Short communication

Synthesis and evaluation of polythiocyanogen (SCN)$_x$ as a rechargeable lithium-ion battery electrode material

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ABSTRACT

Polythiocyanogen, (SCN)$_x$, is a promising lithium-ion battery electrode material due to its high theoretical capacity (462 mAh g^{-1}), safe operation, inexpensive raw materials, and a simple and less energy-intensive manufacturing process. The (SCN)$_x$ was prepared from the solution of trithiocyanate (SCN)$_3^-$ in methylene dichloride (MDC), which was prepared by electrochemical oxidation of ammonium thiocyanate (NH$_4$SCN) in a two-phase electrolysis medium of 1.0 M NH$_4$SCN in 0.50 M H$_2$SO$_4$ + MDC. The (SCN)$_3^-$ underwent auto catalytic polymerization to (SCN)$_x$ during MDC removal. Battery electrodes with (SCN)$_x$ as the active material were prepared, and tested in Swagelok cells using lithium foil as the counter and reference electrode. The cells delivered capacities in the range of 200–275 mAh g^{-1} at the discharge–charge rate of 0.2 C. The cells were tested up to 20 cycles and showed repeatable performance with a coulombic efficiency of 97% at the 20th cycle. The results presented here indicate that (SCN)$_x$ is a promising lithium-ion battery electrode-material candidate for further studies.

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1. Introduction

Lithium ion battery (LIB) technology has advanced along with the growth of the consumer electronic market and rechargeable LIBs are the most popular choice to power devices such as laptops, cell phones, and cameras [1,2]. Moreover, LIBs are now being considered as "green power sources" for automobiles to replace internal combustion engines, mainly to abate global warming by reducing carbon emissions. In current LIBs, graphite is used as the negative electrode and layered lithium metal oxides such as LiCoO$_2$, LiCo$_{0.15}$Ni$_{0.80}$Al$_{0.05}$O$_2$, manganese spinel oxide LiMn$_2$O$_4$, or Olivine-phase lithium iron phosphate (LiFePO$_4$) are used as the positive electrodes [3]. The graphite anode has a theoretical charge–discharge capacity of 372 mAh g^{-1}, and the above-mentioned cathodes have capacities in the range of 150–200 mAh g^{-1} [1–3]. The LIB electrodes are manufactured by energy-intensive ceramic manufacturing processes [4,5]. Lithium insertion potential of the negative electrode is close to that of lithium plating potential, hence, during low-temperature; high-current charging, lithium metal may get plated on the surface of the graphite anode leading to safety issues [6]. In addition, the graphite anode has low volumetric energy density. The layered-oxide positive electrodes, apart from having low capacity, are also the sites of thermal runaway reactions during accidental overcharge [7]. Hence, there is a need for safe, inexpensive, high-capacity LIB electrode materials so that LIBs can compete with traditional power sources in various applications [8,9].

Since lithium (Li) is a versatile element that reacts with a diverse group of elements and their compounds, a large array of new materials are being developed as high-capacity, safe, and inexpensive LIB electrode materials. Some of the materials being investigated include Si [10] and SnO$_2$ [11] as negative electrode materials, sulfur [12] as a positive electrode material, and conducting polymers [13] and organic materials [14–19] as both positive and negative electrode materials. Organic molecules are attractive candidates for LIB electrodes since organic chemical manufacturing processes are well developed and can be easily scaled-up to high volume with better process controls. Organic compounds that include the disulfide (–S–S–) bond in their structure undergo reversible 2e$^-$ reduction of disulfide bond breakage and its reformation during the charge–discharge process in a LIB, and could therefore serve as the electrode in a rechargeable LIB. They are being extensively explored as LIB electrode materials as they are incombustible and have high theoretical capacities [14–19]. Since many of the disulfide organics are soluble in the LIB electrolyte, they are normally used in the form of polymers [14–19]. A large number of compounds have been studied and impressive capacities in the range of 170–400 mAh g^{-1} have been reported.

$$-S–S- \underset{-2e^-}{\overset{+2e^-}{\underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}}}} -S^- + -S^-$$
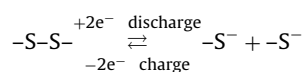
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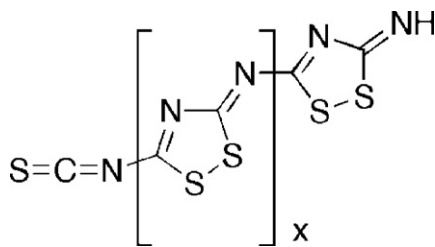
Scheme 1. Structure of polythiocyanogen.

