

Rapid Microwave-Assisted Synthesis and Electrode Optimization of Organic Anode Materials in Sodium-Ion Batteries

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Sodium-ion batteries are commanding increasing attention owing to their promising electrochemical performance and sustainability. Organic electrode materials (OEMs) complement such technologies as they can be sourced from biomass and recycling them is environmentally friendly. Organic anodes based on sodium carboxylates have exhibited immense potential, except the limitation of current synthesis methods concerning upscaling and energy costs. In this work, a rapid and energy efficient microwave-assisted synthesis for organic anodes is presented using sodium naphthalene-2,6-dicarboxylate as a model compound. Optimizing the synthesis and electrode composition enables the compound to deliver a reversible initial capacity of $\approx 250 \text{ mAh g}^{-1}$ at a current density of 25 mA g^{-1} with a high initial Coulombic efficiency ($\approx 78\%$). The capacity is stable over 400 cycles and the compound also exhibits good rate performance. The successful demonstration of this rapid synthesis may facilitate the transition to preparing organic battery materials by scalable, efficient methods.

have attracted considerable attention, particularly led by the commercialization of Li-ion batteries (LIBs).^[2,3] As the scope of applications powered by EES systems keeps widening, there is growing interest in exploring other technologies based on more abundant elements, such as Na-ion batteries (NIBs), to meet rising energy demands sustainably.^[4,5] In principle, NIBs work via a similar “rocking-chair” mechanism to LIBs.^[6] However, owing to the different sizes and mobility of the two ions, there is no direct equivalence of electrode materials from LIBs to NIBs, although NIB is viewed as a drop-in technology from LIB that uses similar manufacturing processes. Organic electrode materials (OEMs) are seen to overcome this issue by their ability to operate seamlessly for insertion

1. Introduction

The quest for global energy security has resulted in ever increasing prominence for electrochemical energy storage (EES) devices.^[1] Among other technologies, rechargeable batteries

of ions having similar characteristics ($\text{Li}^+/\text{Na}^+/\text{K}^+$).^[7–9] In addition, OEMs complement the green energy theme as their precursors can be obtained from biomass or postconsumer waste,^[10–12] and recycling devices containing them is environmentally benign.^[13] Also, OEMs offer over the ability to fine-tune electrochemical properties and allow integration of active groups into several types of solid-state materials.

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In NIBs, there is greater interest in developing anodes, since graphite which is a popular choice for LIBs, is not able to insert Na^+ ions effectively.^[14] Among redox-active organic groups, carboxylates, imines, and azo containing molecules have shown considerable promise as anode materials with low-voltage ion insertion.^[15,16] Typically, organic battery materials are synthesized using conventional solvothermal methods or by mixing reagents in large volumes of solvent for prolonged periods. For instance, sodium-carboxylates are typically prepared using solution-based reaction between sodium hydroxide and the corresponding carboxylic acid. These methods potentially limit the practical utility of these materials. Recently, microwave-based synthesis has garnered immense attention owing to rapid processing, applicability to wide range of precursors and solvents, and promising scalability.^[17–21] Microwave chemistry operates by heating the reagents homogeneously leading to cleaner conversions and higher yields. Additionally, the amount of solvent required for the reaction is relatively low and the reaction has an overall energy advantage.^[22] Also, this approach is seen to offer several benefits in related materials built from

