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Sustainable and high-energy pre-sodiation cathode using $Na_2C_2O_4$ and dry-processing method for sodium-ion batteries[#]

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ABSTRACT

Sacrificial sodium-rich salts are promising pre-sodiation method to compensate the irreversible capacity of SIBs for energy density enhancement. To increase the capacity utilization ratio and decrease the decomposition potential, the particle size of sacrificial salts is generally reduced to lower than 10 um. However, large amounts of solvent are required to disperse the salts in slurry-coating electrodes, which increases the electrode production cost and limits the mass loading of electrode. This work utilizes dry-processing method to achieve sustainable and high-energy pre-sodiation cathode using $Na_2C_2O_4$, which is free of using solvent and able to produce ultra-thick electrodes. The feasibility of $Na_2C_2O_4$ as additive in ultra-thick dry-processing electrode has been demonstrated by electrochemical performance evaluation and electrode structure characterization. The full cells with pre-sodiation achieve large reversible capacity of 101.52 mAh g^{-1} at high areal capacity of 5.4 mAh cm^{-2} under 0.1 C as well as superior energy density of 309.3 Wh kg^{-1} and stable cycling. The novel electrode production strategy is promising for large-scale manufacturing of high-energy-density and low-cost SIBs.

Keywords: Pre-sodiation, Dry-processing electrodes, high energy density, sustainable method, Sodium-ion batteries

NONMENCLATURE

Abbreviations	
$Na_2C_2O_4$	Sodium Oxalate
NVP	$Na_3V_2(PO_4)_3$
HC	Hard carbon
VGCF	Vapor-grown carbon fiber
PVdF	Poly(vinylidene fluoride)
PTFE	Polytetrafluoroethylene
SIBs	Sodium-ion Batteries
SEM	Scanning Electron Microscope

1. INTRODUCTION

Sodium-ion batteries are promising candidates to achieve low-cost energy storage due to unlimited sodium source and sustainable electrode materials[1]. However, the widely application of SIBs is still limited due to the relatively low energy density compared to lithium-ion batteries, which is mainly caused by the low initial coulombic efficiency of hard carbon anode and continuous sodium loss upon cycling[2]. Pre-sodiation could effectively address the problem, which compensate the irreversible consume of sodium and enlarges the sodium inventory of SIBs.

There have been intensive works to develop novel pre-sodiation materials and method. Based on the pre-sodiation rection type[3], these methods could be generally divided into electrochemical pretreatment[4], chemical rection[5] and sacrificial sodium-rich salts[6]. Electrochemical pretreatments method needs to pre-charge the electrodes in half cell to form stable CEI or SEI, disassemble the half-cell to harvest the electrodes, and re-assemble the full cell, which is only applicable in laboratory research. Chemical reaction pre-sodiation needs to operating with sodium metal in glove box, which inevitably increases the production cost and safety issue. As comparison, sacrificial salts could add into the cathode during electrode production method, which is cost-effective and safe for SIBs.

Various types of sodium-rich salts have been reported to use for pre-sodiation, such as inorganic salts of NaN_3[7], $NaCrO_2$[8], and organic salts of Na_2CO_3[9], $Na_2C_2O_4$[10]. To increase the capacity utilization ratio and reduce the decomposition potential, the sacrificial salts

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were treated by reducing size to increase reaction surface area[11], constructing abundant contact with conductive carbon[12], adding catalyst to decrease reaction energy[13]. As a result, the particle size of the sacrificial reaction agents is generally lower than 10 um[10]. Although the performances were well improved, introducing small particle size agents into the slurry-coating electrodes would need large amounts of solvent to disperse[14], which would increase the electrode production cost and limit the mass loading of electrode.

To address the issue of sacrificial salts between electrode production, we report a sustainable and high-energy pre-sodiation cathode using $Na_2C_2O_4$ achieved by dry-processing method. Dry-processing electrodes is free of using solvent and able to produce ultra-thick electrodes with no thickness limitation, demonstrating the sustainability for large-scale manufacturing and potential to increase energy density by reducing inactive materials mass. Combining electrochemical performance evaluation and electrode structure characterization, we verify the feasibility of $Na_2C_2O_4$ as additive in ultra-thick dry-processing electrode, which not only compensate the irreversible capacity, but also slightly increase the pores in electrode to achieve higher rate capability. The novel strategy combining sacrificial salts pre-sodiation and dry-processing electrode can effectively boost the energy density and save production cost of SIBs.

