI^-$ anions giving rise to the exfoliation of the active material [20,24].

In addition, some preliminary FTIR data seem indicate that this primary diamine chemically inserts solvent molecules of the electrolyte as previously observed with secondary diamines [24,25], which could explain the discrepancies observed in the cycling curves when using