# Introduction of Carbonyl Groups: An Approach to Enhance Electrochemical Performance of Conjugated Dicarboxylate for Li-Ion Batteries

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A rational functionalization of conjugated dicarboxylate is reported here to enhance the cyclability and rate capability for Li-ion batteries. Introduction of carbonyl groups between aromatic rings is explored as an alternative way to extend  $\pi$ -conjugation. For the proof of concept, 4,4'-bis(lithiooxycarbonyl)benzil (Li<sub>2</sub>-BZL) was synthesized and compared its lithium storage performance against lithium [1,1'-biphenyl]-4,4'-dicarboxylate (Li<sub>2</sub>-BPDC). The Li<sub>2</sub>-BZL electrode delivers a stable capacity of 165 mAh g<sup>-1</sup> even after 50 cycles at current density of 50 mAh g<sup>-1</sup> whereas, rapid capacity fading was observed in the case of Li<sub>2</sub>-BPDC. Density functional theory (DFT) studies confirmed that the carbonyl groups in the Li<sub>2</sub>-BZL to reduce the bandgap, thereby improving the electrochemical lithium storage performance of Li<sub>2</sub>-BZL electrode in comparision to that of Li<sub>2</sub>-BPDC. (© 2017 The Electrochemical Society. [DOI: 10.1149/2.1581707jes] All rights reserved.

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Secondary lithium-ion batteries (LIBs) have ruled the portable electronic market for past two decades due to their high energy density and long cyclability.<sup>1,2</sup> However, the current inorganic electrode materials such as LiCoO<sub>2</sub>, LiFePO<sub>4</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> etc. are limited in natural abundance, expensive and toxic.<sup>3,4</sup> Use of these materials in huge quantity to meet the growing energy demand causes awful environmental anxieties. Therefore, it is important to explore new electrode materials to develop the next-generation LIBs for power sources in large-scale applications. Recently organic materials have received great attention, as alternative LIB electrode materials, due to their vast natural abundance, low cost synthesis, recyclability and easy molecular engineering.<sup>3–7</sup> Among several kind of redox organic materials, conjugated carboxylates have gained great attention as alternative anode materials for LIBs due to their suitable redox potentials (<1.2 V vs. Li/Li<sup>+</sup>) coupled with low polarization, less strain and low solubility in the electrolyte.4,8-18 However, their poor electronic conductivity limits their cyclibility and rate capability.<sup>3,4</sup> In order to enhance the electronic conductivity of an organic material, many strategies were reported in the literature. Electrode engineering such as compositing with CNTs, r-GO and extending the conjugation of the organic material are the reported ways to improve the electronic conductivity.<sup>9,10,16,18–21</sup> However, electrode engineering by adding the redox inactive conducting medium (like CNTs) reduces the energy density of the LIB. Extending conjugation in the redox active molecule decreases the theoretical specific capacity of the material by increasing molecular weight of the active material. 4,8,19,22,2

Considering all the above discussion, we have introduced redox active chromophoric (carbonyl) groups to reduce the bandgap of the conjugated carboxylate, which enhances the electronic conductivity by shifting the absorption maximum toward higher wave length. We herein introduced two carbonyl groups into the lithium [1,1'-biphenyl]-4,4'-dicarboxylate (Li<sub>2</sub>-BPDC) to yield 4,4'bis(lithiooxycarbonyl)benzil (Li<sub>2</sub>-BZL). The two carbonyl groups in the Li<sub>2</sub>-BZL not only decrease the bandgap but also increase the theoretical specific capacity (345 mAh g<sup>-1</sup>) in comparison to that of Li<sub>2</sub>-BPDC (211 mAh g<sup>-1</sup>). Moreover, the intermediate (Li<sub>4</sub>-BZL) formed upon lithiation of Li<sub>2</sub>-BZL extends the  $\pi$ -conjugation (Fig. 1), which facilitates the further lithiation thereby enhancing the electrochemical performance of the material. In this study we report, synthesis and electrochemical performance of Li<sub>2</sub>-BPDC and Li<sub>2</sub>-BZL as anode materials for LIBs.

## Experimental

*Materials.*—Absolute ethanol (Fisher Scientific), dimethyl [1,1'biphenyl]-4,4'-dicarboxylate (MBPDC, Sigma Aldrich), methyl 4formyl benzoate(Alfa Aesar), Glacial acetic acid (Alfa Aesar) and

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 $\rm LiOH.H_2O$  (Sisco Research Laboratories Pvt. Ltd.) were purchased and used without any further purification.