2. MATERIAL AND METHODS

2.1 Preparation of materials and electrodes

Commercial $Na_2C_2O_4$ were ball-milled to reduce particle size before use, which were milled for 4 hours at a rotating speed of 500 r min^{-1}. $Na_2C_2O_4$ electrodes were made by slurry coating method, which were composed of $Na_2C_2O_4$, Super P and PVdF in a mass ratio of 70:20:10. Slurry-coated cathode electrodes were fabricated by mixing NVP, Super P, PVdF and $Na_2C_2O_4$ in a mass ratio of 95:2:3:10, of which the mass loading is 11 mg cm^{-2}. Dry-processing cathode electrodes were fabricated by hot-calendaring mixed materials powder of NVP, VGCF, PTFE and $Na_2C_2O_4$ in a mass ratio of 90:4:6:10, of which the mass loading is 53 mg cm^{-2}. Dry-processing anode electrodes were fabricated by hot-calendaring mixed materials powder of HC, VGCF and PTFE in a mass ratio of 95:3:2, of which the mass loading is 15 mg cm^{-2}. All electrodes were dried at 80 °C in vacuum overnight before use.

2.2 Electrochemical performance

The half cells were fabricated using sodium metal as counter electrode and 1 M $NaPF_6$ in diglyme as electrolyte. The full cells were composed of NVP as cathode, HC as anode and 1 M $NaClO_4$ in EC/DEC (vol%=1:1) with 5% FEC as electrolyte. All cells were made using CR2032-type coin cells and assembled in argon-filled glove box. Electrochemical performances were evaluated using Neware battery test system (CT-4008T-5V50mA-164, Shenzhen, China).

2.3 Characterization

The morphologies of materials and electrodes were obtained by the scanning electron microscope (SEM, Zeiss Sigma 300, Germany). Height distributions of electrode surface were characterized using optical microscopy (VHX-S90BE).

3. RESULTS AND DISCUSSION

3.1 Ball-milled $Na_2C_2O_4$ as pre-sodiation additive

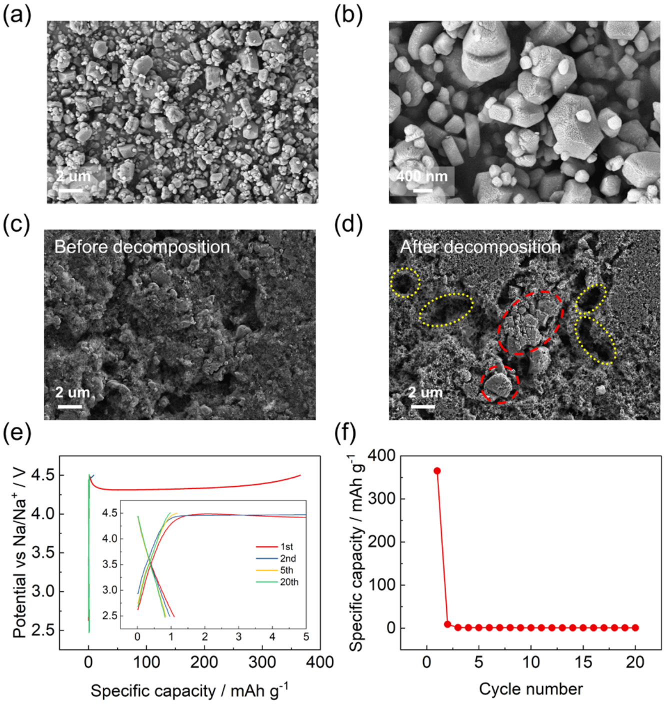

Fig. 1 Morphologies and decomposition capacity of ball-milled $Na_2C_2O_4$ (a-b) SEM images of ball-milled $Na_2C_2O_4$; (c-d) Surface morphologies of $Na_2C_2O_4$ electrodes before and after decomposition; (e) Potential curves of $Na_2C_2O_4$ electrodes during charging and discharging between 2.5 – 4.5 V vs Na/Na$^+$; (f) Charging capacities during 20 cycles of $Na_2C_2O_4$ electrodes