In this paper we introduce a novel inorganic polymer polythiocyanogen, $(SCN)_x$ as the electrode material in a LIB. $(SCN)_x$ is an inexpensive inorganic polymer that has a repetitive –S–S– bond as well as a conjugated electronic structure. Recently, Woolen et al. [20] have confirmed that $(SCN)_x$ is a conjugated polymer of 1,2,4-dithiazole rings linked by nitrogen bridges (Scheme 1). $(SCN)_x$ can be prepared in a single step by chemical oxidation of thiocyanate (SCN^-) anion using Cl_2 or Br_2 as the oxidizing agents, or by electrochemical oxidation [20,21]. The application of $(SCN)_x$ as a semiconductor solar cell electrode material [22], and as a photocatalyst [23] has been studied. However, the application of $(SCN)_x$ as a LIB electrode material has not been explored. $(SCN)_x$ is an attractive LIB electrode material due to its high theoretical capacity of 462 mAh g^{-1}, inexpensive raw materials and simple preparation procedure. In this communication, studies on the application of $(SCN)_x$ as a LIB electrode material are presented for the first time.

2. Experimental

2.1. Materials

Ammonium thiocyanate (NH_4SCN, 99.0%), sulfuric acid (H_2SO_4, 99.50%), methylene dichloride (CH_2Cl_2, 99.0%) polyvinylidene fluoride (PVDF, 99.50%), N-methylpyrrolidone (NMP, 99.50%), copper foil (thickness 25 μm), aluminum foil (thickness 50 μm), all from Sigma Aldrich USA, super-P® conductive carbon from Timcal, lithium foil (thickness 750 μm) from Alfa Aesar USA were used as-received.

2.2. Preparation of $(SCN)_x$

$(SCN)_3{}^-$ was prepared by an electrochemical method reported earlier [21]. Briefly, 65 ml of 1.0 M NH_4SCN in 0.5 M H_2SO_4 + 65 ml MDC were taken in a 200 ml beaker-type electrochemical cell. Two graphite rods (1.0 cm diameter, and 4.0 cm long) were used as the working as well as the counter electrodes. Constant-current electrolysis was carried out at the current density of 25 mA cm^{-2} for 3.0 h at 2 °C by keeping the electrochemical cell in a constant temperature bath. After the electrolysis, organic phase (MDC) was separated from the aqueous phase in a separating funnel, and dried over anhydrous sodium sulfate. The clear solution of $(SCN)_3{}^-$ in MDC was transferred to a rotary vacuum evaporator over a water bath at 50 °C. When all the solvent was evaporated, $(SCN)_3{}^-$ instantly polymerized into an orange-red solid. The solid was scraped from the evaporating flask, dried at 110 °C under vacuum, and used in further experiments.

2.3. Characterization

The $(SCN)_x$ was mixed with potassium bromide (KBr) and compressed to make a pellet. A Thermo Nicolet NEXUS 670 FTIR spectrometer was used to record the FTIR spectrum. FT-Raman spectra of the polymers were acquired with a Nicolet Raman 950 using a neodymium-doped yttrium aluminum garnet (Nd:YAG)

laser operating at 1064 nm. For each sample, duplicate spectra were acquired with multiple scans at a spectral resolution of 8 cm^{-1}. The surface morphology of $(SCN)_x$ powder was examined by scanning electron microscope (SEM), JSM-7400 from JOEL Ltd., Japan. To examine the surface morphology, a pinch of the $(SCN)_x$ powder was adhered on to the SEM sample holder using double-sided tape and a thin layer of Au–Pd was sputtered before observation.