[1,1'-biphenyl]-4,4'-Synthesis.—Synthesis oflithium dicarboxylate (Li2-BPDC).-The Li2BPDC was prepared in two steps; in the first step, dimethyl 4,4'-biphenyl dicarboxylate (MBPDC) was converted into 4,4'-biphenyl dicarboxylic acid (BPDCA) followed by lithiation of BPDCA to yield Li2-BPDC (Scheme 1a). The detailed procedure is as follows; to the solution of MBPDC (600 mg, 2.22 mmol) in 40 mL acetic acid, 20 mL of 4:1 (v/v)  $H_2SO_4/H_2O$  solution was added. Then the reaction mixture was refluxed for 24 h at 120°C. The product was washed thoroughly with ethanol and dried in oven at 80°C overnight (Yield: 520 mg, 96.6%). In the second step, the obtained BPDCA (122 mg, 0.5 mmol) and LiOH.H2O (44 mg, 1 mmol) were added to absolute ethanol and stirred at 60°C for 12 h. The final product Li<sub>2</sub>-BPDC was washed thoroughly with absolute ethanol followed acetone and dried in vacuum oven at 100°C overnight (Yield: 119 mg, 93%, white crystalline powder). NMR spectra: (a) BPDCA. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): § 8.04 (d, 4H, 8.5 Hz, ArH), § 7.85 (d, 4H, 8.5 Hz, ArH). <sup>13</sup>C NMR (500 MHz, DMSO-d<sub>6</sub>): δ 167.52 (-COOH), δ 143.60 (Ar-C), δ 130.80 (Ar-C), δ 130.50 (Ar-C), δ 127.64 (Ar-C). (b) Li<sub>2</sub>-BPDC. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O): δ 7.98 (d, 4H, 8.5 Hz, ArH), δ 7.77 (d, 4H, 8.5 Hz, ArH). <sup>13</sup>C NMR (500 MHz, D<sub>2</sub>O): δ 175.34 (-COOLi), δ 142.40 (Ar-C), δ 135.60 (Ar-C), δ 129.52 (Ar-C), δ 126.87 (Ar-C).



Figure 1. Structural formulae of conjugated dicarboxylates.



Scheme 1. Synthesis of (a) Li<sub>2</sub>-BPDC and (b) Li<sub>2</sub>-BZL.

*Synthesis of 4,4'-bis(lithiooxycarbonyl)benzil (Li<sub>2</sub>-BZL).*—The Li<sub>2</sub>-BZL was synthesized by benzoin condensation and conversion to benzil ester,<sup>24</sup> which is hydrolyzed to corresponding carboxylic acid followed by lithiation (Scheme 1b). Detailed procedure of synthesis is as follows;

(i) Preparation of 4,4'-bis(methyloxycarbonyl)benzoin (2): 300 mg (4.6 mmol) of KCN was added to the solution of absolute ethanol (10 mL) and deionized water (3 mL) containing 2.5 g (15.2 mmol) of methyl 4-formyl benzoate (1). The reaction mixture was stirred for 25 min at room temperature to obtain light yellow colored precipitate.

The precipitate was washed with deionized water several times and dried at 70°C for 12 h followed by recrystallization from ethanol, which gave 1.5 g of 2 (Yield: 60%). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  8.10 (d, 2H, 8Hz, ArH),  $\delta$  8.01 (d, 2H, 7.5 Hz, ArH),  $\delta$  7.91 (d, 2H, 7.5 Hz, ArH),  $\delta$  7.56 (d, 2H, 7.5 Hz, ArH),  $\delta$  6.47 (s, 1H),  $\delta$  6.17 (s, 1H),  $\delta$  3.85 (s, 3H, -OCH<sub>3</sub>),  $\delta$  3.81 (s, 3H, -OCH<sub>3</sub>) <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 500 MHz):  $\delta$  199.03 (-C=O),  $\delta$  166.40 (-COO),  $\delta$  165.93 (-COO),  $\delta$  145.01 (Ar-C),  $\delta$  138.79(Ar-C),  $\delta$  133.75 (Ar-C),  $\delta$  130.70(Ar-C),  $\delta$  130.41(Ar-C),  $\delta$  129.79 (Ar-C),  $\delta$  129.67(Ar-C), 127.96(Ar-C),  $\delta$  76.16 (-C-OH),  $\delta$ 52.96 (-OCH<sub>3</sub>),  $\delta$  52.59 (-OCH<sub>3</sub>).