Figure 1a-b shows the morphologies of ball-milled $Na_2C_2O_4$ particles. The particle size of $Na_2C_2O_4$ particles was reduced to 2 um, contributing to construct efficient contact with the conductive carbon. The decomposition of $Na_2C_2O_4$ was further investigated using slurry-coating electrodes with Super P as conductive carbon. The morphologies of electrode surface were compared using SEM in Figure 1c-d. The $Na_2C_2O_4$ particles were wrapped by mossy Super P, proving the sufficient electron conductive network was built. After charging to 4.5 V vs Na/Na^+, there were abundant pores on surface of $Na_2C_2O_4$ electrodes (highlighted using yellow circle), owing to the decomposition of $Na_2C_2O_4$ generates only carbon dioxide. However, structure damage of slurry-coating electrodes is observed by the generated pores, which would peel off some conductive carbons and cause invalid contact with $Na_2C_2O_4$. As a result, the $Na_2C_2O_4$ was not fully decomposed after charging to 4.5 V, which was still observed in Figure 1d (highlighted in red circle). Under current density of 0.2 C, $Na_2C_2O_4$ can deliver an initial charging capacity of 365.23 mAh g^{-1} and a discharge capacity of 1.09 mAh g^{-1}. During subsequent charging and discharging cycles, the electrodes only showed capacities lower than 1 mAh g^{-1}, proving the feasibility of utilizing ball-milled $Na_2C_2O_4$ as sodium compensation additive. Nevertheless, the utilization capacity is still lower than the theoretical value of 400 mAh g^{-1}, which could be improved by constructing more compact electrode structure using dry-processing electrode.

3.2 Effect of $Na_2C_2O_4$ on electrode morphology

The surface morphologies of electrodes containing 10% ball-milled $Na_2C_2O_4$ made by slurry-coating and dry-processing method were compared in Figure 2a-b. Due to the addition of small size $Na_2C_2O_4$, large amount of solvent NMP is added to form homogenous slurry with well fluidity for coating, of which the solid content is ~40%[14]. However, it is still observed a bumpy surface of electrode after coating process, which might due to the alkaline $Na_2C_2O_4$ triggers gelation[15]. Besides, the thickness of coating layer is limited by the low solid content slurry, further causing low areal capacity of electrodes and long drying time for solvent evaporating. The morphologies were detailly investigated using optical microscopy. As shown in Figure 2c-d, the dried slurry-coating electrodes exhibits large height distribution, which were also proved by the reconstructed color map of three-dimension imaging. As comparison, flat surface is achieved using dry-processing electrodes, which achieves largely reduced height difference in Figure 2e-f. Moreover, dry-processing electrodes is free of using solvent and able to produce ultra-thick electrodes with no thickness limitation, indicating the sustainability for large-scale manufacturing by reducing cost of solvent purchasing and drying process.

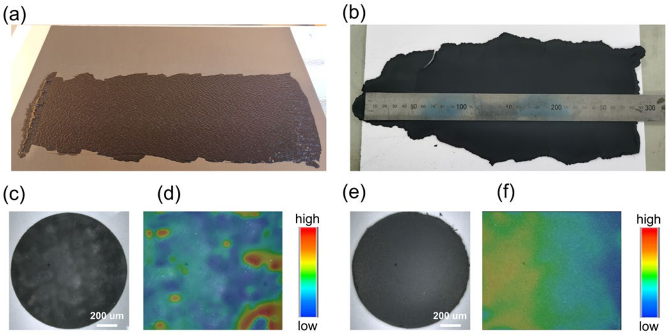

Fig. 2 Morphologies of cathode electrodes containing 10% $Na_2C_2O_4$ (a) slurry-coating electrode after coating process; (b) dry-processing electrode after hot-calendaring process; (c-d) slurry-coating electrode after drying and corresponding height distribution image; (e-f) dry-processing electrodes and corresponding height distribution image

