

Nano-sized carboxylates as anode materials for rechargeable lithium-ion batteries

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Abstract

Nano-sized carboxylates $\text{Na}_2\text{C}_7\text{H}_3\text{NO}_4$ and $\text{Na}_2\text{C}_6\text{H}_2\text{N}_2\text{O}_4$ were prepared and investigated as anode materials for lithium-ion batteries. Both carboxylates exhibit high reversible capacities around 190 mAh/g above a cut-off voltage of 0.8 V vs. Li^+/Li , potentially improving the safety of the batteries. In addition, good rate performance and long cycle life of these carboxylates make them promising candidates as anode materials for lithium-ion batteries.

Key words

carboxylates; $\text{Na}_2\text{C}_7\text{H}_3\text{NO}_4$; $\text{Na}_2\text{C}_6\text{H}_2\text{N}_2\text{O}_4$; anode; lithium-ion batteries

Rechargeable lithium-ion batteries have been widely used in portable electronic devices. To satisfy the coming demand for large scale energy storage in electric vehicles and smart grids, it is urgent to investigate high energy/power density, cost-effective and environmentally friendly electrode materials [1–4]. Organic electrode materials can be made from biomasses or recyclable resources free from expensive elements, and are mostly synthesized via solution phase routes that avoid high-temperature annealing [5–7]. Due to the redox reaction mechanism, theoretical capacities and reaction rates of organic electrodes are sometimes higher than inorganic intercalation electrodes, which endow them with high energy density and power density.

So far, most of the researches on organic electrodes have focused on cathode materials, such as organosulfur compounds [8–11], free radical compounds [12–16], conducting polymers [17–19] and quinone-type carbonyl compounds [20–22]. Their redox potentials are usually above 2 V vs. Li^+/Li . In contrast, there are few reports on organic anode materials, including bipolar conducting polymers [23,24] and conjugated carboxylates [25–27]. The low operating potential of conventional carbon-based anodes may lead to safety issues during overcharge or fast charge [1,28]; therefore anode materials with relatively high potential are needed to avoid the growth of solid electrolyte interphase (SEI) layer and the use of expensive copper current collector. The properties of

organics can be rationally tuned using the well-established principles of organic chemistry, and predicted by calculation based on molecular models [29], thus making them promising candidates for lithium-ion batteries. Among the organic anode materials, conjugated carboxylates show low solubility in liquid electrolyte derived from coordination bonding between metal and oxygen and with proper potential around 1 V vs. Li^+/Li , therefore attracting considerable interest.

In this contribution, two nano-sized carboxylate-based organic materials, disodium 2,5-pyridinedicarboxylate ($\text{Na}_2\text{C}_7\text{H}_3\text{NO}_4$) and disodium 2,5-pyrazinedicarboxylate ($\text{Na}_2\text{C}_6\text{H}_2\text{N}_2\text{O}_4$), are introduced as novel anode materials for lithium-ion batteries. It was found that these carboxylates exhibited high reversible capacities around 190 $\text{mAh}\cdot\text{g}^{-1}$ above a cut-off voltage of 0.8 V vs. Li^+/Li . Besides, the rate performance and cycleability of the two carboxylates were excellent, the $\text{Na}_2\text{C}_7\text{H}_3\text{NO}_4$ electrode delivered a capacity of 168 $\text{mAh}\cdot\text{g}^{-1}$ after 20 cycles at a current rate of 2 C, while a capacity of 180 $\text{mAh}\cdot\text{g}^{-1}$ was obtained for the $\text{Na}_2\text{C}_6\text{H}_2\text{N}_2\text{O}_4$ electrode after 200 cycles at 0.1 C.

The $\text{Na}_2\text{C}_7\text{H}_3\text{NO}_4$ sample was prepared by a liquid-phase reaction between 2,5-pyridinedicarboxylic acid ($\text{C}_7\text{H}_5\text{NO}_4$) and NaOH. NaOH (0.168 g, 4.2 mmol) was dissolved in ethanol (20 mL), and then the solution was slowly injected into a DMSO solution (100 mL) dissolved $\text{C}_7\text{H}_5\text{NO}_4$ (0.3342 g, 2 mmol). White precipitates were obtained and

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then separated out by centrifugation. The as-obtained solid was washed by ethanol and water, and then dried at 60 °C for 12 h. The synthesis process of $\text{Na}_2\text{C}_6\text{H}_2\text{N}_2\text{O}_4$ was similar to that described above, and was carried out by a reaction between 2, 5-pyrazinedicarboxylic acid dehydrate ($\text{C}_6\text{H}_2\text{N}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and NaOH.

Powder X-ray diffraction data were collected on an Bruker D8 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5405 \text{ \AA}$) in the scan range of 5°–60°. The particle sizes were measured by scanning electron microscopy (Hitachi S-4800). Fourier transform infrared spectroscopy measurements were performed on a Bruker Tensor 27 Spectrometer using KBr pellets. The C/Na ratios of the samples were measured by inductively coupled plasma.

Electrochemical studies were performed in swagelok type cells. The cells were assembled in an argon filled glove-box. Electrodes were fabricated by intimately mixing the active material (60 wt%) with the polyvinylidene difluoride binder (10 wt%) and acetylene black (30 wt%) in a 1-methyl-2-pyrrolidinone (NMP) solvent. The mixed slurry was cast onto a copper foil current collector and dried in air at 50 °C for 5 h and dried at 100 °C under vacuum over night. Lithium metal was used as the negative electrode and 1 mol/L LiPF_6 in EC/DMC = 1/1 (in volume) was used as the electrolyte.

