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Benzenediacylates as organic battery electrode materials: Na *versus* Li

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Abstract

This paper discusses investigations of a novel Na-based organic battery electrode material, disodium benzenediacylate (Na₂BDA) in comparison with its Li-ion homologue. Li₂BDA has previously shown promising battery properties, such as stable cycling and good capacity retention. Na₂BDA and Li₂BDA are here successfully synthesized and characterized, and investigated as anode materials in prototype Na- and Li-ion battery cells. Moreover, different electrolytes are screened for the Na-battery material, and a useful operating voltage window is explored. Na₂BDA is shown to possess a higher initial coulombic efficiency (91%) than the Li-homologue, which is uncommon for sodiated organic electrode materials. The Na-compound shows an initial capacity of 177.7 mAh/g, which however decreases to ca. 50 mAh/g after 20-100 cycles depending on cycling rate; a significantly lower capacity retention than that observed for Li₂BDA. The capacity loss can primarily be explained by a decomposition mechanism of the Na₂BDA compound.

Keywords: Na-ion batteries; Organic electrode materials; Electrolyte compatibility; Potential window

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1. Introduction

In the past decades, the development of Li-ion batteries has grown rapidly, and batteries have become a major energy storage solution also outside of portable electronics [1, 2]. For example, the electric vehicle industry is expanding and therefore also increasingly interested in the development of better batteries. Conventional battery chemistries are, however, commonly based on inorganic compounds involving transition metal elements, giving rise to high costs and environmental issues. Life cycle assessment studies of inorganic battery materials (including extraction, processing and recycling) have generally shown significant negative environmental impact [3]. Organic materials issued from biomass, on the other hand, could here constitute an environmentally better option, to decrease the use of non-renewable resources. These materials are often renewable and can be easily synthesized from energetically favorable solution phase routes [4]. In recent years, several such organic compounds have been considered for Li batteries [5-12]. Their less rigid structure can provide higher mobility of the cations as compared to inorganic materials. However, organic electrode materials do possess some important drawbacks such as high solubility in common electrolytes, poor energy density and lack of electronic conductivity.

The rapidly increasing utilization of Li-ion chemistries for energy storage has, at the same time, led to a vast increase in the price of Li metal and other Li compounds in the past years [13], which is also dependent on the geographical constraints on the resources. Since these resources are finite, it will be of importance to also explore battery chemistries based on metals which are cheaper and more widely spread, perhaps at the expense of energy density. In this context, Na has recently attracted a lot of interest as an alternative to Li [14], and many researchers are trying to develop structural homologues to the common lithium battery materials. Though Na cathodes have shown promising results in terms of good cycling stability and convenient rate capability [15, 16], most anode materials still fall short in performance, while it would still be beneficial to replace the dangerous and reactive Na foil. The most important drawback that has to be taken into consideration is the poor kinetics of the Na ion de/insertion reaction mechanism, originating in the relatively large ionic radius of the Na cation (102 pm) in comparison with the Li cation (76 pm).

To date, there exist only a very limited number of organic compounds suitable for Na batteries [17-21], and among these there is an obvious lack of compounds which can work as an anode. Not least sodium carboxylates have been investigated as negative electrode material due to their low average potential. One example is disodium terephthalate [15], which displays a voltage of 0.4 V vs. Na and a reversible capacity of ca. 250 mAh/g. However, the sodium carboxylates reported on so far suffer from a high irreversible capacity during the first cycle, with initial coulombic efficiency values in the 42-65% range. Such performances are significantly (6-20%) worse than their lithium-based counterparts; for example, by comparing disodium terephthalate [15-17] to dilithium terephthalate [5] or $\text{Na}_4\text{C}_8\text{H}_2\text{O}_6$ [22] to $\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$ [23]). A low coulombic efficiency corresponds to a vital energy loss if experienced in a whole-cell. Therefore,

development of sodiated materials with minimum irreversible capacity during the first cycle is required for successful battery implementation.

In this paper, we present a novel Na-based organic battery electrode material, disodium benzenediacylate (Na_2BDA), and compare it with its Li-ion homologue Li_2BDA . Li_2BDA has previously been reported briefly as an example material for electrode formulation strategies for organic Li-ion batteries [24,25], but no in-depth characterization has so far been made. Here, we report the synthesis, characterization of Na_2BDA and Li_2BDA and discuss their electrochemical performance as functional anode materials in Na and Li ion batteries. The compounds can reversibly de/insert two Na or Li cations, resulting in theoretical capacities of 205 mAh/g and 233 mAh/g, respectively. We also report the first case where a sodium salt has a higher initial coulombic efficiency than the Li-homologue, with a value as high as 91%.

2. Experimental

2.1 Materials

All chemicals were purchased from commercial sources and used as received. For synthesis, 1,4-benzenediacylic acid (98% purity) was purchased from Alfa Aesar, sodium hydroxide (98% purity) from VWR International, lithium carbonate (99% purity) from Merck, and ethanol (99.5% purity) from Solveco. For electrode preparation, carbon black and carboxymethylcellulose were purchased from Erachem Comilog N.V. and Leclanché, respectively. Electrolyte salt were purchased from Ferro Corporation (lithium bis(trifluoromethanesulfonyl)imide, LiTFSI), Solvionic (sodium bis(fluorosulfonyl)imide, NaFSI, 99.7%), Alfa Aesar (sodium hexafluorophosphate, NaPF_6 , 99%), and Aldrich (sodium perchlorate, NaClO_4 , 99.9%), while electrolyte solvents were purchased from Novolyte (ethylene carbonate, EC, propylene carbonate, PC, and dimethyl carbonate, DMC), and Aldrich (diethylcarbonate, DEC). The additive used fluoroethylenecarbonate (FEC) was purchased from Aldrich (99% purity). Counter-electrode materials such as high purity lithium foil and sodium cubes (99.9%) were purchased from Cyprus Foote Minerals and Aldrich, respectively.

2.2 Synthesis

Na_2BDA was synthesized using two different routes. Route A involves a modified procedure of the synthesis of sodium terephthalate by Park et al. [16]. Disodium benzenediacylate (Fig. 1) was prepared via the addition of 1,4-benzenediacylic acid to an aqueous NaOH solution at 50-60 °C. Ethanol was thereafter added to the solution at 90 °C to precipitate disodium benzenediacylate in a deionized water-ethanol mixture. After refluxing at 90 °C for 12 h, the compound was hot-filtered and then dried overnight in an oven at 100 °C.

Route B is based on a similar synthesis as the Li-homologue of this compound, presented by Renault *et al.* [24]. Li₂BDA was synthesized by the addition of 1,4-benzenediacyric acid to a Li₂CO₃ solution in an ethanol:water (1:1) solution at 50 °C, stirred for 2 days and then dried in an oven at 100 °C. The synthesis of Na₂BDA resulted, however, in a two-phase mixture of the monosodiated and disodiated compounds. The pure disodiated phase was obtained after recrystallization in water:ethanol (1:1) solution.

