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A polyacetylene derivative with pendant TEMPO group as cathode material for rechargeable batteries

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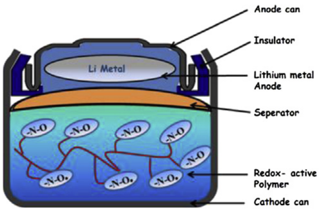
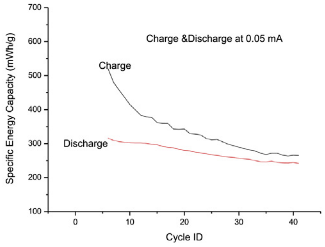
HIGHLIGHTS

- A polyacetylene with pendant TEMPO radical has been used as a cathode active material.
- Graphite-polymer composite material cathode and Li anode have been used.
- The initial specific discharge capacity of the battery is 102.6 mAh g^{-1}.
- The initial specific energy capacity of the battery is 315.9 mWh g^{-1}.
- Battery has retained 77% of its energy capacity after 40 charge–discharge cycles.

GRAPHICAL ABSTRACT





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ABSTRACT

A composite cathode material comprised of a polyacetylene derivative with pendant TEMPO electroactive groups and graphite has been obtained and successfully utilized in a rechargeable battery against a Li anode. The battery has an initial specific discharge capacity of 102.6 mAh/g and an initial specific energy capacity of 315.9 mWh/g. This specific energy capacity is very high compared to today's conventional lithium-ion batteries with cathodes made of $LiFePO_4$, $LiCoO_2$, $LiMnO_2$, etc. The battery has retained 77% of its energy capacity after 40 charge–discharge cycles.

1. Introduction

There is an increasing demand for the development of new and improved rechargeable battery technology in conjunction with today's increasing market demand in portable devices and electric automobiles. In most of the new applications, batteries need to be lighter in weight, to be capable of fast charging, and even to be flexible in addition to having high charge and energy capacities. Most of these characteristics cannot be provided simultaneously by today's conventional rechargeable battery technology which rely on metal based electrodes. The stringent requirements such as moisture and oxygen-free environments, as well as high temperatures required for production of electrode materials make battery production difficult and costly. Polymeric materials offer many advantages over metal based materials such as their ease of

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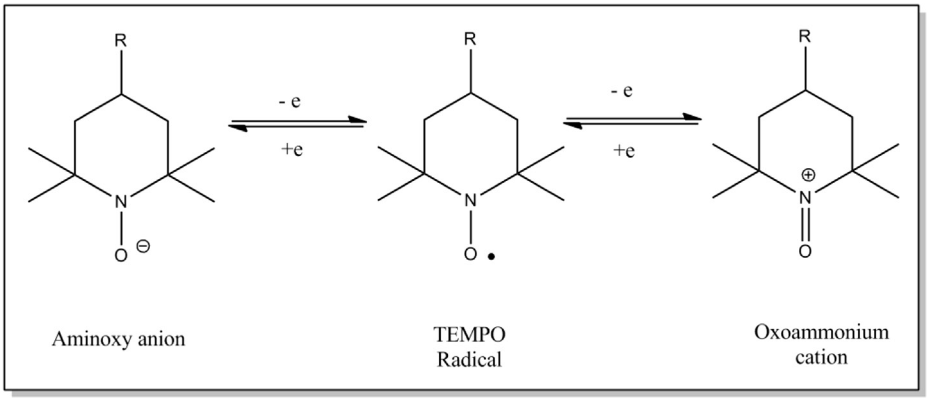

Scheme 1. The two redox couples of TEMPO radical.