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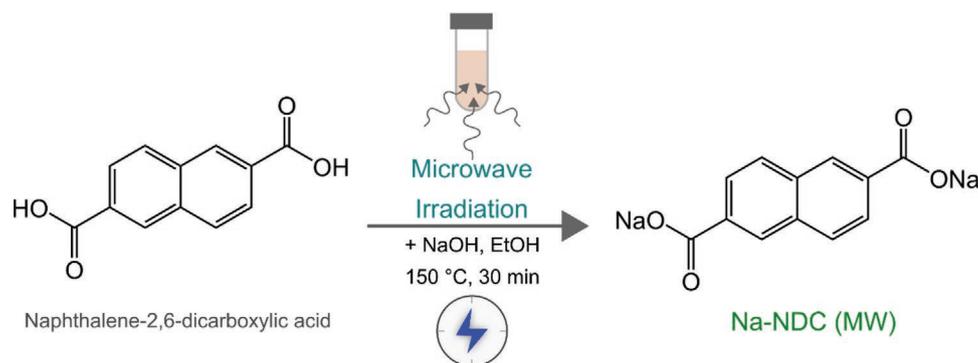


Figure 1. Schematic representation of the reaction for preparing Na-NDC (MW) using microwave irradiation.

organic molecules such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), over those prepared by conventional methods.^[23–26] Microwave-assisted synthesis has been previously trialed successfully for the preparation of other high performing battery electrode materials.^[27–29] Although some challenges remain for large-scale reactors,^[20] microwave technology continues to draw increasing attention as a green and effective method for scale-up. Especially in continuous flow settings, accompanied with engineering improvements,^[19,30] microwave-assisted synthesis is promising as an energy efficient, cost effective method for scaling up a range of materials.^[31–35] To promote the progress of organic battery materials toward practical implementation developing an efficient synthesis process is essential. This is particularly relevant for upscaling and a commercial perspective, as the cost of electrode materials is a major component of the total battery cost.^[36] Applying microwave-assisted synthesis, therefore, is an appealing and hitherto unexplored pathway to study for the preparation of OEMs.

In this work, the rapid and efficient microwave-assisted synthesis of organic anodes for sodium-ion batteries is presented, using sodium naphthalene-2,6-dicarboxylate (Na-NDC) as a model compound (Figure 1). Na-NDC has been previously shown to be a promising anode material with a two-electron redox reaction at a useful working potential.^[37–39] In addition to the synthesis conditions, the compound's electrochemical response is optimized by varying the composition of the electrode and testing different binders. Also, this synthesis method is shown to be extendable to the preparation of other sodium carboxylates, making it a promising general route to synthesize organic battery materials.

2. Results and Discussion

The title compound – Na-NDC (MW), was synthesized by heating a mixture of naphthalene-2,6-dicarboxylic acid (H₂NDCA) and sodium hydroxide (NaOH) in ethanol using microwave irradiation for 30 min (further details in the Experimental Section). The solid product was found to be structurally similar to the Na₂NDC compound obtained using the reflux method (Figure S1, Supporting Information).^[39] The completeness of the reaction was also validated using Fourier transform infrared spectroscopy (FT-IR) which showed

the absence of a broad O–H stretching peak, present in the parent naphthalene-2,6-dicarboxylic acid (Figure 2a). Additionally, the strong peak corresponding to carbonyl (–C=O) stretching at 1685 cm⁻¹ present in H₂NDCA was noticeably shifted in the spectrum for Na-NDC (MW). The morphology of the pristine phase was found to consist of solid particles with crystalline features (Figure S2, Supporting Information). Like the compound obtained using reflux synthesis, Na-NDC (MW) exhibited high thermal stability, with a plateau in the thermogravimetric analysis (TGA) profile up to ≈500 °C, followed by a sharp loss corresponding to the decomposition of the material (Figure S3, Supporting Information). This stability was further evident in a variable temperature powder X-ray diffraction (VT-PXRD) experiment, where the compound heated stepwise up to 500 °C did not show any significant changes (Figure S4, Supporting Information). The subtle shift for peaks at 2θ = 12° and 13.5° is ascribed to the slight framework distortion as previously reported.^[39]