2.3 Characterization

The compounds characterization is based on the following analysis: thermogravimetric analysis (TGA) was performed using a TGA Q500. Proton and carbon (¹H, ¹³C-NMR) spectra were recorded at room temperature on a JEOL ECP-400 spectrometer at 400 MHz and 100 MHz, respectively. Infrared spectra were recorded in the 650-4000 cm⁻¹ range on a Perkin Elmer Spectrum One FT-IR spectrometer equipped with an attenuated total reflectance (ATR) probe. X-ray diffraction was recorded with a Siemens D 5000 diffractometer using CuK α radiation. SEM micrographs were recorded using a LEO 1550 instrument.

2.4 Electrochemistry

Na₂BDA was mixed with carbon black and carboxymethylcellulose (CMC) as binder to form a slurry at a weight ratio of 60:33:7. The slurry was casted on a Cu foil and dried overnight in the oven at 100 °C. Electrodes of 20 mm \varnothing were cut from the foil and dried in a vacuum oven at 120 °C overnight. The cell assembly was performed in an Ar glove-box, using glass fiber as separator and Na foil as counter electrode. A series of different electrolytes were tested: 1 M sodium bis(fluorosulfonyl)imide (NaFSI) in EC: DEC 1:1.5, 1 M sodium hexafluorophosphate (NaPF₆) in EC:DEC 2:1, 1 M NaPF₆ in propylenecarbonate (PC), 1 M NaPF₆ in EC:PC 1:1, 1 M sodium perchlorate (NaClO₄) in PC, 1 M NaClO₄ in EC:DEC 1:1, 1 M NaClO₄ in PC+fluoroethylenecarbonate (FEC). The electrochemical performance of the Na-batteries was tested using an Arbin BT 2043 system. 2 V (*vs.* Na/Na⁺) was used as high cut-off voltage, while low cut-off values of 0.1, 0.3 and 0.5 V were investigated in galvanostatic cycling tests. The preparation of the electrodes and electrochemical performance of the Li homologue were discussed in previous papers [24,25]. Cyclic voltammograms (CV) of the electrodes were recorded for 1 M LiTFSI in DMC and 1 M NaFSI in EC:DEC, respectively at a scan rate of 0.1 mV/s between 0.9-3 V and 0.1-2 V respectively.

3. Results and discussions

The synthesis of Na₂BDA according to route A, illustrated in Fig. 1, gave a crystalline white solid powder with a yield of 87 %. Route B, equivalent to the synthesis strategy for the Li homologue, gave on the other hand a yield of only 76 %. This yield is significantly smaller than the results for

both route A and the 98 % observed for the Li compound [24]. The value is, however, reasonable considering that route B includes one extra step in the purification of the compound. In all further analysis, compounds synthesized using route A was therefore used.

Li₂BDA has previously been synthesized and used successfully in Li-ion batteries [24,25]. It has then been shown that electrodes based on this compound can be significantly improved by tailoring the particle size and structure, as well as the amount of carbon in the electrode. In this context, Na₂BDA can be considered to constitute a cheaper and more environmentally friendly battery material analogue. Also Li₂BDA is a crystalline white powder, characteristic for the carboxylated Li compounds. The white colour is indicative of the poor electronic conductivity in this type of compounds, but which can be overcome by using a carbon-coating method in a liquid medium or by freeze-drying techniques.

The morphology of electrodes based on Na₂BDA was determined using SEM. As seen in the SEM micrograph in Fig. 2, the materials present a rather homogeneous carbon repartition and a relatively high surface area with an acceptable particle sizes for Na-batteries; the largest particles being around 6 μm in diameter. If comparing with the Li compound, where the particle size was between 2 and 10 μm, it can be concluded that the compounds have similar morphologies despite the difference in cation size.

The TGA data (Fig. 3) for Na₂BDA shows only one significant weight reduction at ca. 480 °C, indicating that the compound is phase-pure after synthesis. A weight loss of ~2% appears at 100 °C, most likely corresponding to H₂O residuals. This small amount of extra water might prove difficult to get rid of by simple oven drying. TGA data of the Li compound display a dramatic weight loss around 380 °C, indicating that the Li compound is somewhat less stable than the Na compound which decomposes at higher temperatures. The remaining ca. 30 and 40% of the original weight represents Li₂CO₃ and Na₂CO₃, respectively, formed after pyrolysis of the synthesized compounds, as seen with the matching IR spectra of the pyrolysed compounds with commercial Li₂CO₃ and Na₂CO₃, respectively (cf. Fig. S1 and Fig. S2 in the Supporting Information). The experimental and theoretical ratio of Na₂CO₃/Na₂BDA has the same value of ~0.4, from which it can be concluded that the compound is completely transformed to carbonate after pyrolysis. This formation is also confirmed by FTIR characterization of the remaining sample after heat treatment to 600 °C (see Fig. 4 and associated discussion). It can also be observed that the Li compound contains more than 2% H₂O, suggesting that the compound might be more hygroscopic than the Na homologue.

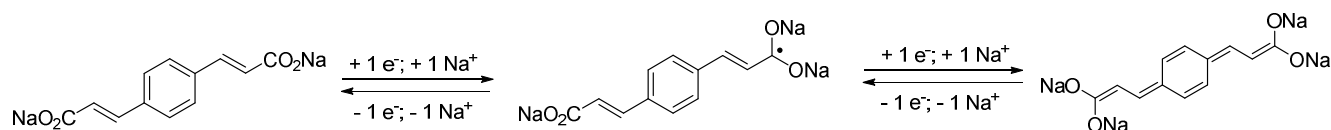
In the IR spectrum (Fig. 4) of Na₂BDA, some characteristic peaks can be seen, such as a 1639 cm⁻¹ C=C symmetric stretch, 1553-1510 cm⁻¹ C=O stretch vibrations, 1422-1390 cm⁻¹ C=C stretchings from the phenylene group, a 1250 cm⁻¹ C-O stretch, a 969 cm⁻¹ C-H stretch characteristic of the alkene group and at 850 cm⁻¹ a bending peak, corresponding to the 1,4-disubstituted aromatic rings. In the IR spectrum of the pyrolysed Na₂BDA, well-known signals for Na₂CO₃ [26] can be observed such as the strong stretching of the C=O bond at 1410-1421 cm⁻¹

¹ and a more narrow signal at 850 cm⁻¹. No obvious signals of contaminants could be detected in the spectra.

XRD patterns from the two carboxylate compounds can be found in the Supporting Info. Interestingly, the replacement of Li with Na changes the XRD pattern significantly, which can not only be attributed to the difference in cationic radius. The compounds are thus most likely not iso-structural, which can be indicative of different electrochemical behavior. Moreover, the signals are much weaker for the Na-compound despite equal measurement times, indicating a higher degree of amorphicity, which can lead to easier dissolution in the electrolyte solvents.

