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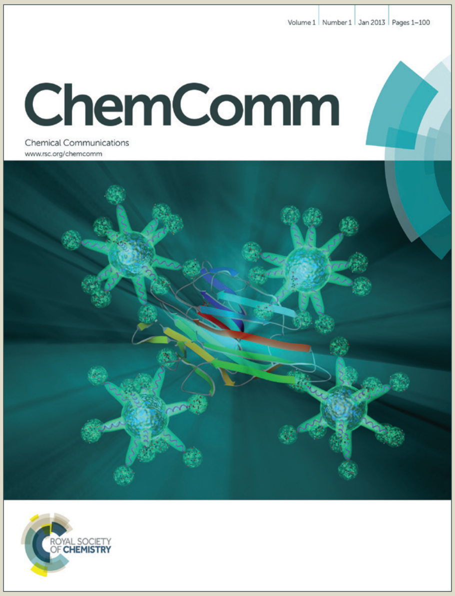

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ARTICLE TYPE

Disodium Salt of 2,5-dihydroxy-1,4-benzoquinone as Anode Material for Rechargeable Sodium Ion Batteries

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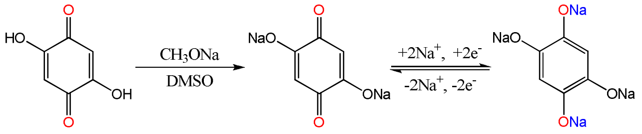
Disodium salt of 2,5-dihydroxy-1,4-benzoquinone has been prepared and proposed as anode material for rechargeable sodium ion batteries for the first time, showing an average operation voltage of ~1.2 V, reversible capacity of ~265 mAh g^{-1}, long cycle life (300 cycles), and high rate capability.

Lithium ion batteries (LIBs) have indeed represented the state-of-the-art battery system,[1,2] but developing sodium ion batteries (SIBs) have recently captured much research interest because of the natural abundance and 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, structure 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 polyimides.[27] In comparison, only few organic carbonyl compounds are suitable candidates for anode materials.[28] For example, sodium terephthalate and its derivatives have been proposed as anode for SIBs,[29–31] showing cycle life up to 100 cycles with reversible capacity in the range of 170-300 mAh g^{-1}. More recently, the sodiation/desodiation behaviour of graphene oxide wrapped croconic acid disodium salt has also been tested.[32] It rendered an initial capacity of ~290 mAh 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, 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 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 electrode for SIBs. The as-prepared Na_2DBQ exhibits high reversible capacity (265 mAh 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 5C, rendering it 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 Supporting Information). The raw material of H_2DBQ is commercial available. The products were characterized by NMR (Fig. S1), FTIR (Fig. S2), and elemental analysis, all confirming the successful synthesis of the target Na_2DBQ.



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

The resulting Na_2DBQ is in the form of dull red powders and exhibits irregular morphology with average size in submicron range as observed in the scanning electron microscope (SEM) image (Fig. 1a). The BET specific surface area of Na_2DBQ was 27.2 m^2/g (Fig. S3), which is favorable toward 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). The thermal stability is acceptable for practical application concerning the safety issue.[34]

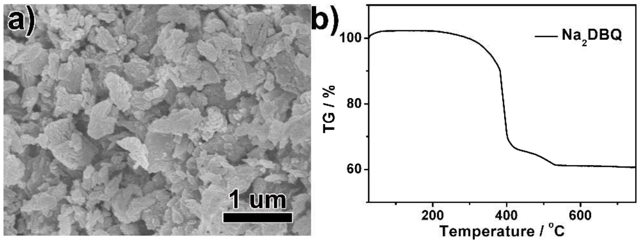


Fig. 1 (a) SEM image (b) and TG curve of prepared Na_2DBQ.

Na_2DBQ contains two carbonyl groups as redox centers and can afford a high theoretical capacity of 291 mAh 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 counter electrode. The working electrodes consist of Na_2DBQ (60 wt%), conductive carbon (30 wt%), and 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). 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 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 0.1 C rate (1C=291 mAh g^{-1}). The first discharge curve exhibits a long plateau at about 1.22 V, giving an initial discharge capacity of 398 mAh 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 an indicative of an activation process associated with the large volume expansion during the first sodiation. Such phenomenon assembles 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 with 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 kept 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. Note that the capacity of the second cycle reaches 265 mAh g^{-1}, which is comparable with previous proposed carbonyl-based anode materials.[29–32] Furthermore, the Na_2DBQ electrode can offer satisfied cycle performance. The capacity maintained at 231 mAh 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 suppressing dissolution.[13] Additionally, the coulombic efficiency quickly increased to 99% after initial a few cycles, even though it was relative low at the first cycle. It should be pointed out that a very recent work demonstrated that polymerization of organic salt could completely prevent the active material from dissolving.[23] It is believed that this strategy should be also 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 0.1C rate, the obtained capacity reaches 265 mAh g^{-1}. When the current density became 10 times higher (1C), a specific capacity of 248 mAh g^{-1} can still be achieved with small polarization. Even at a rate of 5C, 60% of the capacity delivered at 0.1C 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