To explore the synthesis further, several control experiments were carried out. A lower ratio of reagents (metal/ligand ratio) led to the formation of the target material along with unreacted H₂NDCA, with no evidence of any side product formation (Figure S5, Supporting Information). In the above-described process, NaOH functions both as the Na-ion source and the base for deprotonating the carboxylic acid. This was reinforced when the same reaction was attempted using other Na-salts such as Na₂SO₄ (sodium sulfate) or NaCl (sodium chloride). In neither of these cases was the desired product formed under the specified reaction conditions (Figure S6, Supporting Information). Further, the effect of reaction time was studied by reducing it to 10 and 20 min of heating. The target material could be prepared even at these lower times with no evidence of unreacted starting compound (Figure 2b). This can be deemed to be a significant improvement over conventional preparation methods for organic battery materials and is also highly attractive from a commercial point of view. The efficacy of the method was further tested to prepare two other sodium-carboxylates that have previously demonstrated excellent electrochemical properties as anode materials. By employing the same reaction protocol, both Na-BDC (MW) (BDC—benzene-1,4-dicarboxylic acid) and Na-BPDC (MW) (BPDC—biphenyl-4,4'-dicarboxylic acid) were prepared. The products showed similar PXRD patterns to the corresponding fully sodiated compounds and no presence of partially sodiated solids or unreacted precursors (Figure S7,

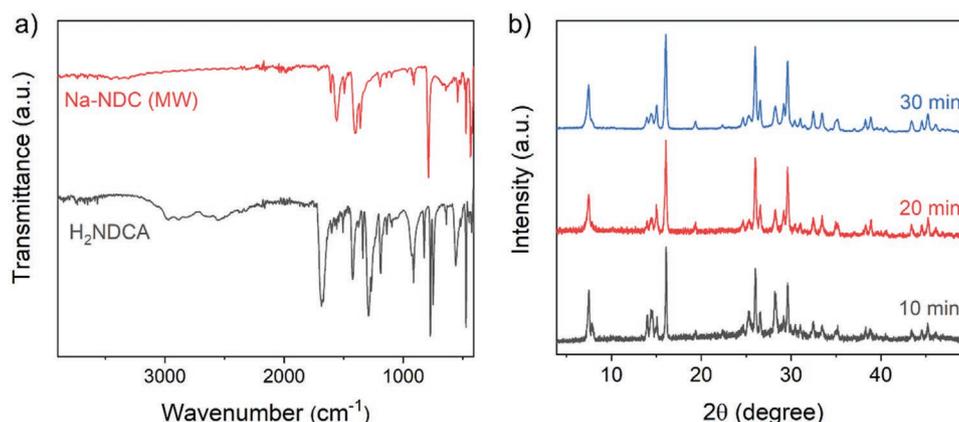


Figure 2. a) FT-IR spectra for naphthalene-2,6-dicarboxylic acid (H₂NDCA) (gray) and as-synthesized phase of Na-NDC (MW) (red). b) PXRD patterns for synthesis at different heating time—10 min (gray), 20 min (red), and 30 min (blue).

Supporting Information).^[40–43] This emphasizes the efficacy of using microwave-assisted synthesis in preparing organic materials in general for rechargeable batteries.

Electrochemical studies on Na-NDC (MW) were initially carried out on an electrode mix prepared using conductive carbon (Super C65—30%) and PVDF (polyvinylidene fluoride) as the binder (10%). Upon drying, the PXRD profile of the electrode resembled that of the pristine material (Figure S8, Supporting Information). When cycled at a low current density of 25 mA g⁻¹, in potential window of 0.05–2.5 V, a capacity of 330 mAh g⁻¹ was observed for the first discharge (Figure S9, Supporting Information). On subsequent charge, a capacity of 166 mAh g⁻¹ was reached. The excess capacity in the first discharge could be assigned to the solid-electrolyte interphase layer formation and irreversible capacity contribution from the conductive carbon.^[44,45] However, in the following cycles, a rapid capacity fade was observed, suggesting the incompatibility of PVDF binder with this material.