The purity of the synthesized Na₂BDA compound was further confirmed by ¹H-NMR and ¹³C-NMR spectroscopy. The spectra show single phase signals from the carboxylate as well as the phenylene groups of Na₂BDA (Fig. 5, Fig. 6). ¹H NMR (400 MHz, D₂O) δ(ppm): 6.51 (d, 2H, 16 Hz, HC=HC-CO₂), 7.35 (d, 2H, 16 Hz, HC=HC-CO₂), 7.59 (s, 4H, C₆H₄). ¹³C NMR (100 MHz, D₂O) δ (ppm): 125.0 (HC=C_βH-CO₂), 128.3 (CH, phenylene), 136.5 (C_α-CH=CH-CO₂), 140.2 (C_βH=CH-CO₂), 175.7 (CO₂). From the coupling constants obtained from ¹H-NMR, it can be concluded that the Na₂BDA synthesized is the *trans* isomer, because the range of *trans* coupling is 11-18 Hz and 16 Hz being the typical value, while the *cis* should be in the range 6-14 Hz. *Cis/trans*-isomerism can be of large importance for the electrochemical performance of batteries based on organic compounds, as recently shown by Walker *et al.* [7].

A proposed mechanism for the insertion/deinsertion of Na ions in Na₂BDA during battery operation, similar to the lithium compound, is presented in Scheme 1. It is in this context noteworthy that the sodium ions are inserted in two different steps, which most likely will correspond to two different electrochemical potentials.



Scheme 1. Expected mechanism for insertion/deinsertion of Na in Na₂BDA.

Since the Na homologue of the BDA compound has never been tested before as a battery material, finding an appropriate electrolyte and cut-off voltage values had to be taken into consideration before further electrochemical characterization. While the upper cut-off voltage was set to 2 V for all experiment, lower cut-off voltages of 0.5, 0.3 and 0.1 V (*vs.* Na/Na⁺) were investigated; Na metal dendrite formation can be expected at even lower potentials. The most satisfying results in terms of cycling stability and obtained efficiency from the material were achieved for 0.1 V. As seen in the CV data in Fig. 7, the higher low cut-off voltages will not allow the material to complete the insertion process of Na during reduction. The reduction process starts at ca. 1.2 V, and a clear reduction peak is observed from 0.5 V. The increase in current between 1.2 and 0.5 V can probably be ascribed to electrolyte reduction and SEI formation, while the large peak below 0.5 V is due to sodium insertion into the electrode.

Obviously, the sodiation is therefore very limited when the cycling is stopped at 0.5 V, while the process is allowed to continue somewhat longer when stopping at 0.3 V. An oxidation reaction can then also be visible. However, if the cut-off voltage is decreased to 0.1 V the compound has time to complete the reduction, and the corresponding oxidation peak also increases significantly. When using 0.3 V as a cut-off, the corresponding capacity is ca. 63 mAh/g and 43 mAh/g during reduction and oxidation, respectively, while these values grow to 79 mAh/g and 66 mAh/g for the 0.1 V cut-off.

Fig. 8 shows CV data for one constant potential window (2-0.1 V vs Na/Na⁺) for Na₂BDA during the first three cycles. A clear difference in electrochemical behavior can be observed between the first cycle and the followings. During reduction, the first cycle presents first a small peak which can be attributed to SEI layer formation, then a clear reduction peak at 0.4 V with a shoulder at 0.25 V. This lower voltage peak and the corresponding shoulder can be attributed to the reduction of the compound and the insertion of two Na ions. Similar features can be observed for subsequent cycles, but with less SEI layer formation. A sharp peak with a shoulder can be visible also during oxidation. However, the first presents a somewhat different shape than the following, with one large peak at 0.9 V and a second small peak at 1.6 V. The peak at 0.9 V most likely corresponds to the deinsertion of Na ions from BDA while the 1.6 V can perhaps be attributed to decomposition products formed during reduction. This second peak decreases significantly during subsequent cycles. The most striking feature in Fig. 8 is perhaps that the first cycle oxidation peak displays a much lower capacity in comparison to other cycles. This intensity difference might be explained by an activation step which the material experience during the first cycle, making it achieve full capacity only after passing this barrier. This activation barrier might also be explained by a layer loss in the first cycle as a consequence of the dissolution process of the compound in the electrolyte.

In comparison, the Li analogue compound presents a more consistent cycling voltammogram (Fig. 9). Although the investigated potential window is large, it can be noticed that the compound can complete the reaction reversibly within less than 1 V. Moreover, the reduction peak is as high as ~1 V vs Li/Li⁺, in comparison with 0.25-0.4 vs Na/Na⁺ for Na₂BDA, which might be explained by the smaller atomic radius of Li⁺ which makes insertion easier. Keeping this potential difference in mind, it is also more likely that the Li complex formed is more stable than the Na analogue, since the latter possess a weaker bond with the complex in comparison to Li. On the other hand, it is important to note that the peaks are clearly decreasing during cycling for Li₂BDA, corresponding to a capacity decrease not observed in the CV for Na₂BDA. This might indicate a dissolution or decomposition, process of the active material into the electrolyte. From recent studies on the Li compound [27], it has also been shown that Li₂BDA rather suffers from material decomposition during cycling than from dissolution into the electrolyte.

Another key issue to address is the choice of electrolyte. It is well-known that the electrolyte plays an important role for determining battery life and performance [28]. This is perhaps especially true for organic electrode materials, where dissolution of active material into the

electrolyte constitute a significant drawback [5]. Moreover, during the first battery cycles, the electrolyte is often spontaneously partially reduced to form a solid electrolyte interphase (the SEI layer) which suppress further degradation of the electrolyte. In order to find a good electrolyte for this particular system, a series of electrolytes with different compositions of salts and solvents were tested. The salts used were NaPF_6 , NaClO_4 and NaFSI while the solvents were PC, and different combinations of EC:DEC and EC:PC (see Table 1). The electrolyte giving the best cycling stability and capacity retention was 1 M NaFSI in EC:DEC; this electrolyte was therefore being used in further electrochemical characterization studies. The EC:DEC solvent mixture is generally used since EC displays a broad electrochemical stability window and possess a high dielectric constant, while DEC has low viscosity and melting point. PC has similar properties as EC but lower melting point and viscosity, and could therefore well constitute an alternative. The FEC electrolyte additives have shown improvement in the performance of the electrolyte when combined with PC for inorganic battery systems [29,30] but did here not result in any improved capacity retention. Nevertheless, the results clearly indicate that the battery performance is less dependent on the solvent, but rather on the Na-salt used, with NaFSI being the only salt displaying acceptable capacity retention. This is likely due the fact that NaFSI is a more stable salt in this potential window than the other salts used. For the Li homologue, the only electrolyte tested was 1 M LiTFSI in DMC, which also displayed acceptable capacity retention of 180 mAhg^{-1} . The DMC solvent could be considered an option also for Na_2BDA but is less likely to display any significant improvement considering that its properties are generally similar to DEC.