2.4. Electrochemical studies

A paste was prepared by mixing the $(SCN)_x$ active material, polyvinylidine fluoride as binder, and super-P® carbon conducting additive in the wt% ratio of 60:10:30, unless or otherwise mentioned, using N-methylpyrrolidine as the solvent for use as the electrode coating. The paste was coated on copper and aluminum foil current collectors. The active material loading was 4–5 mg cm^{-2}. The electrolyte was 1.0 M LiPF$_6$ in a (1:1, wt%) mixture of ethylene carbonate and dimethyl carbonate (Novolyte, USA). The Swagelok cell (Hockson, Japan) was assembled with a lithium-foil counter electrode and a Celgard 2400 (Cellgard Corporation, USA) separator inside a helium-filled glove-box. The cells were discharged and charged between fixed voltages vs. Li/Li$^+$ reference electrode using a VERSASTAT3 potentiostat/galvanostat from Princeton Applied Research (USA). All the reported voltages are with respect to Li/Li$^+$ reference electrode.

3. Results and discussion

The FTIR spectrum of the prepared $(SCN)_x$ is plotted in Fig. 1(a). The spectrum shows one very broad band in the range of 950–1300 cm^{-1}, and many small overlying shoulders. The spectrum exactly matches the FTIR spectrum reported for $(SCN)_x$ in the literature [24,25]. The strong, broad band around 1200 cm^{-1} is the confirmation of $(SCN)_x$, the shoulder at 1520 cm^{-1} is due to =C=N– conjugated vibration, and signals at 1620–1640 cm^{-1} are due to symmetric and asymmetric stretching of the =C=N– group [24,25]. Hence, the FTIR spectrum confirms that the $(SCN)_x$ prepared in this work is similar to that reported earlier by other researchers. The FT-Raman spectrum of $(SCN)_x$ is given in Fig. 1(b). The FT-Raman spectrum nicely matches with the one reported by Woolen et al. [20]. They have assigned the peaks in the 400–480 cm^{-1} to –S–S– vibrations and the peak at 650 cm^{-1} to C–S– vibrations. They have also reported that the FT-Raman spectrum of the $(SCN)_x$ is different from linear $S_n(CN)_2$ molecules and closely matches with that of the 1,2,4-thiadiazole compounds. The SEM micrographs at two magnifications are shown in Fig. 2. The $(SCN)_x$ in the micrograph show a fluffy film-type morphology; the $(SCN)_x$ is amorphous in nature and totally agglomerated. The agglomerated morphology is probably due to strong aggregation in $(SCN)_x$ due to intermolecular interaction between the molecular chains [26].

Cyclic voltammograms (CV) of cells assembled with the bare Al current collector, as well as that of $(SCN)_x$ coated over the Al current collector are given in Fig. 3(a). Large reduction current around 0 V vs. Li/Li$^+$ in the blank voltammogram is due to the formation of Li–Al alloys [27]. However, the current magnitude in the blank voltammogram is negligible when compared with that in the presence of $(SCN)_x$. In the voltammogram of $(SCN)_x$, four oxidation peaks (O_I–O_{IV}) are observed in the 0–4.0 V range during the forward sweep, and the current increases exponentially beyond 4.0 V. During the reverse sweep, a hump at 3.45 V (R_{III}) and a small reduction peak at 2.93 V (R_{II}) are observed. The reduction current slowly increases below 2.50 V, and then increases exponentially below 1.5 V. The large redox currents in the potential range of 0–2.00 V reveal that the –S–S– bonds in the $(SCN)_x$ are electroactive in the above potential range and the $(SCN)_x$ could serve as a potential