Moving toward more environmentally friendly water-soluble binders, carboxymethyl cellulose (CMC) and sodium alginate were tested as suitable options. Prior to electrode preparation, a recrystallization test from water was performed to mimic the casting and drying process and check the stability of the compound. The recrystallized solid exhibited big crystalline particles, owing to faster kinetics and possible aggregation promoted by the hydrophobic core of the molecule (Figure S10, Supporting Information). The PXRD pattern showed crystalline nature, with slight differences from parent phase, suggesting some hydration (Figure S11, Supporting Information). This was validated by the TGA profile, which exhibited ~6% weight loss corresponding to presence of water in the material (Figure S12, Supporting Information). The recrystallized solid was further heated under vacuum, which transformed completely to the pristine phase (Figure S11, Supporting Information). Subsequently, electrodes were prepared using Super C65 (30%) and the respective binder (10%). The scanning electron microscope (SEM) images for the electrode cast using CMC showed homogeneous distribution of block shaped recrystallized active material (Figure S13, Supporting Information), while the PXRD pattern of the dried electrode exhibited a similar trace to that for the anhydrous Na₂NDC (Figure S14, Supporting Information).

A similar morphology was observed for electrodes prepared using sodium alginate (Figure S15, Supporting Information). It is worth noting that the use of water-soluble binders strongly complements the green synthesis and sustainability aspect of battery electrode preparation.^[46]

Galvanostatic cycling studies at low current rate (25 mA g⁻¹) showed high first discharge capacities of 318 and 302 mAh g⁻¹ for CMC and sodium alginate-based electrodes, respectively (Figure S16, Supporting Information). Significantly higher initial Coulombic efficiency (ICE) was seen for electrode prepared from CMC binder (77.8%) for the first cycle over sodium alginate (59%). This ICE value for the CMC-based electrode is noteworthy from a commercial standpoint as these values for half cells are usually very low, making the transition to full cell studies difficult.^[47] From the second cycle onward, gradual capacity fading was observed for sodium alginate-based electrode, whereas in the case of CMC, a stable reversible capacity was delivered over 400 cycles (Figure 3a). Therefore, further electrochemical studies were carried out using CMC binder-based electrodes. As observed in the previous synthesis,^[39] Na-NDC (MW) exhibited a one-step redox reaction from the second cycle with discharge and charge peaks at 0.38 and 0.48 V, respectively (Figure S17, Supporting Information). The minor redox couple close to 0 V could be ascribed to presence of conductive carbon, as observed in electrodes prepared using only Super C65 (90%) and binder (10%, CMC) (Figure S18, Supporting Information). Based on the stable discharge capacity for this cell, an approximate capacity contribution of 37.33 mAh g⁻¹ could be ascribed to the electrodes prepared using 30% conductive carbon. Na-NDC (MW) cells cycled at current rates of 200 and 500 mA g⁻¹ delivered high capacities with low polarization and little fade over 75 cycles (Figure 3b and Figure S19, Supporting Information). Also, for these current densities, very low irreversible capacity loss for the first cycle was observed. This performance is comparable with previous studies on Na₂NDC prepared using solution-based methods.^[37–39] Additionally, there is improvement in terms of first-cycle Coulombic efficiencies and long term cyclability. Na-NDC (MW) was found to have excellent rate capability when the current rate was increased step wise from 25 to 500 mA g⁻¹, and the cycling capacity was retained when it was lowered back to 25 mA g⁻¹ (Figure 3c).