Table 1. Capacity retention of batteries using different electrolytes.

| Salt | Solvents | Capacity retention after 10 cycles (mAhg^{-1}) | Performance |
|----------------------|---------------|---|--|
| 1 M NaClO_4 | PC | 80 | Capacity is fading very fast after first 4 cycles, especially when EC:DEC is used as a solvent. A better performance can be recorded in the case of the PC solvent. Using FEC as an additive does not improve the performance of the PC solvent in combination with NaClO_4 . |
| | EC:DEC (1:1) | 30 | |
| | PC + FEC (2%) | 60 | |
| 1 M NaPF_6 | PC | 10 | Generally poor capacity retention. PC and EC:DEC display lower capacity than the EC:PC |
| | EC:DEC (2:1) | 8 | |

| | | | |
|-----------|----------------|----|---|
| | EC:PC (1:1) | 45 | mixture, which has a similar performance as NaClO ₄ in PC. |
| 1 M NaFSI | EC:DEC (1:1.5) | 85 | The best capacity retention observed. |

When cycling Na₂BDA, an initial capacity of 177.7 mAh/g can be observed; see Fig 10 inset. This recorded capacity almost reaches the theoretical capacity value of 205 mAh/g. Moreover, the capacity does not decrease dramatically during the second cycle, indicating that no severe SEI layer formation has taken place. There is, however, a clear decrease in capacity during the first 10 cycles, which then levels out, and the battery cycles with a more stable but modest discharge capacity of ca. 50 mAh/g. In the galvanostatic cycling (Fig. 10), the compound displays a plateau at 0.6 V which can be ascribed to the reduction of the carbonyl groups for Na cation insertion, where C=O is transformed into ⁻C-O-Na. Upon recharge, the electrode initially delivers a capacity of 161.7 mAh/g, indicating a coulombic efficiency of 91 %. This value is significantly higher than for other organic Na-materials, and also higher than the 79% experienced for the Li homologue. This value increases to ~95 % after 40 cycles (Fig. 10 inset). The capacity fading experienced is a well-known problem for many organic electrode materials, and is often attributed to the dissolution of active material in the electrolyte. Tailoring the electrolyte system can help overcoming this problem; in this context, the electrolyte solvents are generally developed for Li-based systems. Another factor which can explain the higher dissolution of the Na- than the Li-compound can be the higher degree of amorphicity of the previous BDA-analogue. Furthermore, it should be noted that as the cycle number increases, the probability of side-reactions such as decomposition mechanisms also increases, which can explain the capacity fading. Recent studies [31] have shown that a strong sodiation of carbonyl groups indeed destabilizes organic molecules to a higher degree than equivalent lithiation mechanisms, leading to electrode decomposition processes.

The electrochemical characterization was performed for Na₂BDA at three different C rates (see Fig. 11); the results at a comparatively high C-rate (C/10) being very similar to those at the lower rate of C/40. Interestingly, though, if the C rate (corresponding to the speed at which sodium was inserted and deinserted) was increased to C/4, the capacity fading become much less pronounced. The curves meet after 8 cycles, after which the capacity is higher per cycle number for C/4. This can be explained by the fact that the C/40 and C/10 cells are used during 462 h and 113 h, respectively, while the C/4 is cycled for only 44 h to achieve the same cycle number. These observations can be understood by a specific decomposition reaction or dissolution being responsible for the capacity fading, primarily related to the time the battery is under operation and less dependent on cycle number. The BDA compound has a lot of time to dissolve or react chemically with the electrolyte or polymerize when cycling at C/40 or C/10, forming secondary products which increase the loss of material. The similarity between in capacity retention behaviour between C/40 and C/10 cycling can be due the rate constant of this decomposition reaction. When cycling at C/4 or at higher rates, on the other hand, there is less time for the

radicals to participate in side-reactions. It can also be noted that while the compound is losing capacity fast initially when at a slower rate, the performance is rather stable after approximately 20 cycles. However, when the compound is cycled faster, the capacity has a slow but constant decrease.

Similar electrochemical characterization was performed for the Li salt at three different C rates (C/20, C/2 and C), shown in Fig.12. In comparison with the Na salt, the Li salt has a different behavior. While the Na salt displays increasing capacity with increasing C rate, the capacity for the Li salt electrode decreases with increasing the C rate, similar to most inorganic electrode materials. Nevertheless, the capacity at a C/20 rate decreases with cycling also for the Li₂BDA electrode. The latter is an indication of possible side reactions of the Li salt, such as salt dissolution or decomposition. These side reactions are however slower, than in the case of the Na compound, and cycling at higher rates (shorter cycle time) provides better capacity retention.

Conclusions

A novel organic battery electrode material, Na₂BDA, has here been synthesized and compared to its Li homologue. The electrochemical behavior in Na-ion batteries has been investigated by first developing an appropriate electrolyte and exploring a useful operational potential window. It is clear from this study that design of Na-based carboxylate electrode materials constitutes additional challenges as compared to the Li-based, which display higher capacity and better capacity retention. On the other hand, Na₂BDA experience a higher initial coulombic efficiency, which is promising. This study thus clearly highlights that transferring from Li-based to Na-based battery chemistries is less straightforward, but involves an associated chemical complexity.

Nevertheless, although the Na-material likely undergoes dissolution or a decomposition reaction under battery operation, the capacity stabilizes at a value of ca. 40-50 mAh/g after an initial drop and display these values for >100 cycles. Moreover, a considerable amount of work has been conducted on Li₂BDA [24,25] to improve its particle size and electrode morphology, thereby achieving useful battery properties, and associated methods could well be investigated also for the Na-compound, for example tailoring the quantity of the carbon additive or exploring a wider range of possible Na-electrolytes [32]. Further research on the electrochemistry of these compounds can also give a better understanding of the mechanistic behavior during cycling.

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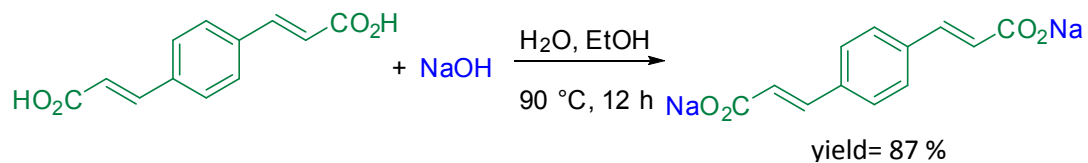


Fig. 1 Schematic diagram for the synthesis of disodium benzenediacylate.