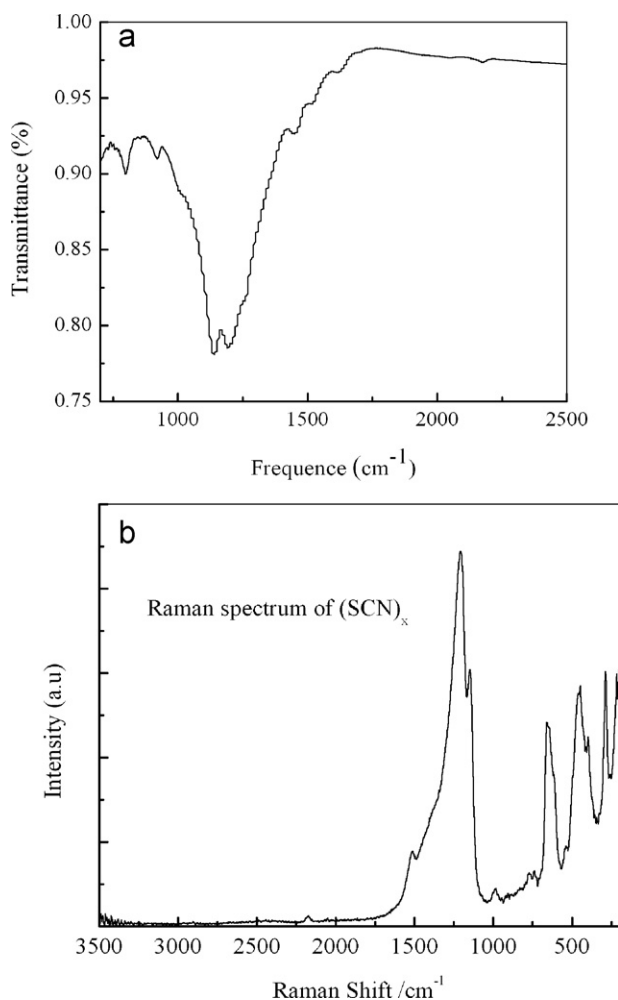**Fig. 1.** (a) FTIR and (b) FT-Raman spectrum of polythiocyanogen $(SCN)_x$.

Fig. 2. SEM micrographs of the prepared polythiocyanogen $(SCN)_x$ at magnifications of (a) 2000, (b) 10,000.

anode material in LIB. This is a very interesting fact since most of the reported –S–S– compounds undergo reduction in the potential range 1.0–2.5 V vs. Li/Li^+ [16–19], and hence were studied as potential cathode materials. Due to the very negative redox potential of the –S–S– bonds, $(SCN)_x$ is an interesting anode material to fabricate high-voltage rechargeable lithium-ion batteries by coupling with high-voltage cathodes such as $LiMn_2O_4$.

We could assign the O_{II}/R_{II} redox couple to the reversible doping and de-doping of the polymer chain by the PF_6^- anion present in the $LiPF_6$ electrolyte. The anion doping of the conjugated conducing polymers like polyaniline is well known [28]. In fact, there are many reports of doping $(SCN)_x$ with iodine (I_2) [22,23]. It has also been reported that I_2 doping leads to increased conductivity of $(SCN)_x$. The oxidation peaks O_{III}, O_{IV} and the exponential increase of oxidation current beyond 4.0 V could be due to the irreversible oxidation of the $(SCN)_x$ polymer. Bowmaker et al. [25] have reported that $(SCN)_x$ undergoes irreversible oxidation resulting in the degradation of the $(SCN)_x$ film at potentials higher than 4.0 V vs. Li/Li^+.