(ii) Preparation of 4,4'-bis(methyloxycarbonyl)benzil (**3**): To the solution of **2** (740 mg, 2.25 mmol) in dimethyl sulfoxide (10 mL), 3 mL of 48% hydrobromic acid was added under stirring. The reaction mixture was stirred at 55°C for 24 h followed by adding 20 mL deionized water. The obtained yellow colored precipitate was washed with water and dried at 70°C overnight (Yield of 3: 710 mg, 96.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.06 (d, 4H, 8.4 Hz, ArH),  $\delta$  7.93 (d, 4H, 8.4 Hz, ArH),  $\delta$  3.85 (s, 6H, -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  192.86 (-C=O),  $\delta$  165.81 (-COOH),  $\delta$  135.76 (Ar-C),  $\delta$  135.55(Ar-C),  $\delta$  130.16(Ar-C),  $\delta$  129.86 (Ar- C),  $\delta$ 52.65 (-OCH<sub>3</sub>).

(iii) Preparation of 4,4'-bis(hydroxycarbonyl)benzil (4): 10 mL of 4:1 (v/v)  $H_2SO_4/H_2O$  solution was added to the solution of **3** (300 mg, 0.92 mmol) in acetic acid (25 mL). The reaction mixture was refluxed and stirred for 10 h. Then 20 mL of deionized water was added and cooled in ice bath. The obtained pale yellow colored precipitate was washed with water and dried at 70°C overnight (Yield of 4: 270 mg, 93.7%). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  8.13 (d, 4H, 8.5 Hz, ArH),  $\delta$  8.06 (d, 4H, 8.5 Hz, ArH). <sup>13</sup>C NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  193.85 (-C=O),  $\delta$  166.78 (-COOH),  $\delta$  136.91(Ar-C),  $\delta$  135.50 (Ar-C),  $\delta$  130.56 (Ar-C),  $\delta$  130.52 (Ar-C).

(iv) Preparation of 4,4'-bis(lithiooxycarbonyl)benzil (5): 32 mg of LiOH.H<sub>2</sub>O was added to the mixture of **4** (100 mg, 0.33 mmol) and 15 mL of absolute ethanol. The reaction mixture was stirred at 60°C for 24 h. The obtained pale yellow color solution was concentrated under reduced pressure and washed with acetone several times to obtain a light yellow colored solid, which was dried in vacuum oven at 100°C overnight (Yield of 5: 95 mg, 91.3%). <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O):  $\delta$  8.02 (d, 4H, 8 Hz, ArH),  $\delta$  7.94 (d, 4H, 8 Hz, ArH). <sup>13</sup>C NMR (500 MHz, D<sub>2</sub>O):  $\delta$  130.20 (Ar-C),  $\delta$  129.23 (Ar-C).

Material characterization and electrochemical measurements. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at Bruker AVANCE 500 MHz spectrometer. The morphologies of the compounds Li<sub>2</sub>-BPDC and Li<sub>2</sub>-BZL were analyzed by a high resolution scanning electron microscope (HRSEM) FEI Quanta FEG 200. The working electrodes were prepared by coating slurry on copper foil. The slurry was obtained by mixing of 55 wt% of active material, 35 wt% of acetylene black (AB) and 10 wt% of polyvinylidene fluoride (PVDF) in Nmethyl-2-pyrrolidone (NMP). The loading of the active materials in the electrodes is  $\sim 2 \text{ mg cm}^{-2}$ . Swagelok cells were fabricated in argon filled glove box. Cells were galvanostatically cycled by using an Arbin BT-2000, galvanostat. The specific capacities were calculated by taking the active materials weight alone. Cyclic voltammetry (CV) were done using Biologic science instruments VSP model. The sample preparation for ex-situ <sup>13</sup>C NMR experimental procedure is as follows: two Swagelok cells were assembled with electrodes containing  $\sim 3$  mg of Li<sub>2</sub>-BZL and cycled at a current density 50 mA g<sup>-1</sup>. These cells were dismantled in the argon filled glove box after the first charge. The electrodes were cleaned and soaked in the dimethyl carbonate solvent for 24 h in order to remove the residual electrolyte from the electrode surface. Next, the dried electrodes were transferred to a vial containing 1 mL of D<sub>2</sub>O solvent and subjected to sonication to extract the active material into D<sub>2</sub>O, and then the vials were allowed to stand for 24 h. The supernatant solution was collected with a micro syringe to carry out <sup>13</sup>C NMR analysis. The optimized geometries and electronic properties (HOMO, LUMO and  $E_{p}$ ) of Li<sub>2</sub>-BPDC and Li<sub>2</sub>-BZL, Li<sub>4</sub>-BZL were computed by using Kohn-Sham density functional theory (DFT) in Gaussian 09 suite.

