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Biphenyl-lithium-TEGDME solution as anolyte for high energy density non-aqueous redox flow lithium battery

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ABSTRACT

Non-aqueous redox flow batteries, because of larger operating voltage, have attracted considerable attention for high-density energy storage applications. However, the study of the anolyte is rather limited compared with the catholyte due to the labile properties of redox mediators at low potentials. Here, we report a new strategy that exploits high concentration organic lithium metal solution as a robust and energetic anolyte. The solution formed by dissolving metallic lithium with biphenyl (BP) in tetraethylene glycol dimethyl ether (TEGDME) presents a redox potential of 0.39 V versus Li/Li^+, and a concentration up to 2 M. When coupled with a redox-targeted $LiFePO_4$ catholyte system, the constructed redox flow lithium battery full cell delivers a cell voltage of 3.0 V and presents reasonably good cycling performance.

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1. Introduction

Large-scale energy storage is increasingly in great demand for power grids, in order to mitigate the impact of electricity from the waving renewable energies, such as wind and solar energy [1,2]. Redox flow battery is one of the most suitable energy storage systems for grid-scale applications because of their unique architecture that separates the energy storage and power generation units, and affords high safety and operation flexibility. Unlike conventional batteries, which store energy in active materials coated on electrodes, redox flow batteries store energy in dissolved redox species in two different electrolyte fluids: the higher potential catholyte and the lower potential anolyte. The energy density of redox flow battery is determined by the concentration of redox species and cell voltage. Aqueous redox flow batteries, such as all-vanadium, zinc-bromine and iron-chromium flow batteries, have been developed for decades [3]. Voltage of aqueous flow batteries is limited within the electrochemical window of water (~1.29 V) to avoid H_2/O_2 evolutions. Thus, non-aqueous electrolytes are attracting considerable attention due to their wider electrochemical window than water. In recent years, various redox active species have been investigated for Li^+-based non-aqueous redox flow batteries, including metal complexes [4–14], organic molecules [15–22], and ionic liquids [23], etc. However, most of those studies are focused on the catholyte. There have been very few studies on non-aqueous anolyte, adopting redox species with potentials in the range from 1.50 to 2.50 V versus Li/Li^+ [6–8,11,16,17], which are however too positive to render a high cell voltage. In addition, the solubility of these redox species is generally limited compared to their aqueous counterparts. Yu and coworkers reported an aluminum-based deep-eutectic-solvent, which had 3.2 M concentration. But the potential, 2.2 V versus Li/Li^+, was still relatively high for an anolyte [24,25]. As a result, these systems still fall short of energy density. Another popular choice for the anode is metallic lithium due to its extremely high capacity and low potential. Hybrid lithium redox flow batteries employing metallic lithium anode and flowable catholyte have been reported by several groups [14,20,26–33]. But these hybrid systems sacrifice the flow mode on the anodic side, which results in compromised operation flexibility. In addition, the metallic anode suffers from poor cycling performance upon repeated stripping and plating due to the formation of dendrites. So, to achieve high energy density while keeping flowable anolyte, it is desirable to find a proper anolyte with high concentration and low redox potential concurrently.

Organic alkali metal solution, which has been discovered for nearly a century, provides a novel approach for anolyte for redox flow batteries. It has been found that alkali metals could directly react with certain aromatic hydrocarbons in organic solutions, mostly ethereal solvents to form charge transfer complexes [34,35], computational and experimental studies have been conducted on these systems [36–39], which were reported to be strong reducing agents, and have been used for synthetic chemistry [40,41]; such a strong reduction property presents a good indication of low redox potential for these solutions. Recently, sodium

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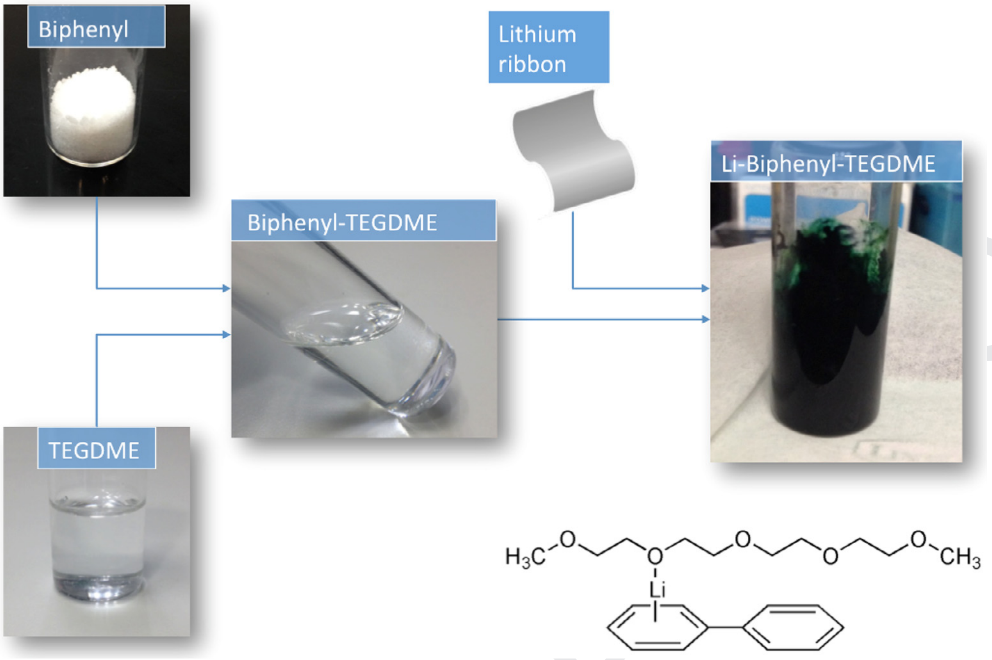