Initial charge–discharge experiments were carried out with the $(SCN)_x$ coated over Al current collector to assess the possibility of using $(SCN)_x$ as LIB cathode material. Since the $(SCN)_x$ polymer has conjugated tertiary nitrogen atoms similar to polyaniline, it should be possible to charge $(SCN)_x$ by anion doping as discussed in ref. [28]. The assembled cells show an open circuit voltage of around 2.4–2.7 V. We were able to repeatedly charge–discharge the cell in the 3.70–2.50 V range, showing that $(SCN)_x$ could also be employed as the cathode. However, the capacities obtained were very low
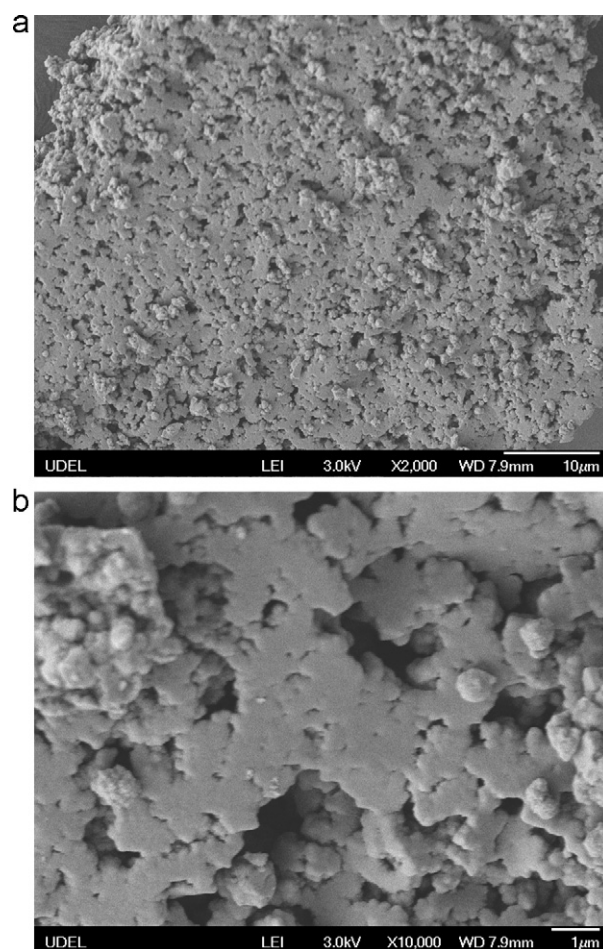
(around 10–15 mAh g^{-1}) hence, it was decided to investigate its suitability as anode in the further experiments using copper as the current collector. The CV of the $(SCN)_x$ coated over Cu current collector in the 0–3.10 V range vs. Li/Li^+ is given in Fig. 3(b). The CV of $(SCN)_x$ on Cu current collector is different from that of $(SCN)_x$ coated over Al current collector (Fig. 3(a)). The reason for the difference is not clear; probably it could be due to the catalytic effect of Cu. With the Cu current collector, the peaks are well resolved especially below 2.0 V. We can identify three reversible couples $(O_I/R_I, O_{II}/R_{II}, O_{III}/R_{III})$ and two irreversible oxidation peaks (O_{IV}, O_V) in the voltammogram. As discussed earlier, the couples O_I/R_I and O_{II}/R_{II} are below 1.5 V, and are due to the reversible formation and reduction of –S–S– bonds in $(SCN)_x$. The couple O_{III}/R_{III} could be due to the reversible doping and de-doping of the PF_6^- anion. The irreversible oxidation peaks O_{IV}, O_V could be due to the oxidation of the $(SCN)_x$ polymer.

Since $(SCN)_x$ is a semiconducting inorganic polymer, sufficient quantity of electrically conducting carbon additives need to be incorporated in the electrode formulation to have the required electrical conductivity in the $(SCN)_x$. electrode so that it could be charged and discharged at a suitable rate without much ohmic resistance. The charge–discharge curves of the $(SCN)_x$ electrodes with 10 wt% super-P® carbon additive are presented in Fig. 4. The observed capacities were very low and the charge–discharge could not be carried out at a reasonable rate. Hence, further experiments were carried out with 30 wt% of super-P® carbon as conductive additive. In the first set, discharge–charge experiments were carried out at the rate of 0.2 C in the 0–3.1 V range
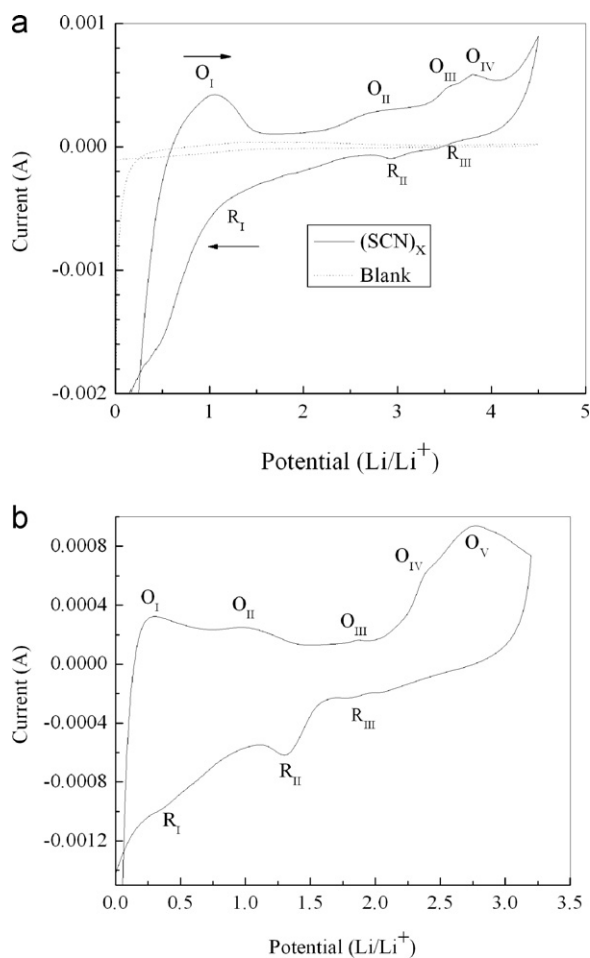
Fig. 3. Cyclic voltammogram of polythiocyanogen $(SCN)_x$. Sweep rate $0.5\,mV\,s^{-1}$ with: (a) aluminum current collector, (b) copper current collector.

