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The disodium salt of 2,5-dihydroxy-1,4-benzoquinone as anode material for rechargeable sodium ion batteries†

Zhiqiang Zhu, Hao Li, Jing Liang, Zhanliang Tao and Jun Chen*

The disodium salt of 2,5-dihydroxy-1,4-benzoquinone has been prepared and proposed as anode material for rechargeable sodium ion batteries for the first time, showing an average operation voltage of ∼1.2 V, a reversible capacity of ∼265 mA h g^{-1}, a long cycle life (300 cycles), and high rate capability.
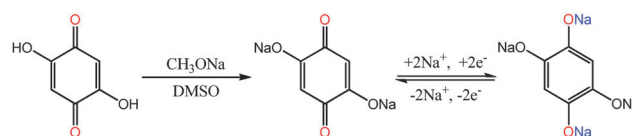
Lithium ion batteries (LIBs) indeed represent the state-of-the-art battery systems,[1,2] but developing sodium ion batteries (SIBs) have recently captured much research interest because of the natural abundance and the low cost of sodium.[3–5] So far, the investigation of electrode materials for SIBs is mainly focused on transition-metal inorganic compounds[6–8] or alloy-based materials,[9–11] which are synthesized from limited resources and thus give rise to the problem of cost and availability concerns. In contrast, organic materials without expensive elements are potential low cost and sustainable electrodes.[12–16] In this regard, various electrochemical dopable polymers have been studied for SIBs and gained recent achievements.[17,18] The energy density of these materials is limited by doping levels as well as the anion–cation doping–de-doping mechanism which requires a large excess of electrolytes.[19] Meanwhile, organic carbonyl compounds are also attractive electrodes because of their processability, redox stability, structural diversity, and high theoretical capacities.[20–23] Like in LIBs, most organic carbonyl compounds are designed for cathode application, such as $Na_2C_6O_6$,[24] indigo carmine,[25] 3,4,9,10-perylene-tetracarboxylicacid-dianhydride (PTCDA),[26] and a series of dianhydride-based poly-imides.[27] In comparison, only a few organic carbonyl compounds are suitable candidates for anode materials.[28] For example, sodium terephthalate and its derivatives have been proposed as anodes for SIBs,[29–31] showing cycle life up to 100 cycles with reversible capacity in the range of 170–300 mA h g^{-1}. More recently, the

sodiation–desodiation behaviour of a graphene oxide wrapped croconic acid disodium salt has also been tested.[32] It rendered an initial capacity of ∼290 mA h g^{-1} with ∼45% capacity retention after 100 cycles at a current density of 20 mA g^{-1}. Therefore, exploiting new carbonyl compound anode material is still needed.

In 2008, a dilithiated 2,5-dihydroxy-1,4-benzoquinone (Li_2DBQ) based coordination polymer was reported as cathode material for LIBs with an average potential of ∼1.65 V (*vs.* Li^+/Li).[33] As the redox potential of Na/Na$^+$ (−2.71 V *vs.* SHE) is higher than that of Li analogues (−3.04 V *vs.* SHE), the sodium derivative Na_2DBQ should possess lower operation potential (*vs.* Na/Na$^+$), which might make it a suitable anode for SIBs. Moreover, it could also offer good stability due to its highly ionic nature.[13] Herein, we firstly reported the application of Na_2DBQ as an electrode for SIBs. The as-prepared Na_2DBQ exhibits high reversible capacity (265 mA h g^{-1}) with an average storage voltage of ∼1.2 V (*vs.* Na$^+$/Na). Furthermore, Na_2DBQ also demonstrates high cyclability up to 300 cycles and high rate capability up to 5 C, rendering it a promising anode for SIBs.

Na_2DBQ was synthesized through a simple one-pot reaction of H_2DBQ with sodium methylate in dimethyl sulfoxide (DMSO) solution (left part of Scheme 1, see details in the ESI†). The raw material of H_2DBQ is commercial available. The products were characterized by NMR (Fig. S1, ESI†), FTIR (Fig. S2, ESI†), and elemental analysis, all confirming the successful synthesis of the target Na_2DBQ.

The resulting Na_2DBQ is in the form of dull red powder and exhibits irregular morphology with an average size in the sub-micron range as observed in the scanning electron microscope (SEM) image (Fig. 1a). The BET specific surface area of Na_2DBQ

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin, 300071, People's Republic of China. E-mail: chenabc@nankai.edu.cn; Fax: +86-22-23509571; Tel: +86-22-23506808
† Electronic supplementary information (ESI) available: The synthetic procedure of Na_2DBQ, ^{1}H NMR spectrum, FTIR spectrum, and elemental analysis of prepared Na_2DBQ. See DOI: 10.1039/c4cc08220f
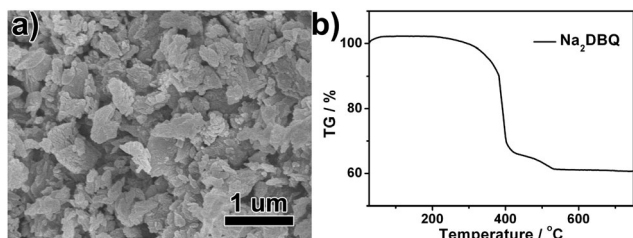

Scheme 1 The synthetic route (left part) and the proposed electrochemical redox mechanism (right part) of Na_2DBQ.