Fig. 1. Preparation of BP-Li-TEGDME solution.

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metal solution has been reported, and demonstrated as a safe and stable liquid anode [42]. However, the electrochemical activities of organic lithium solution as the anolyte of non-aqueous redox flow batteries have yet been studied.

Here we report on the electrochemical properties of an organic lithium solution and its novel use as the anolyte of non-aqueous redox flow lithium batteries. The solution is prepared by dissolving metallic lithium with biphenyl (BP) in tetraethylene glycol dimethyl ether (TEGDME) at room temperature, which forms an organic redox active solution (hereafter denoted as BP-Li-TEGDME). The lithium concentration of the solution is as high as 2.0 M, which delivers a low redox potential close to the metallic lithium, making it a suitable anolyte for non-aqueous redox flow battery. The interactions and bonding structures for the formation of BP-Li-TEGDME charge transfer complex are investigated by spectroscopic and density functional theory. Extensive electrochemical studies demonstrate great promise for its application as an intriguing anolyte system for high energy density flow batteries.

2. Experimental

2.1. Preparation of Li-BP-TEGDME solution

Lithium ribbon (99.9% trace metals basis, Sigma-Aldrich), biphenyl (BP, ≥99%, Sigma-Aldrich) and tetraethylene glycol dimethyl ether (TEGDME, ≥99%, Sigma-Aldrich) were used as purchased without further purification. Biphenyl was first dissolved in TEGDME, and a colorless BP-TEGDME solution was obtained (Fig. 1). The BP-TEGDME solution was dehydrated by adding molecular sieves (4 Å) and standing for 24 h. Then lithium metal was added in the BP-TEGDME solution, followed by vigorous stirring for 10 min. The metal was cut in the form of slices of 2–3 mm before added into the solution. The whole preparation process was conducted in an argon-filled glove box.

2.2. Electrochemical test

The cyclic voltammetry (CV) measurements were conducted with a multichannel potentiostat (Metrohm Autolab, PGSTAT302N) in an argon-filled glove box. A three-electrode electrochemical cell was employed, in which a gold disk electrode, a platinum wire and a silver wire was used working, counter and quasi-reference electrodes, respectively. The potential of the quasi-reference electrode was calibrated with ferrocene (Fc/Fc^+) and calculated against Li/Li^+. 1.0 M $LiClO_4$ in TEGDME was used as supporting electrolyte. The galvanostatic measurement was carried out in a two-electrode static stack cell with lithium metal as the counter electrode and a Li^+-conducting PVDF membrane as the separator. The current density was 0.025 mA cm^{-2}.

2.3. FTIR and UV–vis test

FTIR measurement was performed with an infrared spectrophotometer (Shimadzu, IRTracer-100). The FTIR sample was prepared by sealing the BP-Li-TEGDME solution between two KBr pellets to protect the solution from oxygen and moisture. The measurement was conducted with spectral range from 400 to 1300 cm^{-1}. The UV–vis absorption measurement was conducted on BP-Li-TEGMDE solution in an airtight optical cell. The spectra were collected using a UV–vis-NIR spectrophotometer (Shimadzu, Solidspec-3700) in the range of 300–1600 nm. All the measurements were conducted at room temperature.

2.4. Redox flow lithium battery test

The battery performance test was carried out with a multichannel potentiostat (Metrohm Autolab, PGSTAT302N). 2 mL solution of BP (2 M)-Li (1 M)-TEGDME was used as the anolyte with 1.0 M $LiClO_4$ as the supporting electrolyte. A sheet of nickel foam was used as the current collector for the anode. The catholyte consisted of 10 mM ferrocene (Fc) and 10 mM dibromoferrocene ($FcBr_2$) dissolved in 2 mL 1.0 M $LiClO_4$/TEGDME solution. 8 mg $LiFePO_4$ granules, equivalent to 25 mM, were placed in the cathodic storage tank. A piece of carbon felt was used as the cathode current collector. A Li^+-conducting PVDF membrane (2 cm × 2 cm in area) was used as the separator. The preparation of the PVDF membrane has been previously reported [43]. All the battery tests were performed in an argon-filled glove box at room temperature.

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