vs. Li/Li⁺, the results for 4–8 cycles are given in Fig. 5. The cell delivered capacities in excess of $400\,mAh\,g^{-1}$ during the initial cycles. The discharge–charge capacities for the 4th cycle were 557 and $345\,mAh\,g^{-1}$, respectively. After 8 cycles, the discharge–charge capacities reduced drastically to only 190 and $140\,mAh\,g^{-1}$, respectively. On dismantling the cell, it was observed that the $(SCN)_x$ coating on the Cu current collector had become loose and a black-
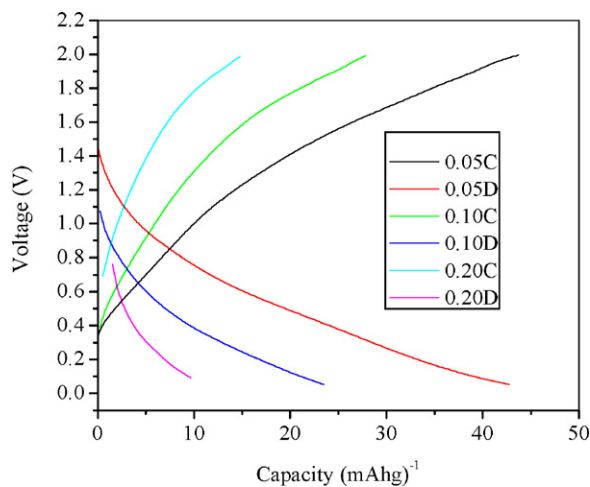

Fig. 4. Charge–discharge curves at different C rates with 10 wt% conductive carbon additive.
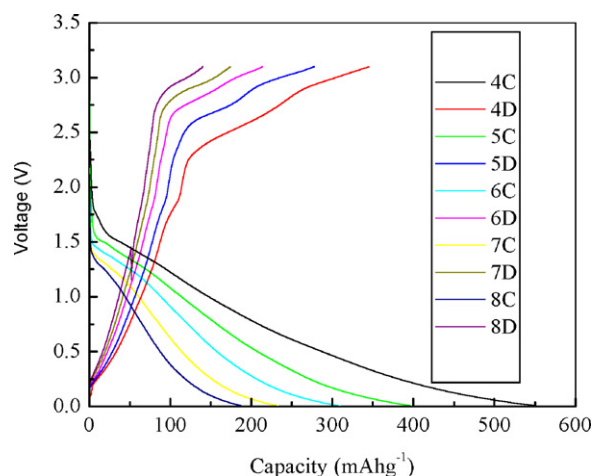
Fig. 5. Charge–discharge curves in the voltage range of 0–3.1 V at 0.2 C. C – charge, D – discharge cycles 4–8.