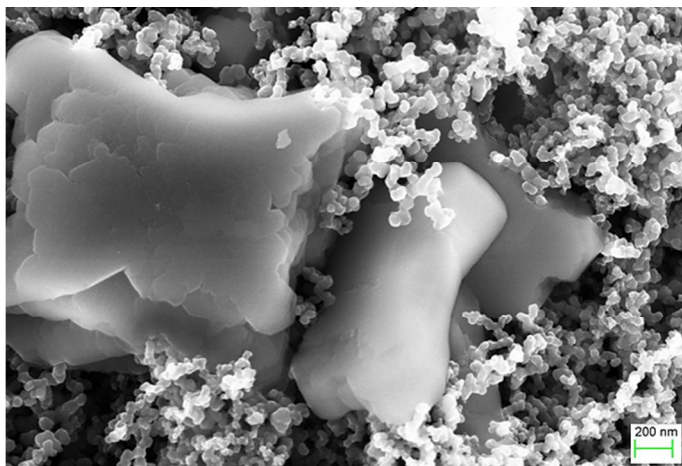


Fig. 2 SEM micrograph of an Na-battery electrode mixture of Na₂BDA and Carbon SP (33 wt%).

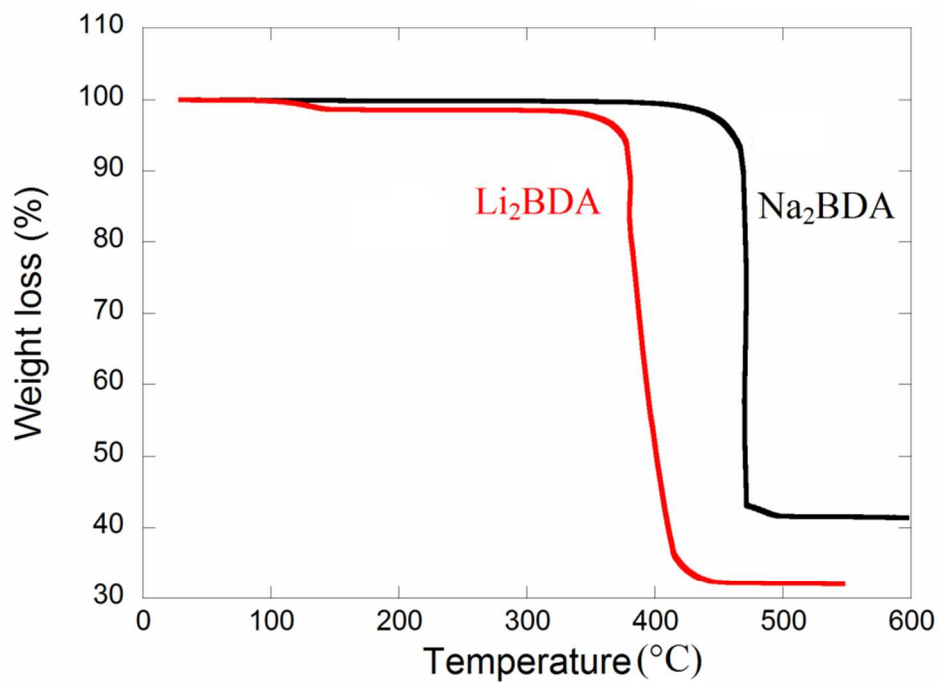


Fig. 3 TGA thermograms for Na₂BDA and Li₂BDA.

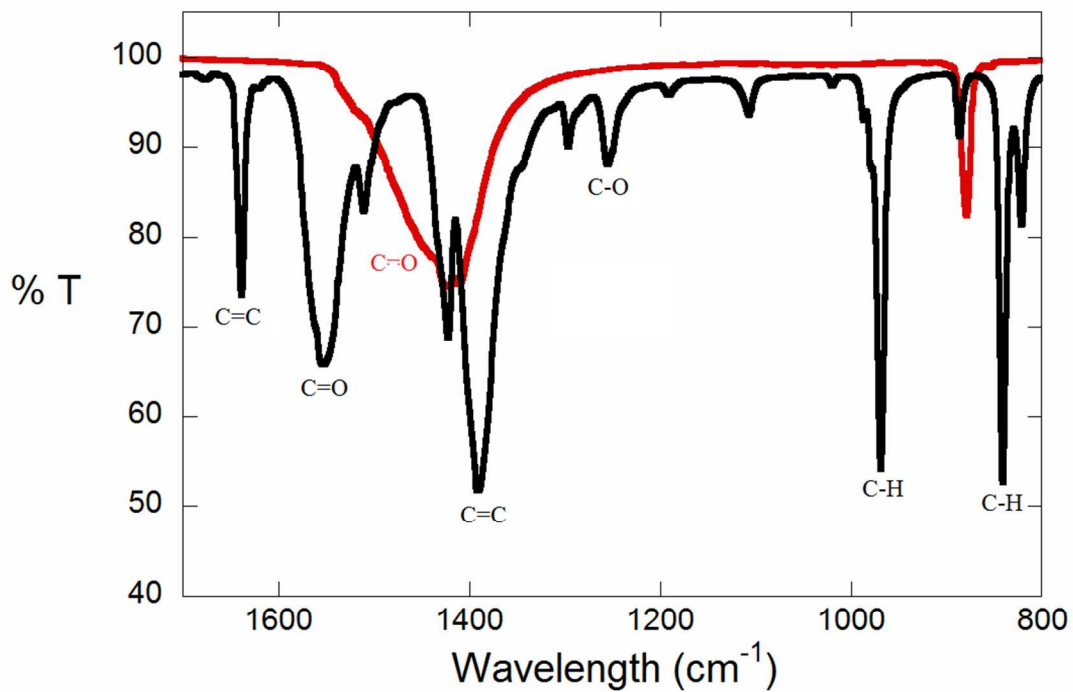


Fig. 4. IR spectra for Na₂BDA (black line) and its remains after pyrolysis at 600 °C (red line).