3.3 Improvements by dry-processing method

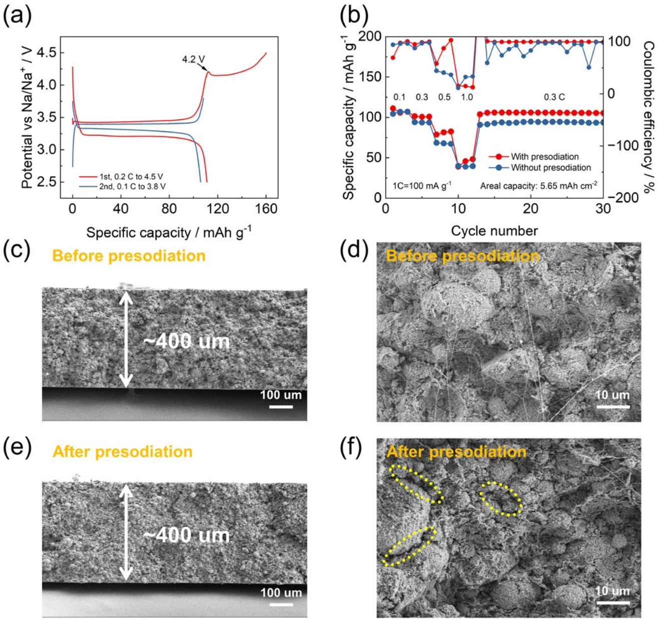

Fig. 3 (a) Potential curves during initial two cycles of cathode as charging to 4.5 V vs Na/Na^+; (b) Rate capability of cathode with and without pre-sodiation; (c-d) Cross-sectional morphology of cathode without pre-sodiation; (e-f) Cross-sectional morphology of cathode with pre-sodiation

To investigate the applicability of pre-sodiation using $Na_2C_2O_4$ for dry-processing electrodes, 400 um-thick dry-processing electrodes containing 10% ball-milled $Na_2C_2O_4$ were fabricated and evaluated in Figure 3, which could deliver a reversible capacity of 5.65 mAh cm^{-2}. Figure 3a shows the potential curves of pre-sodiation process and subsequent cycling process. The flat plateau at high potential verifies the decomposition of $Na_2C_2O_4$ in dry-processing electrodes, where decomposition potential was reduced to 4.2 V, and decomposition capacity was enhanced to 440.6 mAh g^{-1} comparing to slurry-coating $Na_2C_2O_4$ electrodes (Figure 1e). Rate capabilities of electrodes with and without pre-sodiation were compared in Figure 3b, which were charged to 4.5 V and 3.8 V in the initial cycle. Electrodes with pre-sodiation deliver larger capacities of 100.9, 82.55, 48.17 and 105.98 mAh g^{-1} under current densities of 0.3, 0.5, 1.0 and back to 0.3 C, comparing to value of 93.65, 67.17, 39.73 and 93.86 mAh g^{-1} for electrodes without pre-sodiation, which indicates pre-sodiation could reduce the electrode resistance. The electrode structure was further evaluated to illustrate the capacity improvement. From overview of cross-sectional images of electrodes in Figure 3c and 3e, compact structure is retained after pre-sodiation, attributing to high mechanical and flexible skeleton constructed by the 1-dimmensional VGCF and PTFE fibers. Moreover, in Figure 3d and 3f, larger spacing between particles was observed due to decomposition of $Na_2C_2O_4$ (highlighted using yellow circle), which could slightly increase the porosity of dry-processing electrodes and further reduce the diffusion resistance by enhance electrolyte wetting. Therefore, pre-sodiation using $Na_2C_2O_4$ is proved applicable for dry-processing electrodes, which could also enhance the performance of dry-processing electrodes by introducing pores in the electrode.

Table. 1 Performance comparison of pre-sodiation cathodes

	Production	*Method*	*Potential V*	*Loading mg cm^{-2}*	*Ref*
$Na_2C_4O_4$	Slurry	--	3.6	5.6	6
DTPA-5Na	Slurry	--	3.61	3	16
$Na_2C_2O_4$	Slurry	Carbon Catalyst	3.97	4.8	10
Na_2O-NiO	Slurry	catalyst	2.8	2	17
This work	**Dry**	**--**	**4.21**	**54.36**	**-**

Compared to the published works in Table 1, the proposed pre-sodiation cathode achieve full-degree decomposition of $Na_2C_2O_4$ without introducing additional conductive agents and catalysts. Importantly, this dry-processing electrode retained high capacity at 10 times the mass loading, which is free of using solvent for dispersing and achieves sustainable and low-cost production.