ish coating had formed on the Li foil counter electrode. These observations led us to conclude that the $(SCN)_x$ might be getting decomposed at potentials higher than 2.0 V during charging. As, mentioned above, the $(SCN)_x$ might be irreversibly oxidizing above 2.0 V (oxidation peaks O_{IV}, O_V observed in Fig. 3(b)).
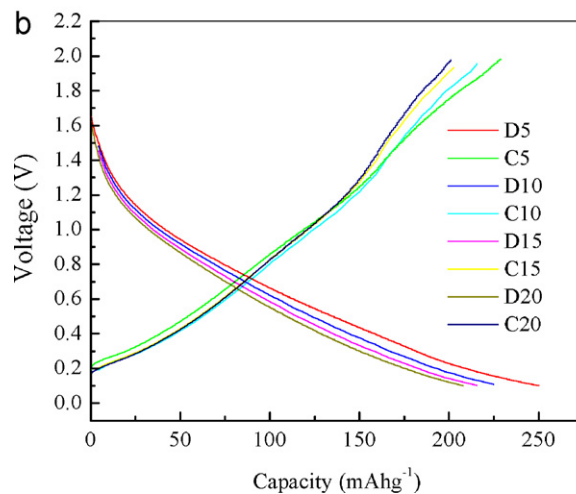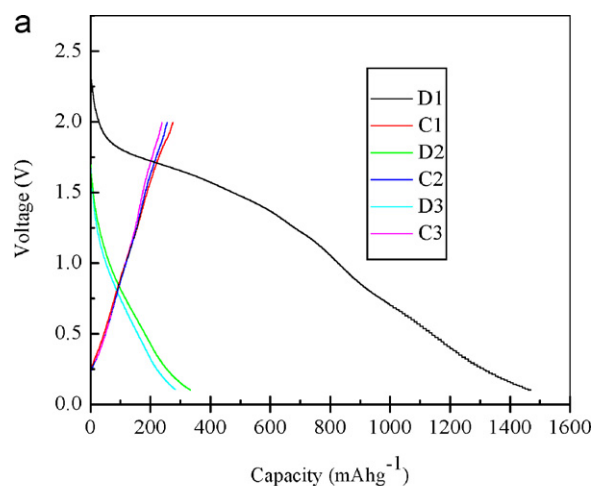
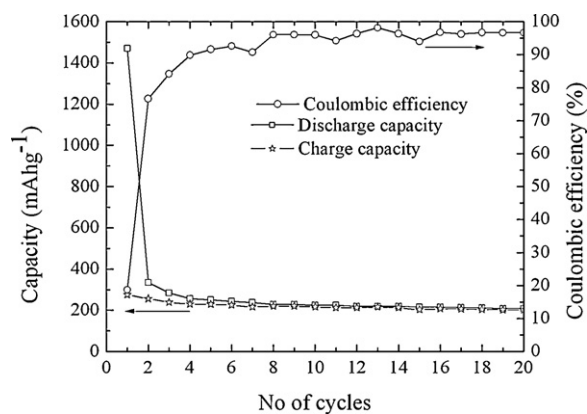**Fig. 6.** Charge–discharge curves at 0.2 C. C – charge, D – discharge cycles: (a) 1–3; (b) 5, 10, 15 and 20.

Fig. 7. Cycling performance and coulombic efficiency at 0.2 C rate.

In order to avoid the decomposition of $(SCN)_x$ on the electrode surface, the voltage range was restricted to 0–2.0 V vs. Li/Li$^+$ in the next set of experiments. The voltage profile vs. capacity for the first three discharge–charge cycles are shown in Fig. 6(a). The large irreversible capacity in the first cycle is due to SEI formation. The coulombic efficiency improved greatly from the second cycle onwards. In the 5th cycle, the discharge–charge capacities were 250 and 229 mAh g^{-1}, respectively. The capacities of 5–20th cycles are plotted in Fig. 6(b). It could be seen that the drop in capacity is very less when compared that observed when the potential range was 0–3.1 V. In fact there is very little drop in performance between 15th and 20th cycles. The cyclic performance along with coulombic efficiency for the 20 cycles is shown in Fig. 7. The discharge–charge capacities at the 20th cycle were 208 and 201 mAh g^{-1}, respectively, with the coulombic efficiency of about 97%. The results show that the $(SCN)_x$ is very stable even after 20 repeated cycles. The initial results presented in this communication have demonstrated that $(SCN)_x$ could be an excellent, inexpensive material for LIB electrodes.

4. Conclusions

The synthesis and evaluation of polythiocyanogen, $(SCN)_x$, as a lithium-ion battery electrode material has been studied for the first time. The redox reactions of the –S–S– bonds in the $(SCN)_x$ occur at negative potentials of 0–1.5 V vs. Li/Li$^+$, and hence $(SCN)_x$ could serve as an inexpensive anode for the fabrication of high-voltage lithium-ion rechargeable batteries. The fabricated cells delivered capacities around 200 mAh g^{-1} after 20 cycles with the coulombic efficiency of 97%. The initial results are very promising for the further development of $(SCN)_x$ as an inexpensive electrode material for rechargeable lithium-ion batteries.

Acknowledgements

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