#### **Results and Discussion**

Both <sup>1</sup>H and <sup>13</sup>C NMR spectra (ESI, Fig. S1-S6) reveal the successful synthesis and purity of the Li<sub>2</sub>-BPDC and Li<sub>2</sub>-BZL materials. The morphologies of both Li<sub>2</sub>-BPDC and Li<sub>2</sub>-BZL samples were shown in Fig. 2. The SEM images of the Li<sub>2</sub>-BPDC and Li<sub>2</sub>-BZL reveal the formation of agglomerated micron sized pillar like particles. To verify our assumption that two carbonyl groups (chromophoric groups) in the Li<sub>2</sub>-BZL enhances the electronic conductivity by lowering the



Figure 2. HRSEM images of the Li2-BPDC (a, b) and Li<sub>2</sub>-BZL(c, d) at different magnifications.

bandgap in comparison to that of Li<sub>2</sub>-BPDC and the intermediate Li<sub>4</sub>-BZL formed upon lithiation of Li<sub>2</sub>-BZL facilitate further lithiation process, density functional theory (DFT) calculations were carried out at B3LYP/6-31G (d) level using Gaussian 09 program. The lowest-unoccupied molecular orbital (LUMO) energy of the Li<sub>2</sub>-BZL (-2.27 eV) is lower than that of Li<sub>2</sub>-BPDC (-1.25 eV) (Fig. 3), indicating easy electronic reduction of Li<sub>2</sub>-BZL (4.01 eV) versus Li<sub>2</sub>-BPDC (4.68 eV), indicates higher electronic conductivity of the former. In addition, bandgap (2.06 eV) of the intermediate Li<sub>4</sub>-BZL is further decreased, which enables further lithiation of the carbonyl group of the carboxylate in Li<sub>4</sub>-BZL into Li<sub>6</sub>-BZL.

Electrochemical lithiation/delithiation performance of samples (Li<sub>2</sub>-BPDC and Li<sub>2</sub>-BZL) were investigated by using two electrode Swagelok cells. Lithium metal disc served as both reference and counter electrode and a borosilicate glass fiber sheet separator soaked



Figure 3. Energy level diagram and frontier orbitals of Li<sub>2</sub>-BPDC, Li<sub>2</sub>-BZL and Li<sub>4</sub>-BZL generated from Gaussian 09 at B3LYP/ 6-31G (d) level.



Figure 4. Cyclic voltammograms of (a) Li<sub>2</sub>-BPDC and (b) Li<sub>2</sub>-BZL at a scan rate of 0.1 mV s<sup>-1</sup> in the potential window 0.5–3.0 V vs. Li/Li<sup>+</sup>.

with 1 M LiPF<sub>6</sub> in 1:1(v/v) of ethylene carbonate and dimethyl carbonate (EC&DMC) solution as the electrolyte. Fig. 4 depicts typical cyclic voltammograms (CV) of Li<sub>2</sub>-BPDC and Li<sub>2</sub>-BZL half cells. The CV curves of Li<sub>2</sub>-BPDC (Fig. 4a) shows a broad peak around 0.71 V (vs. Li/Li<sup>+</sup>) in the 1st cathodic scan and it is disappeared in the 2<sup>nd</sup> cycle, which could be ascribed to the irreversible formation of solid electrolyte interphase (SEI) layer. The peak around 0.6 V (vs. Li/Li<sup>+</sup>) during the 1<sup>st</sup> cathodic scan corresponds to insertion of Li-ions and the two anodic peaks around 0.75 and 1.0 V (vs. Li/Li<sup>+</sup>) suggest extraction of Li-ions from lithiated Li2-BPDC. In the case of Li<sub>2</sub>-BZL during the reduction a broad peak around 0.65 V (vs. Li/Li<sup>+</sup>) corresponding to lithiation and two oxidation peaks at 0.88 and 0.94 V (vs. Li/Li<sup>+</sup>) attributing to delithiation (Fig. 4b) were observed. It is widely accepted that multi-electron transfer electrochemical reaction to occur in multistep, but only a broad peak is observed in cathodic scans could be due to the merging of reduction peaks.<sup>15,25</sup>