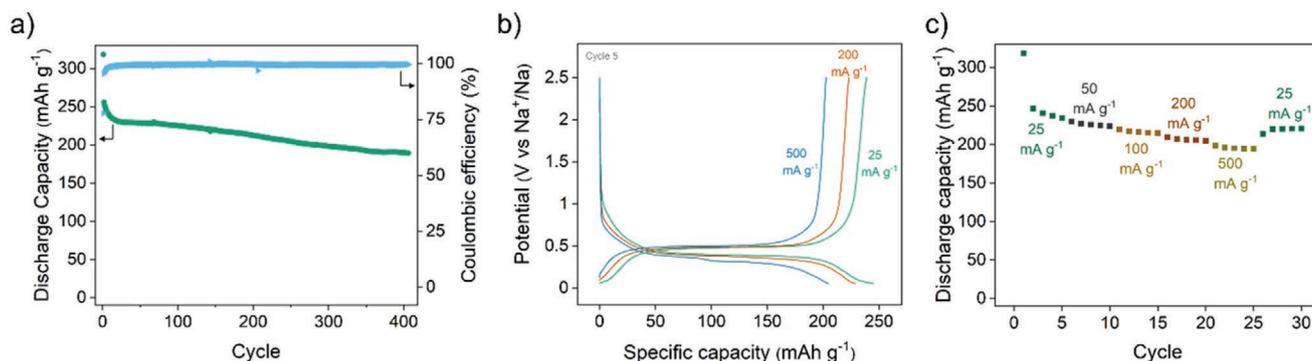


Figure 3. a) Discharge capacity (green) and Coulombic efficiency (blue) for Na-NDC (MW) cycled between 0.05–2.5 V at a current rate of 25 mA g⁻¹. b) Galvanostatic charge/discharge curves for Na-NDC (MW) (5th cycle) at different current densities. c) Rate performance for Na-NDC (MW) cycled at different current rates for five times at each step.

Another aspect in electrode fabrication is to enhance the content of active material and reduce the amount of conductive carbon.^[48] In this regard, electrodes were fabricated using CMC as the binder (10%) and different ratios of Na-NDC (MW) and Super C65—70:20 and 80:10. SEM images of the electrodes before cycling revealed similar crystalline morphology of the active material, but with greater aggregation of the crystallites (Figure S20, Supporting Information). Cycling studies exhibited retention of electrochemical features at both ratios with moderate capacities and moderately high ICE values (Figures S21 and S22, Supporting Information). The capacities, however, dropped slightly compared to electrodes with the previous composition, which may have resulted from weaker contact with conductive carbon. Nonetheless, in both these cases the cycling was stable over several cycles.

3. Conclusion

In summary, a rapid and efficient synthesis route has been demonstrated for preparing an organic anode—Na-NDC. The compound can be synthesized in a short time, within 10 min, and other characterizations validated the retention of properties as compared to the compound prepared by conventional synthesis but with enhanced ICE. This method was shown to work for the preparation of two other organic anode materials. Among different binders studied for fabricating electrodes of Na-NDC (MW), water-soluble binders—CMC and sodium alginate, were seen to offer distinctly superior performance. The electrode prepared using CMC delivered high initial reversible capacity of ≈ 250 mAh g⁻¹ at 25 mA g⁻¹, with notably high ICE (77.8%). This successful approach of using a rapid and energy efficient microwave-assisted synthesis can further drive research on organic battery materials toward practical implementation.

4. Experimental Section

Materials: The reagents—naphthalene-2,6-dicarboxylic acid (95%, Sigma-Aldrich), sodium hydroxide (99.09%, Fisher Chemical), ethanol (VWR), methanol (Fisher Chemical), sodium chloride (99.5%, Fisher Chemical), sodium sulfate (>99%, Fisher Chemical),

4,4'-biphenyldicarboxylic acid (98%, Acros Organics), and terephthalic acid (98%, Sigma-Aldrich) were obtained commercially and used as received. The chemicals for electrochemical studies—Super C65 (Imerys Graphite and Carbon), sodium carboxymethyl cellulose (degree of substitution 1.2, Sigma-Aldrich), sodium alginate (Sigma-Aldrich), PVDF (Solef), and *N*-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) were also obtained from commercial sources.