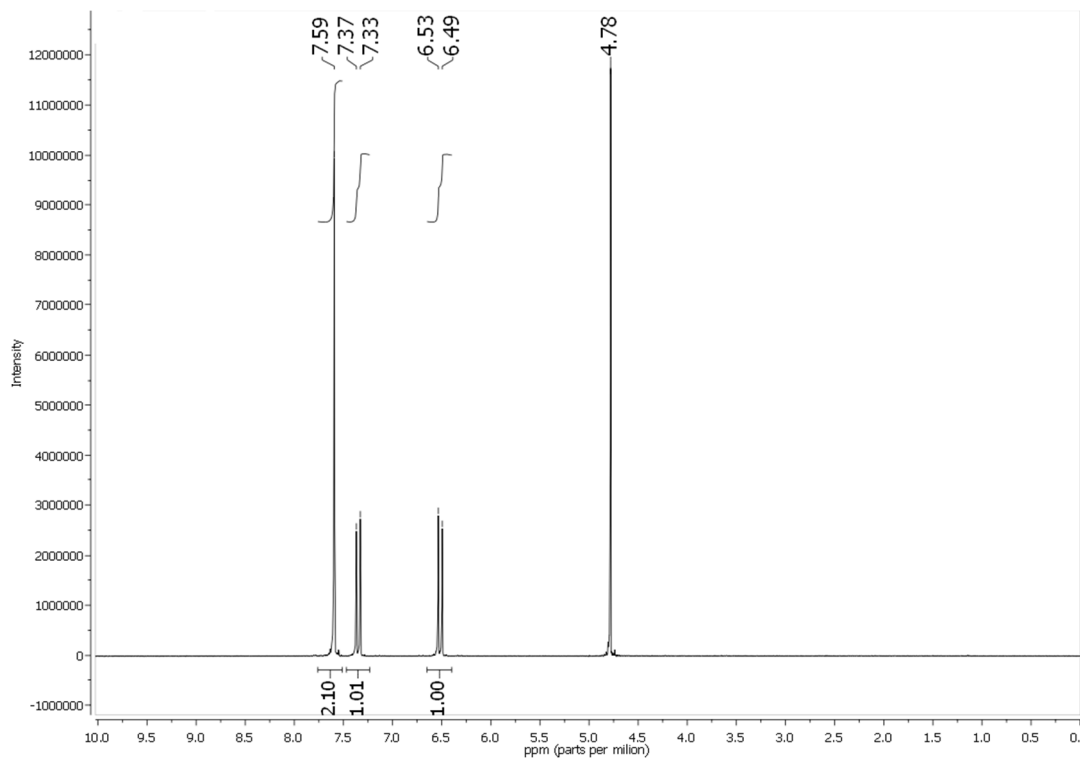


Fig. 5. ¹H-NMR spectrum of Na₂BDA in D₂O at 400 MHz

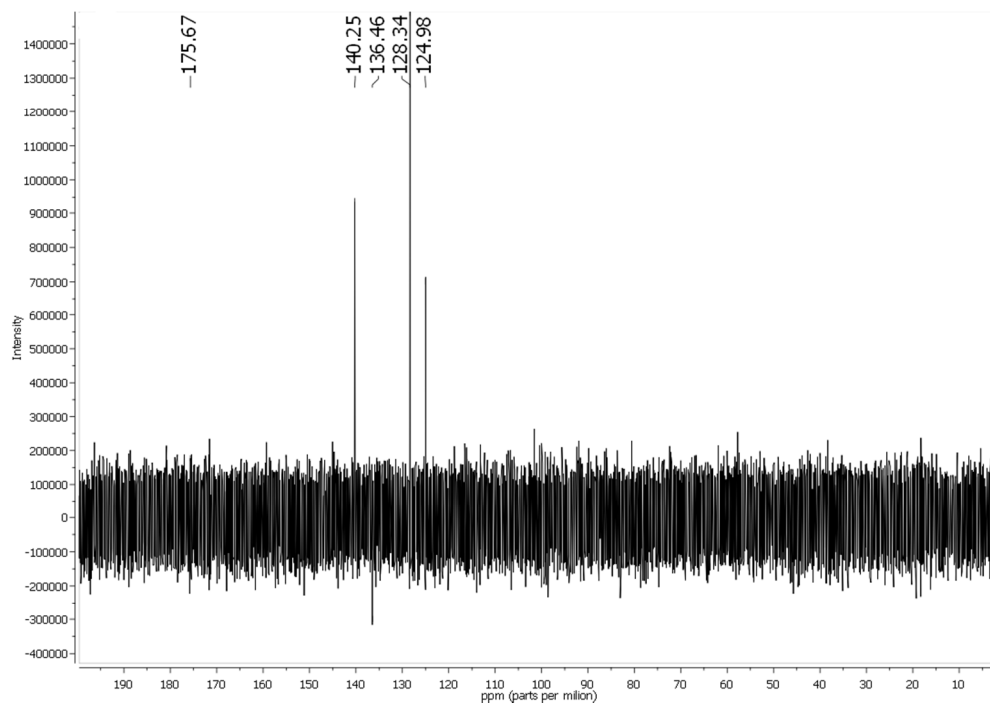


Fig. 6. ^{13}C -NMR apt (attached proton test) spectrum of Na_2BDA in D_2O at 100 MHz

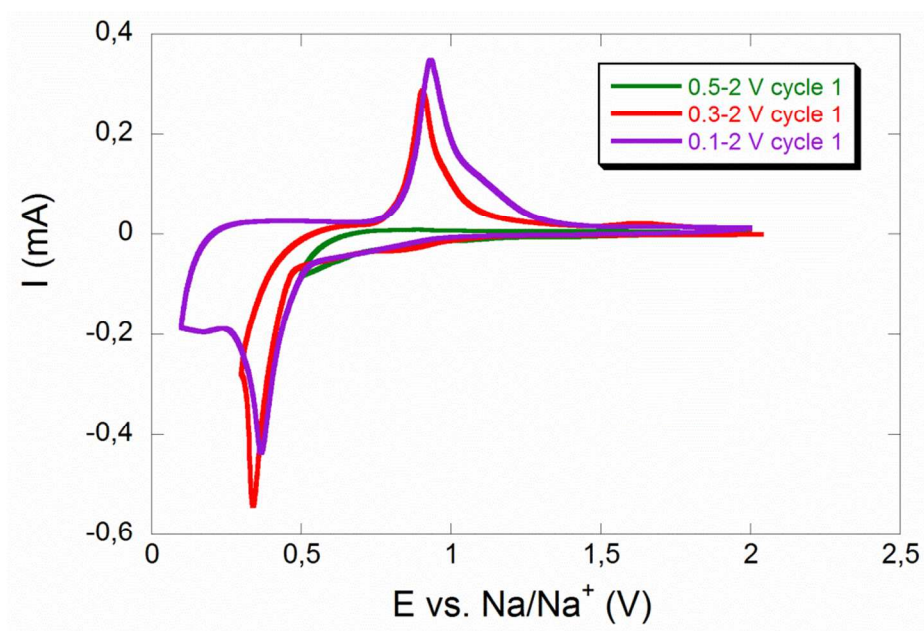


Fig. 7. Cyclic voltammograms of Na_2BDA at 0.1 mV/s, first cycle, for different cut-off potentials. All cycles started at ≥ 2 V.