Fig. 5a shows discharge-charge/voltage profiles of the Li<sub>2</sub>-BPDC in the potential window 0.5-3.0 V vs. Li/Li<sup>+</sup> at a current density of 50 mA  $g^{-1}$ . The specific capacity of 351 mAh  $g^{-1}$  is observed during the first discharge, which is more than the expected theoretical specific capacity of 211 mAh g<sup>-1</sup> for 2 Li<sup>+</sup> insertion. In addition, the first discharge process shows two regions: a slope between 1.5 to 0.8 V and a plateau at  $\sim 0.65$  V. The slope does not appear in the 2<sup>nd</sup> discharge onwards, which is ascribed to the formation of SEI layer. The plateau corresponds to the reaction of lithium with Li<sub>2</sub>-BPDC. The formation of SEI layer and insertion of Li<sup>+</sup> into conductive carbon could be the reasons for excess capacity observed in the first discharge, which is a general phenomenon for anode materials.<sup>4,9,10,14,17,19,21–23,28,29</sup> To account the AB contribution to the specific capacity of the electrode, discharge/charge cycling experiment has been carried out on the electrode containing 90 wt% of AB and 10 wt% of PVDF at a current density of 50 mA  $g^{-1}$  in the potential window 0.5–3.0 V (ESI, Fig. S7). The initial discharge and charge capacities are 190 and 61 mAh  $g^{-1}$  respectively. Considering the AB weight percentage (35%) in the Li2-BPDC and Li2-BZL electrodes, AB's contributes about 74 mAh  $g^{-1}$  during first discharge and 24 mAh  $g^{-1}$  during the first charge. Hence, the capacity corresponding to AB is very less in comparison to that of the total electrode after the first discharge. A capacity of 172 mAh g<sup>-1</sup> is noticed upon the first charge of lithiated Li<sub>2</sub>-BPDC with two plateaus at around 0.72 and 0.98 V. These results are well consistent with the observations from CV studies. A rapid capacity fading is noticed upon cycling and a capacity of only 80 mAh g<sup>-1</sup> retained after 50 cycles. On the other hand, at the same current density and potential window, the Li<sub>2</sub>-BZL delivers a capacity of 440 mAh g<sup>-1</sup> during the first discharge against theoretical specific capacity 345 mAh g<sup>-1</sup> for 4 Li<sup>+</sup> insertion (Fig. 5b). The differential capacity plots (ESI, Fig. S8) of Li2-BZL clearly show two step lithiation/delithiation mechanism and it supports our assumption that two reduction peaks are merged in the cathode scan of the CV profiles. It is to be noted that the carboxylate carbonyl groups (-COOLi) of the Li<sub>2</sub>-BZL do not undergo reduction (lithiation) unless the reduction of the carbonyl groups (dione) introduced between the two aromatic rings happens, otherwise, delocalization of the radical anion is not possible which will result in decomposition of the electrode material via dimerization. Hence, the first discharge must be a four-electron (lithium) transfer process. The frontier orbitals diagrams shown in Fig. 3 demonstrates that the electron density in the LUMO of Li<sub>2</sub>-BZL is more around the dione carbonyl groups than the carboxylate carbonyl groups, it supports the possibility of reduction of dione -C=O prior to the carboxylate -C=O. Unfortunately, during the first charge, a capacity of 185 mAh  $g^{-1}$  only observed, which upon correcting for AB's contribution reduces to 161 mAh g<sup>-1</sup>, corresponding to almost 1.9 Li<sup>+</sup> de-insertion (The theoretical capacity of Li<sub>2</sub>-BZL for 2 Li<sup>+</sup> de-insertion is 172). The extent of lithiation/delithiation of an organic material does not only depend on a number of active reduction centers present in the molecule but also on the crystal structure, as it is observed in the case of some conjugated carboxylates reported in the literature.<sup>14,23,29–31</sup> Therefore, the plausible lithiation/delithiation mechanism of Li2-BZL is a four-electron (lithium) transfer process during first discharge followed by a two-electron reversible process during the first charge and in the subsequent cycles (Scheme 2). However, a better reversibility and good capacity retention are observed after the first cycle. A reversible capacity of 165 mAh  $g^{-1}$  noticed even after 50 cycles, which is more than two times that of the Li<sub>2</sub>-BPDC. The obtained capacity retention with Li<sub>2</sub>-BZL is better than that of the similar extended  $\pi$ -conjugated system (lithium 4,4'-tolanedicarboxylate) reported by Walker et al. as anode material for LIBs.<sup>23</sup> In addition, there is a reduced polarization in the case of Li<sub>2</sub>-BZL in comparison to that of Li2-BPDC electrode. These results indicate that presence of the carbonyl groups in Li2-BZL has enhanced the cyclability and round trip energy by increasing electronic conductivity of the molecule. Moreover, the amount of lithium irreversible associated with Li2-BZL after its first discharge (as this leads to increase in the polarity) could also be one of the reasons for stable capacity by decreasing solubility. To probe the lithiation/delithiation mechanism of Li<sub>2</sub>-BZL, the ex-situ <sup>13</sup>C NMR studies were carried out on pristine