Synthesis of Na-NDC (MW): Naphthalene-2,6-dicarboxylic acid (H₂NDC) (216 mg, 1 mmol) and sodium hydroxide (100 mg, 2.5 mmol) were added as solids to a microwave reaction tube with a stirrer bar. Ethanol (4 mL) was then added and the tube was capped. The mixture was subsequently heated using microwave (Biotage initiator) irradiation at 150 °C for 30 min, after preheat stirring for 10 min. Upon cooling, a white precipitate was obtained which was filtered off and washed several times with ethanol (4 mL \times 5) and methanol (4 mL \times 2). The solid was collected and dried in an oven at 80 °C overnight. The yield of the product was ≈ 140 mg. Anal. calcd. for Na₂NDC: C, 55.40; H, 2.32. Found for Na-NDC (MW): C, 54.25; H, 2.36.

For time-control experiments, the procedure was unchanged, except heating the mixture for shorter time—10 and 20 min. The above-described protocol was also employed for reaction at lower ratio of reagents, by changing the amount of sodium hydroxide (44 mg, 1.1 mmol). For syntheses using different sodium-salts, the same procedure was followed except using respective salts—NaCl (2.5 mmol) or Na₂SO₄ (1.25 mmol).

Recrystallization Test: The product—Na-NDC (MW) (20 mg) was dissolved in water (2 mL) in a glass vial. This solution was left to dry in an oven at 80 °C for 4 h. The recrystallized solid was scraped off and used for further analysis.

Structural Characterization: PXRD patterns were recorded on STOE STADI/P diffractometer using Cu K α radiation at room temperature from 3°–50° (2 θ). Variable temperature PXRD was recorded in air on a PANalytical Empyrean X'Celerator real-time multiple strip detector diffractometer using Mo K α ,₂ radiation in an alumina sample holder. The measurement was performed from 2° to 25° (2 θ) with heating/cooling rate of 5 °C min⁻¹. TGA was recorded in air on Stanton Redcroft STA-780 from room temperature to 700 °C, with heating rate of 5 °C min⁻¹. IR spectroscopy was carried out using Shimadzu IR affinity-1 FTIR spectrophotometer in transmittance mode from 400 to 4000 cm⁻¹. SEM images were collected using a JEOL JSM-IT200 or JEOL JSM-IT800 microscope. The powdered samples were placed on carbon tape and gold coated using Quorum Q150R ES sputter coater (10 mA, 30 s) prior to recording.

Electrochemical Characterization: The working electrodes were prepared by mixing active material (60%), conductive carbon (Super C65, 30%), and CMC (10%) or sodium alginate (10%) as the binder. The slurry was prepared by hand grinding active material and conductive carbon which was added to the binder solution in water and stirred for

4 h. The slurry was cast onto aluminum foil (Advent Research) using a doctor blade and air dried for 2 h. Electrodes were then punched (diameter \approx 12 mm) and dried overnight in a vacuum oven at 110 °C. The approximate active mass loading was 1.7 and 1.55 mg cm⁻² for CMC and sodium alginate-based electrodes, respectively. The same procedure was followed for preparing electrodes with higher content of active material. For PVDF based electrodes, the ratios were retained (60% active, 30% Super C65, and 10% PVDF), but NMP was used for the preparation of the slurry and electrodes were dried overnight under vacuum at 80 °C. Solid state characterization for the air-dried electrode phase was performed by scraping off the solid mixture from the Al-foil. Coin cells (CR2325) were assembled using sodium metal (Sigma-Aldrich) as the counter electrode, glass fiber separator (Whatman GF/F) and NaPF₆ in ethylene carbonate and diethyl carbonate (1:1, v/v) (Kishida Chemical) as the electrolyte, in an argon-filled glovebox (MBraun) with oxygen and water content <1 ppm. Electrochemical studies were performed at 30 °C in a potential window of 0.05–2.5 V (vs Na⁺/Na) on a Biologic BCS-805 modular battery testing system and the data were analyzed using BT-Lab software.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Keywords

microwave, organic anode, rapid synthesis, sodium carboxylate, sodium-ion batteries

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