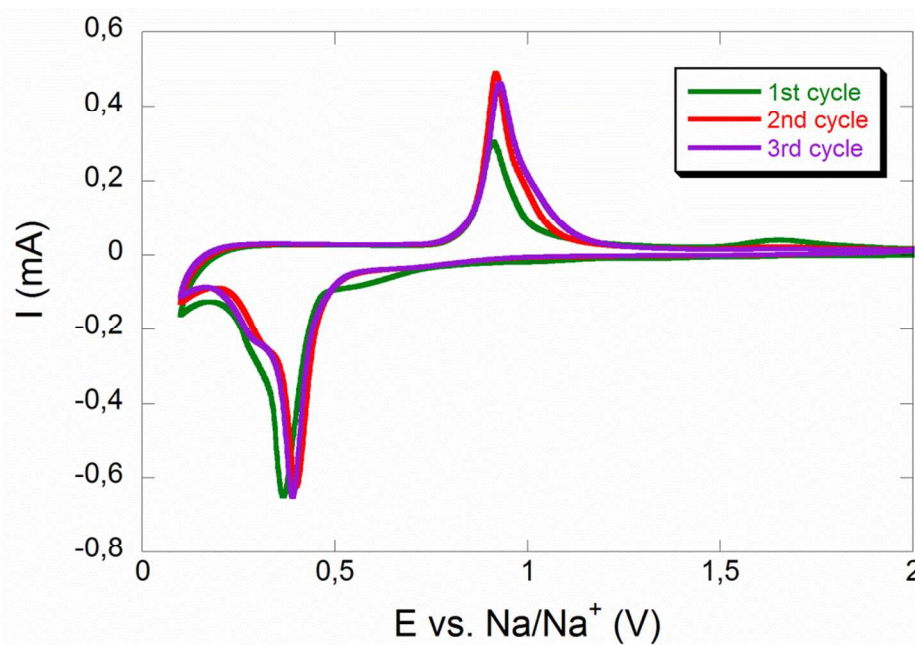


Fig 8. Cyclic voltammogram of Na₂BDA at 0.1 mV/s in the potential window 0.1-2 V *versus* Na/Na⁺ for the 3 first cycles. All cycles started at ≥ 2 V.

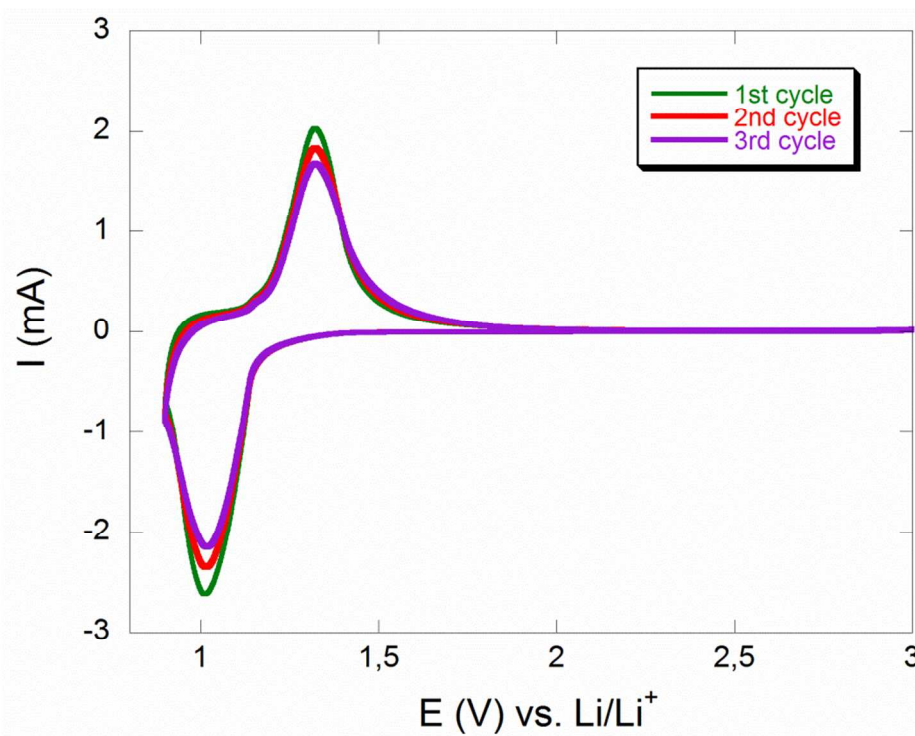


Fig. 9. Cyclic voltammogram of Li₂BDA at 0.1 mV/s in the potential window 0.9-3 V vs. Li/Li⁺ for the first 3 cycles. All cycles started at ≤ 3 V.

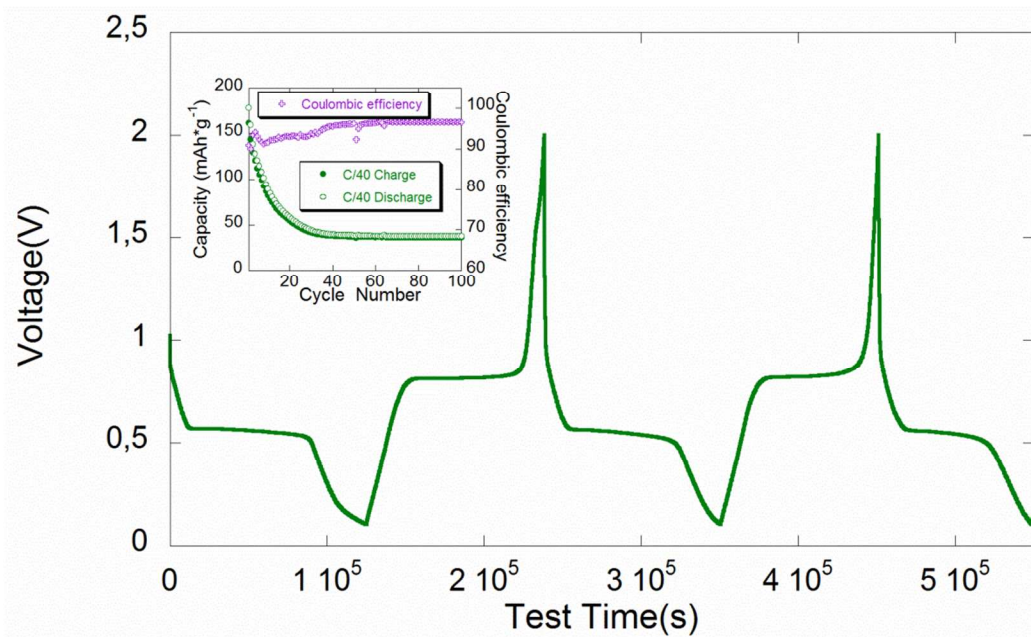


Fig. 10. Electrochemical behaviour of a Na|| Na₂BDA cycled galvanostatically between 0.1 and 2 V at a rate of 1 Na⁺/20 h (C/40) in 1 M NaFSI/EC:DEC. Inset: corresponding capacity and coulombic efficiency curves.