Fig. 1 (a) SEM image (b) and the TG curve of prepared Na_2DBQ.

was 27.2 m^2 g^{-1} (Fig. S3, ESI†), which is favorable for the electrode–electrolyte contact. Also, the small particle size could shorten the ion diffusion path and thus help to achieve high rate performance. In addition, thermogravimetric (TG) analysis of Na_2DBQ demonstrates that no obvious mass loss is observed up to around 255 °C (Fig. 1b). Thermal stability is acceptable for practical application concerning the safety issue.[34]

Na_2DBQ contains two carbonyl groups as redox centers and can afford a high theoretical capacity of 291 mA h g^{-1} through reversible uptake of two sodium ions per formula unit (right part of Scheme 1). On the other hand, because of the ionic nature of Na_2DBQ, the dissolution issue of low molecular organic compounds is expected to be restrained.[35] To prove this concept, the electrochemical performance of Na_2DBQ was evaluated using CR2032 coin-type half cells with sodium foil as a counter electrode. The working electrodes consist of Na_2DBQ (60 wt%), conductive carbon (30 wt%), and the PVdF binder (10 wt%). The mass loading of the active material on the electrode is about 1.2 mg cm^{-2}. The thickness of the electrode is about 20 μm (Fig. S4, ESI†). The electrolyte was 1 M $NaClO_4$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). Glass fiber was used as an electrolyte. The cell was cycled in the voltage window of 0.5–2.5 V. The specific capacity values are calculated on the basis of the mass of the active materials.

Fig. 2a shows the initial three discharge–charge profiles of the assembled cell at a 0.1 C rate (1 C = 291 mA h g^{-1}). The first discharge curve exhibits a long plateau at about 1.22 V, giving an initial discharge capacity of 398 mA h g^{-1}. However, only 67% of the capacity is reversible. Meanwhile, the discharge curves changed significantly in the following cycle, showing two plateaus at ~1.28 and ~1.20 V, respectively. This is indicative of an activation process associated with the large volume expansion during the first sodiation. Such a phenomenon shows the results of some organic electrodes with large volume changes such as croconic acid.[32] The two discharge plateaus in the subsequent cycles should correspond to a two-step 2e$^-$ reduction reaction of the quinonoid carbonyl groups, accompanied by the insertion of Na^+ into Na_2DBQ. Moreover, these two processes are reversible in the charge process. Two distinct plateaus located at 1.28 and 1.59 V can be clearly seen in the charge curves. The shape of the voltage profiles remained nearly unchanged after the first cycle, demonstrating good redox reversibility. The reversible reaction is further confirmed by the cyclic voltammetry as shown in Fig. S5 (ESI†). Note that the capacity of the second cycle reaches
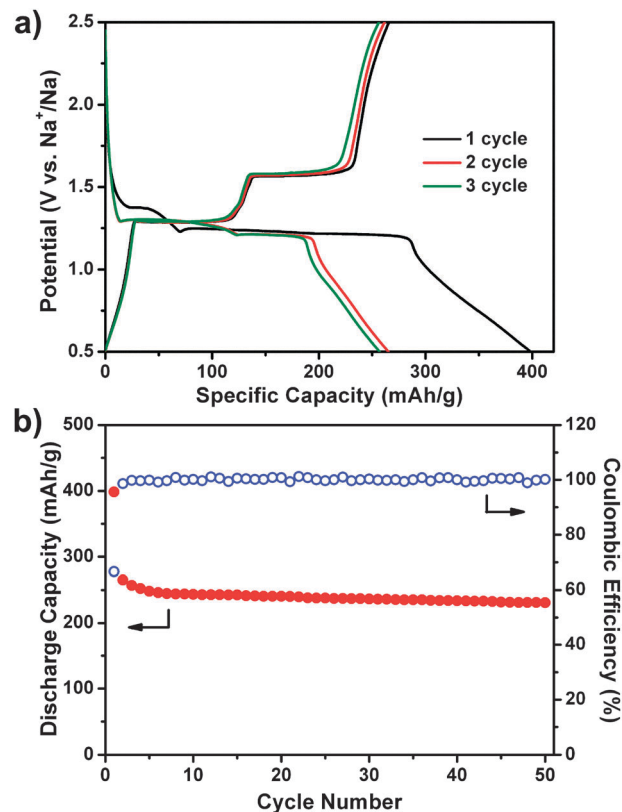

Fig. 2 (a) Initial three voltage profiles and (b) cycling performance of Na_2DBQ in the voltage range of 0.5–2.5 V at a 0.1 C rate.