Electrochemical measurements were carried out using a Land BT2000 battery test system (Wuhan, China) at room temperature. To examine the electrochemical reaction of the cells, cyclic voltammetry was performed on a CHI600D Electrochemical Workshop (Shanghai, China) at a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$.

X-ray diffraction (XRD) powder patterns collected for $\text{Na}_2\text{C}_7\text{H}_3\text{NO}_4$ and $\text{Na}_2\text{C}_6\text{H}_2\text{N}_2\text{O}_4$ samples shown in Figure 1 are similar to disodium terephthalate [30], especially the position and relative intensity of the peaks at 9.3° and 16.9°, suggesting the similarity in crystal structure between these carboxylates. The wide full widths at half-maximum of the two spectra impede further structure refinement. According to the definitive structure of disodium terephthalate, they may crystallize in $\text{Pbc}2_1$ and the planar aromatic ring packing resembles the β packing of hydrocarbons with Na in trigonal prismatic positions. The scanning electron microscopy (SEM) images shown in Figure 1 reveal that the average size of both the $\text{Na}_2\text{C}_7\text{H}_3\text{NO}_4$ and $\text{Na}_2\text{C}_6\text{H}_2\text{N}_2\text{O}_4$ samples is 50 nm, which is much smaller than the carboxylates synthesized by other methods reported before [25]. The nanometer particle sizes are in good agreement with the wider peak widths in their XRD patterns.

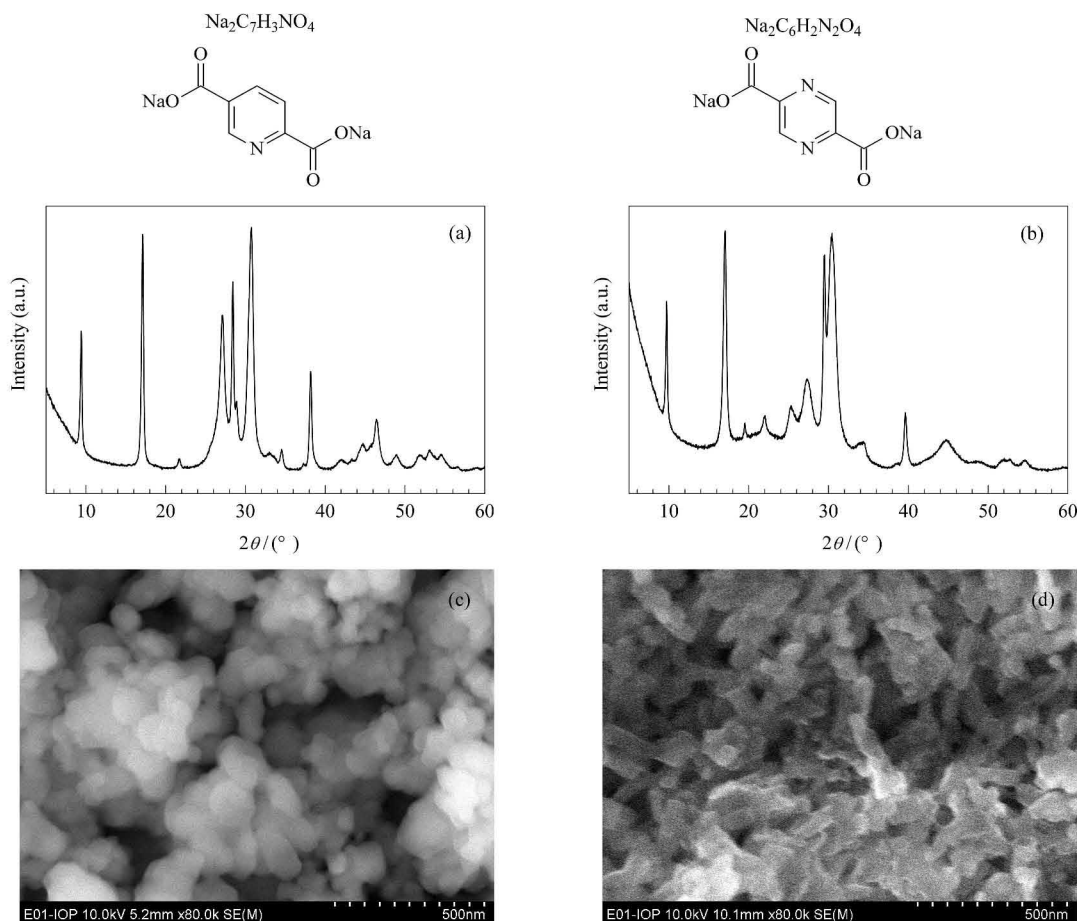


Figure 1. Chemical structures and XRD patterns of $\text{Na}_2\text{C}_7\text{H}_3\text{NO}_4$ (a) and $\text{Na}_2\text{C}_6\text{H}_2\text{N}_2\text{O}_4$ (b) samples, and SEM images of $\text{Na}_2\text{C}_7\text{H}_3\text{NO}_4$ (c) and $\text{Na}_2\text{C}_6\text{H}_2\text{N}_2\text{O}_4$ (d) samples

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