production, processibility and tunability of their properties by chemical modification of monomer structures. The concepts of polymer electrodes and polymer batteries have attracted considerable attention after the pioneering discovery of Shirakawa that conjugated polyacetylene (PA) can become conductive when doped [1]. Conducting polymers such as polyacetylene, polythiophene and polyaniline have been investigated as potential electrode materials [2]. Their use in rechargeable batteries has been hampered because they exhibit low doping levels (leading to lower capacities) and slow electrode kinetics (which limit their charge–discharge rates). As an alternative, redox polymers with pendant electro-active functional groups which can be reversibly oxidized or reduced may be used as electrode materials. Here, the redox centers, not the polymer backbone, govern the redox behavior. However, in conjugated polymers with optional groups (substituents) attached to their backbone the spectrum of redox states offered by the polymer chain may merely be modified. Ferrocene (Fc) [6–8], carbazole groups (Cz) [9,10], tetrathiafulvalene (TTF) [3], triphenylamine (TPA) [11,12], polyoxyphenazine, and the adduct-forming polyamides and polyvinyl polymers are the general types of redox polymers. Conductivity arises when these centers can exchange charge, e.g., on account of mixed valency [3–5]. A different example of redox active functional groups is the nitroxide radical. Among nitroxides, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) is known to be a very robust radical and therefore has been chosen as the first electro-active pendant functional group to be used in redox polymers. TEMPO radical has two redox couples, as shown in Scheme 1, which makes it even more attractive since this gives it a propensity to be used both as an n-type (anode) material and as a p-type (cathode) material. The first attempt on the use of an organic radical as an electrode-active group for charge storage in a lithium battery was made by Nakahara's group in 2002 [13]. Polymers with pendant nitroxide radicals have been successfully utilized as cathode materials recently [14–17].

PA has been extensively studied and it has been used in a variety of battery types. Since PA can be both n-doped and p-doped, it can be used as the anode or cathode material [18–23]. Test cells using PA can exhibit specific charge densities in the range of 100–300 mAh/g. The specific energy for PA-based electrodes ranges from about 100 to 300 mWh/g. The open circuit voltage (OCV) of cells using PA as cathode depends on the counter ion. Cells using PA as the cathode and Li as the anode are generally expected to have an OCV between 3.5 and 3.9 V [24,25]. When both electrodes are PA in a cell and Li^+ is used as the counter ion at the anode, the OCV is stable at ca. 3.5 V. However, it drops significantly to ca. 2.5 V when tetrabutylammonium (Bu_4N^+) is used instead of Li^+ as the counter ion [26–28]. Although there have been extensive studies on utilization of PA in batteries in the past, there has been a only very limited amount of work on this subject recently, possibly due to stability issues and processing difficulties. However, there have been recently some important reports of cathode materials made of derivatives of PA with pendant nitroxide groups. Masuda and Katsumata reported synthesis of TEMPO and 2,2,5,5-tetramethyl-1-pyrrolidinyloxy (PROXYL)-carrying polyacetylenes by direct polymerization of TEMPO containing acetylenes with a rhodium-based transition metal catalyst [29–31]. These nitroxide radical containing PAs displayed reversible charge–discharge processes when cycled in a voltage range of 2.5–4.2 V, with capacities varying between 66 and 112 mAh/g (higher capacities obtained for PA with monomer units carrying more than one TEMPO radical unit or smaller sized PROXYL unit). Large majority of them showed a promising cycle life, that is, the capacity hardly deteriorated even after 100 cycles. Most of these polymers have displayed a gradual reduction in their discharge capacities as current densities withdrawn from batteries have been increased, presumably due to polarization effects.

In this study, we have demonstrated the use of a novel PA derivative with a pendant TEMPO radical group as a cathode active material in a rechargeable battery. The battery had an initial specific discharge capacity of 102.6 mAh/g and a specific energy capacity of 315.9 mAh/g when discharged at the rate of 0.3 C.

2. Experimental

2.1. Chemicals

All chemicals purchased were used as supplied without further purification unless stated otherwise. Solvents used for reactions

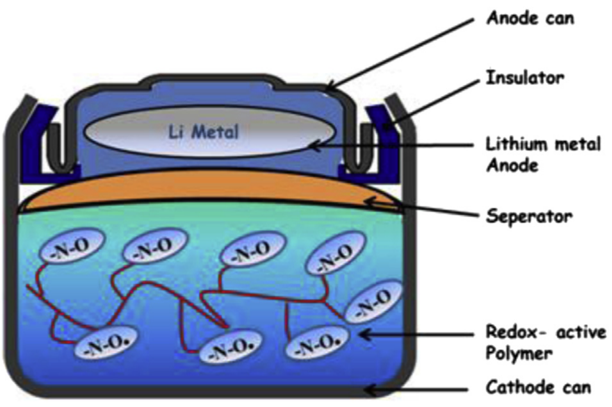

Fig. 1. Cell construction.