Figure 5. Discharge-charge/voltage profiles of (a)  $Li_2$ -BPDC, (b)  $Li_2$ -BZL at a current density of 50 mA  $g^{-1}$  and (c) cycling performance of  $Li_2$ -BPDC and  $Li_2$ -BZL at different current densities, (d) cyclability at a current density of 100 mA  $g^{-1}$ .

Li<sub>2</sub>-BZL and after the first charge (ESI, Fig. S9). The <sup>13</sup>C NMR spectra of the active materials obtained after the first charge does not have a peak around 196 ppm corresponding to dione carbonyl carbon, which confirms that only carboxylate carbonyl groups involve in the lithiation/delithiation process after first discharge and the lithium enolate (=C–OLi) groups corresponding to dione are inactive after first discharge as it is shown in the Scheme 2. The intensity of chemical shift corresponding to =C–OLi was below detectable limit probably due to the low abundance of <sup>13</sup>C carbon or/and increased noise obscured the peak.

In order to examine the impact of carbonyl groups on rate capability, the Li<sub>2</sub>-BPDC and Li<sub>2</sub>-BZL electrodes were subjected to discharge-charge cycling at various current densities (Fig. 5c). With increasing current density from 50 to 400 mA g<sup>-1</sup>, the specific capacity of Li<sub>2</sub>-BPDC decreases dramatically from 186 to 52 mAh g<sup>-1</sup>. In contrast, remarkably, the Li<sub>2</sub>-BZL electrode retains a capacity of 132 mAh g<sup>-1</sup> even at a high current density of 400 mA g<sup>-1</sup>. When the current density was back to 50 mA g<sup>-1</sup>, a capacity of 162 mAh g<sup>-1</sup> is recovered, which is 85% of the first charge capacity. Fig. 5d shows cyclability of both Li<sub>2</sub>-BPDC and Li<sub>2</sub>-BZL electrodes at a current density of 100 mA g<sup>-1</sup>. Most strikingly, the Li<sub>2</sub>-BZL electrode

delivers a reversible capacity of 150 mAh g<sup>-1</sup> with 99% of coulombic efficiency even after 70 cycles, which is a quite good capacity retention and cyclability of an organic anode material for LIBs without any detailed electrode optimization and engineering.<sup>4,11,16,19,32–35</sup> On the other hand, Li<sub>2</sub>-BPDC electrode retains a capacity of only 71 mAh g<sup>-1</sup> after 50 cycles. Hence, it is clear that the carbonyl groups in the Li<sub>2</sub>-BZL are capable of enhancing the capacity retention, cyclability as well as the rate capability.

### Conclusions

In conclusion, we have demonstrated a novel concept of introducing redox active carbonyl groups into conjugated dicarboxylates rather than extended  $\pi$ -conjugation to improve the electrochemical performance. The rationally designed Li<sub>2</sub>-BZL electrode delivers a capacity of 165 mAh g<sup>-1</sup> even after 50 cycles with low polarization and high coulombic efficiency. Remarkably, Li<sub>2</sub>-BZL shows superior rate capability and capacity retention in comparison to that of Li<sub>2</sub>-BPDC. This concept could be applicable to wide range of conjugated carboxylate anode materials for Li and Na-ion batteries.



Scheme 2. Plausible lithiation/delithiation mechanism of Li2-BPDC and Li2-BZL.

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