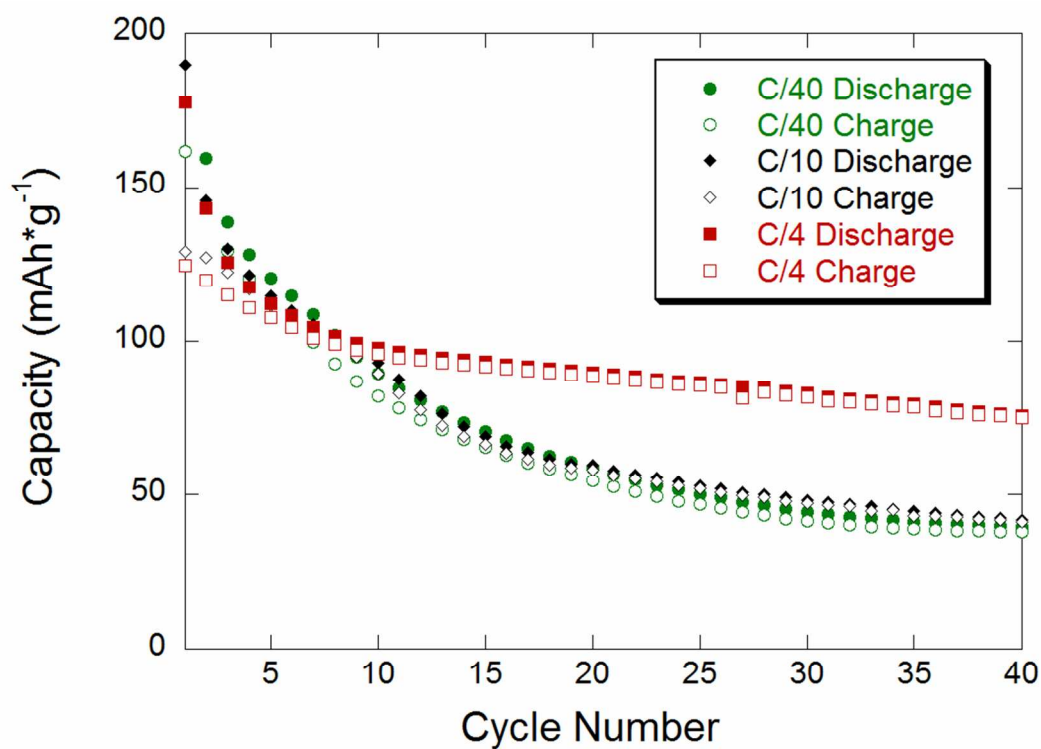


Fig. 11. Electrochemical behaviour of a Na|| Na₂BDA cycled galvanostatically between 0.1 and 2 V at a rate of 1 Na⁺/20 h (C/40), 1 Na⁺/5 h (C/10) and 1 Na⁺/2 h (C/4) in 1 M NaFSI/EC:DEC.

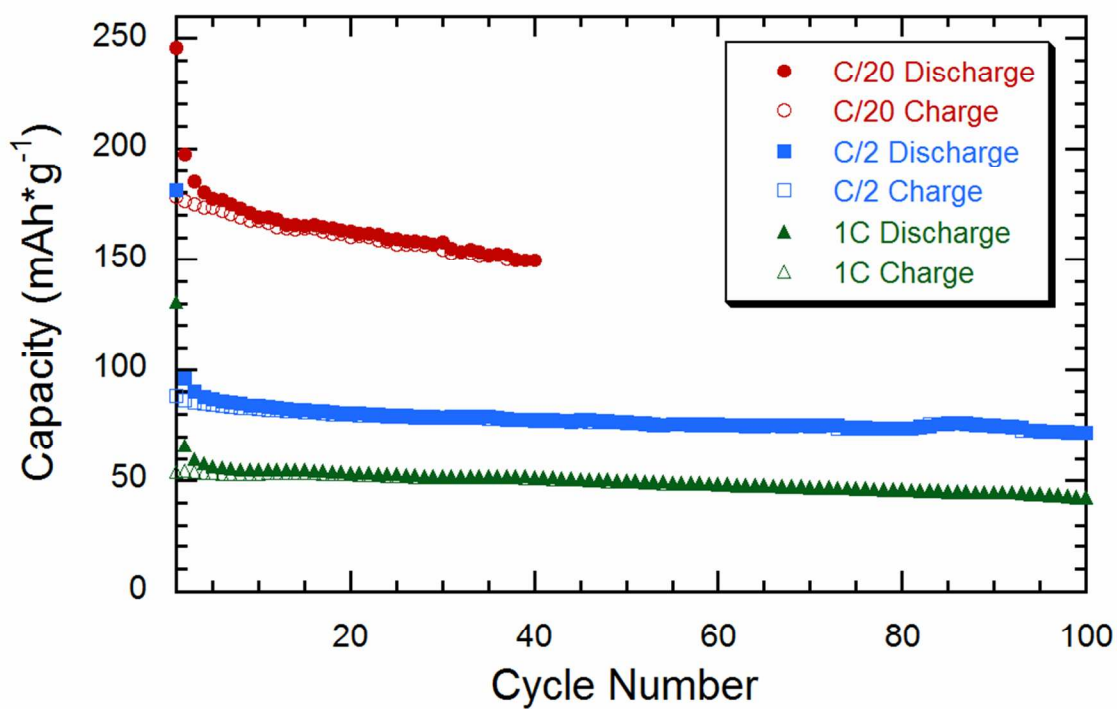


Fig. 12. Electrochemical behaviour of a Li|| Li₂BDA cycled galvanostatically between 0.9 and 3 V at a rate of 1 Li⁺/10 h (C/20), 1 Li⁺/1 h (C/2) and 1 Li⁺/0.5 h (1C) in 1 M LiTFSI in DMC.

Benzenediacylates as organic battery electrode materials: Na *versus* Li

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Abstract

This paper discusses investigations of a novel Na-based organic battery electrode material, disodium benzenediacylate (Na₂BDA) in comparison with its Li-ion homologue. Li₂BDA has previously shown promising battery properties, such as stable cycling and good capacity retention. Na₂BDA and Li₂BDA are here successfully synthesized and characterized, and investigated as anode materials in prototype Na- and Li-ion battery cells. Moreover, different electrolytes are screened for the Na-battery material, and a useful operating voltage window is explored. Na₂BDA is shown to possess a higher initial coulombic efficiency (91%) than the Li-homologue, which is uncommon for sodiated organic electrode materials. The Na-compound shows an initial capacity of 177.7 mAh/g, which however decreases to ca. 50 mAh/g after 20-100 cycles depending on cycling rate; a significantly lower capacity retention than that observed for Li₂BDA. The capacity loss can primarily be explained by a decomposition mechanism of the Na₂BDA compound.

Keywords: Na-ion batteries; Organic electrode materials; Electrolyte compatibility; Potential window

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