3.4 Electrochemical performance of full cells

Full cells were tested using all-dry-process NVP and HC electrodes as cathode and anode to further demonstrating the applicability of using $Na_2C_2O_4$ as sodium compensation additive. As shown in Figure 4a, larger capacities were delivered for SIBs with pre-sodiation, which are 101.52, 83.92 and 59.12 mAh g^{-1} at current densities of 0.1, 0.3 and 0.5 C, comparing to 62.91, 54.54 and 44.47 mAh g^{-1} of SIBs without pre-sodiation. The potential curves of initial two cycles were shown in Figure 4b, the large irreversible capacity was observed for original SIBs with low initial coulombic efficiency of 59.23%, which is originating from solid electrolyte interface growth in HC anodes. As comparison, irreversible capacity was successfully compensated by $Na_2C_2O_4$ decomposition, by which SIBs with pre-sodiation show high reversible capacities. Hence, attributing to the improved capacity, SIBs with pre-sodiation achieves largely improved energy densities of 309.3, 250.1 and 171.3 Wh kg^{-1} (based on NVP mass), comparing to 183.68, 155.6 and 125.2 Wh kg^{-1} for SIBs without pre-sodiation. The above electrochemical measurements prove the feasibility of $Na_2C_2O_4$ as a cathode pre-lithiation additive in full cells.

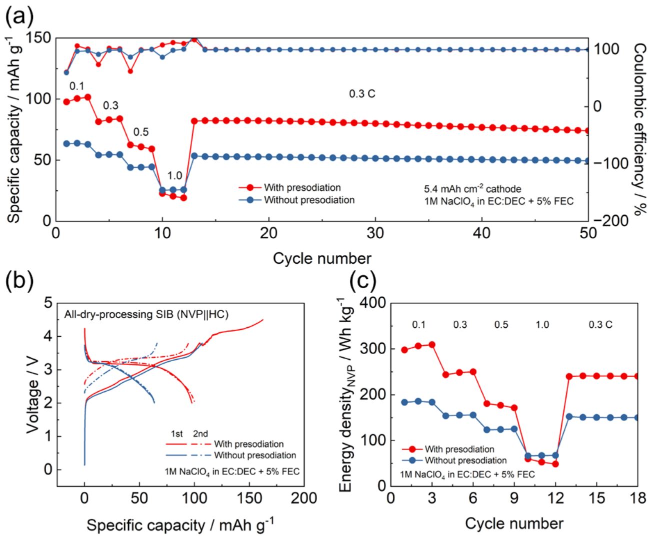

Fig. 4 Electrochemical performance of full cells (a) rate and cycle performance; (b) potential curves of initial two cycles; (c) comparison of energy densities

4. CONCLUSIONS

In this work, we introduced dry-processing method to achieve sustainable pre-sodiation using $Na_2C_2O_4$ and high energy cathode. Dry-processing method enable electrode production without using organic solvent NMP, contributing to fabricating ultra-thick electrode with smooth surface and reducing the production cost of purchasing and drying solvent, which makes feasible for adding $Na_2C_2O_4$ in electrodes for large-scale manufacturing. Evaluation of cathode verified the effective decomposition of $Na_2C_2O_4$ in thick dry-processing electrode without structure damage. Additionally, the porosity of dry-processing electrodes was slightly increased by decomposition of $Na_2C_2O_4$, which would reduce the diffusion resistance by enhance electrolyte wetting, contributing to higher rate capacity. The full cells were further fabricated to demonstrate the feasibility, which exhibits large reversible capacity of 101.52 mAh g^{-1} along with high areal capacity of 5.4 mAh cm^{-2} under 0.1 C, achieving superior energy density of 309.3 Wh kg^{-1} and stable cycling. The novel electrode fabrication strategy is of great importance for achieving high-energy-density and low-cost SIBs.

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