265 mA h g^{-1}, which is comparable with previous proposed carbonyl-based anode materials.[29–32] Furthermore, the Na_2DBQ electrode can offer satisfactory cycle performance. The capacity remained at 231 mA h g^{-1} after 50 cycles. Thus, the capacity retention reaches 87% from the second cycle to the fiftieth cycle. The good cycle stability is benefited from the increased polarities through salt formation which can effectively suppress dissolution.[13] Additionally, the coulombic efficiency quickly increased to 99% after initial few cycles, even though it was relatively low at the first cycle. It should be pointed out that a very recent work demonstrated that polymerization of an organic salt could completely prevent the active material from dissolving.[23] It is believed that this strategy should also be very useful for further increasing the cycling stability of Na_2DBQ.

The rate performance of Na_2DBQ was also investigated. Fig. 3a presents the typical discharge and charge profiles of Na_2DBQ at various current densities. At a 0.1 C rate, the obtained capacity reaches 265 mA h g^{-1}. When the current density became 10 times higher (1 C), a specific capacity of 248 mA h g^{-1} can still be achieved with small polarization. Even at a rate of 5 C, 60% of the capacity delivered at 0.1 C can be realized. The good rate capability should be ascribed to the large surface area and short ion diffusion length provided by the small Na_2DBQ particles. Furthermore, organic molecules usually possess less rigid crystal structure compared to inorganic compounds, thus favoring Na^+ insertion–deinsertion.[30] As a result, Na_2DBQ can operate at high current
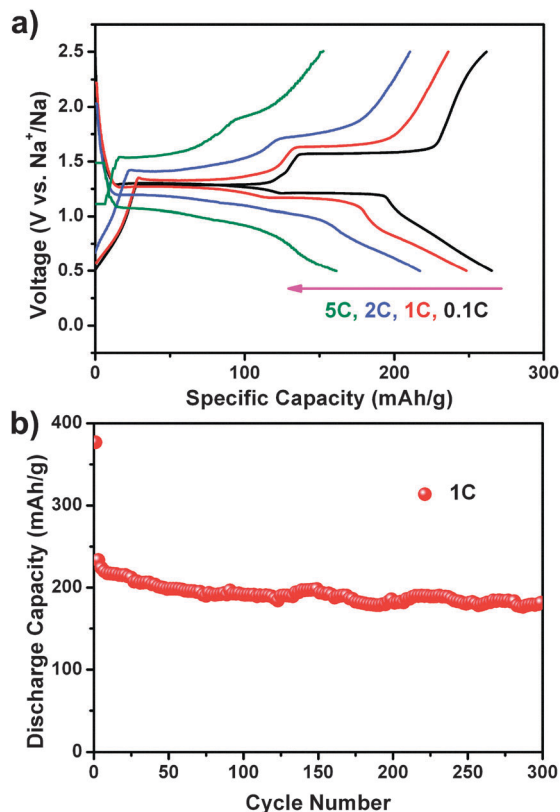
Fig. 3 (a) Typical discharge and charge profiles of Na_2DBQ at various current densities. (b) Cycle performance of Na_2DBQ at a 1 C rate.

density for long-term cycling. As shown in Fig. 3b, after the first activation process, Na_2DBQ can preserve 81% of the capacity from the 2nd cycle (236 mA h g^{-1}) to the 100th cycle (192 mA h g^{-1}). Remarkably, the capacity can remain at 181 mA h g^{-1} even after 300 cycles.

Na_2DBQ in addition to exhibiting relatively high voltage as anode material, which would result in low energy density in full cells, shows high capacity, good cyclability and high rate capability. It should be pointed out that no extra treatment such as surface modification[29,32] is needed to gain the present electrode performance. More importantly, Na_2DBQ possesses advantages of low cost, renewability, and environmentally-benign synthesis. Therefore, Na_2DBQ holds promise as anode material for SIBs.

In summary, the disodium salt of 2,5-dihydroxy-1,4-benzo-quinone was prepared through a simple one-pot solution method using commercial available raw materials and found to be suitable as anode material for SIBs for the first time. Without any modification, Na_2DBQ can operate at an average discharge voltage of ∼1.2 V with good electrochemical performance, including high capacity (∼265 mA h g^{-1} at 0.1 C), a long cycle life (up to 300 cycles at 1 C), and high rate capability (160 mA h g^{-1} at a 5 C rate). These results shed light on the application of organic carbonyl compounds as electrode materials for SIBs.

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