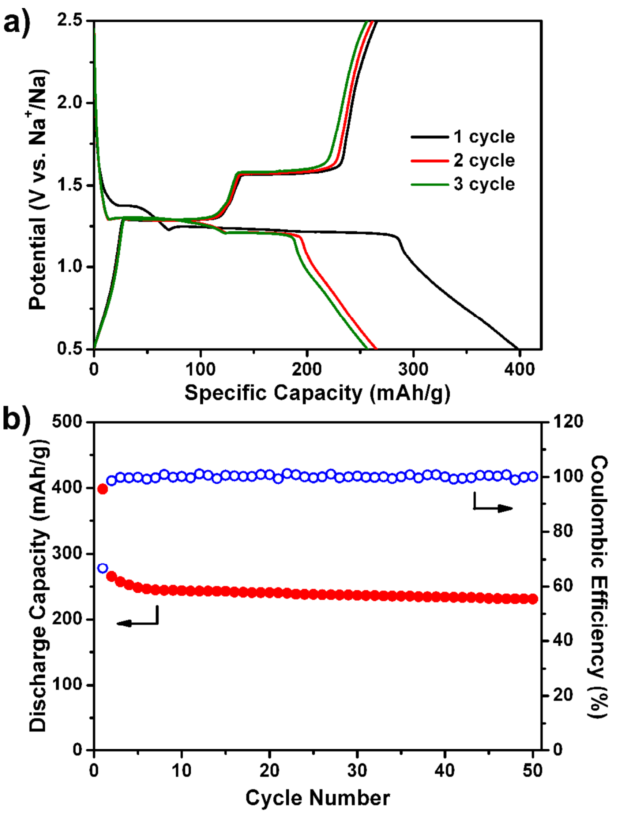


Fig. 2 (a) Initial three voltage profiles and (b) cycling performance of Na_2DBQ in the voltage range of 0.5-2.5V at 0.1C rate.

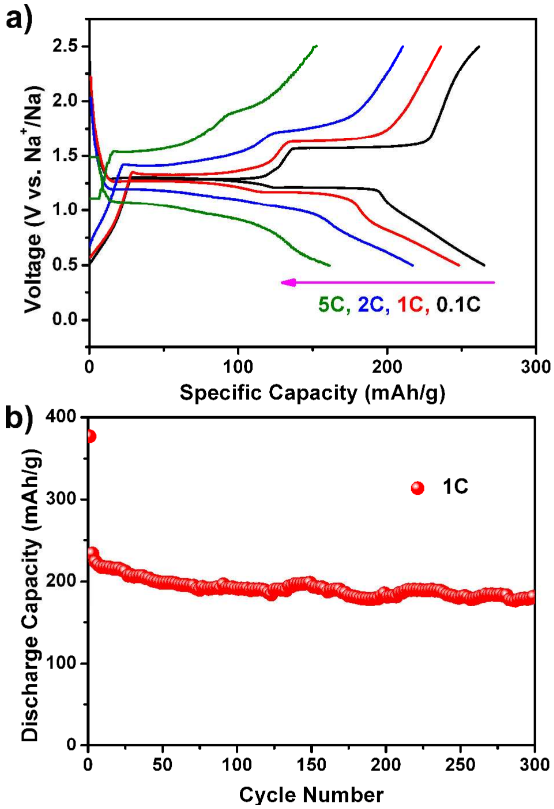


Fig. 3 (a) Typical discharge and charge profiles of Na_2DBQ at various current densities. (b) Cycle performance of Na_2DBQ at 1C rate.

current 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 mAh g^{-1}) to 100th cycle (192 mAh g^{-1}). Remarkably, the capacity can retain at 181 mAh g^{-1} even after 300 cycles.

Despite that Na_2DBQ exhibits relative high voltage as anode material, which would result in low energy density in full cell, it 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 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.

Conclusions

In summary, disodium salt of 2,5-dihydroxy-1,4-benzoquinone 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 mAh g^{-1} at 0.1C), long cycle life (up to 300 cycles at 1C), and high rate capability (160 mAh g^{-1} at 5C rate). These results shed light on the application of organic carbonyl compounds as electrode material for SIBs.

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Notes and references

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† Electronic Supplementary Information (ESI) available: the synthetic procedure of Na_2DBQ, ^1H NMR spectrum, FTIR spectrum, and elemental analysis of prepared Na_2DBQ. See DOI: 10.1039/b000000x/

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