Alkaline Earth Metal Terephthalates $\text{MC}_8\text{H}_4\text{O}_4$ (M=Ca, Sr, Ba) as Anodes for Lithium Ion Batteries

Liping Wang, Chengxu Mou, Bo Wu, Jing Xue, Jingze Li^{*}

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

Abstract

Carboxylate-based metal organic frameworks are popular lithium storage electrode materials by using carbonyl groups as redox centers. In this study, alkaline earth metal terephthalates $\text{MC}_8\text{H}_4\text{O}_4$ (M=Ca, Sr, Ba) are prepared and applied as anodes for lithium ion batteries. The structure differences in terms of crystallography and molecular structures and electrochemical differences resulting from alkaline earth metal ionic radii are explored. It is found that electrostatic interactions between the alkaline metal cations and the terephthalate anions are important to the crystal structure, although these three organic matters consist of alternating layers of terephthalate anions and polyhedrally coordinated metal cations, but do not form iso-structure. Moreover, terephthalate salt with smaller cationic radius is featured with ionic bond behavior, lower discharge potential vs. Li/Li^+ and higher discharge capacity with good capacity retention behavior.

Keywords: Terephthalate salts, Metal-organic frameworks, Organic electrodes, Lithium ion batteries, Anodes

^{*} Corresponding authors. Tel.: +86 28 83207620; Fax: +86 28 83202569.

E-mail addresses: lijingze@uestc.edu.cn (J.Z. Li)

1. Introduction

Lithium ion battery technologies are flagships in the applications of portable electronics, electric vehicles, and possible grid storage. The commercial electrode materials are normally inorganic compounds, such as LiCoO_2 , $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-z}\text{O}_2$, LiFePO_4 , and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [1-5], which are partly expensive for limited mineral resource or toxic. With the increasing demand in market, it would be essential to develop eco-friendly, sustainable, and low-cost electrode materials. Organic materials are the leading contenders. Till now, organosulfur compounds, radical polymers, carbonyl compounds are the most reported organic electrodes [6-9]. Among them, carbonyl-based organic terephthalate salts are widely investigated due to easy synthesis, high thermal stability, moderate operational voltages (~ 0.8 V vs. Li/Li^+) [9-12]. The corresponding lithium storage/release mechanism is shown in **Scheme 1**, where the redox active center is carbonyl group $\text{C}=\text{O}$. In the charge process, the $\text{C}=\text{O}$ functional group absorbs Li^+ to form enol in companying with the acceptance of electron via external circuit for maintaining charge neutralization of the active material and vice versa in the discharge process [7, 13]. Apparently, the electrochemical energy storage mechanism is interpreted on the level of molecular structure.

As is known to us, the small molecular weight organic material exists in the form of crystalline generally, which can be indexed from the CCDC database (Cambridge Crystallographic Data Center). Considering the carbonyl-based terephthalates as shown in **Scheme 1**, the metal cations and the terephthalates anions are bonded together via electrostatic interactions to form metal organic frameworks (MOFs) with

high crystallinity [14-15]. Thus it is obvious that a single organic molecule could not elaborate all the lithium storage information, and the contribution from periodic crystal structure of organic electrode material should be included [7, 13, 16-17]. For example, how does the lithium ion transport in the MOFs structure, and what is the chemical environmental effects on the C=O functional groups so as to influence the operational voltage and kinetics? Can the crystalline structure be remained in the charge-discharge process? In a word, the structure-properties correlations still remain to be unveiled.

According to the literature, the inorganic electrodes such as LiFePO_4 [18] and CuF_2 [19] can form isostructural crystal by doping (metallic element exchanged by Mn, Fe *et al.*) while the electronic structure can be tuned leading to the optimized electrochemical properties including operational voltage and cycling performance. On the other hand, the conventional organic electrodes show improved electrochemical performances by virtue of isomeric effects [20], such as introducing heavy metal atoms [10] and grafting other chemical groups [21]. Inspired by these achievements, we here systematically study the alkaline earth metal terephthalates MTPA (M= Ca, Sr, Ba) for better understanding the composition-structure-property relationships. Their basic information of cation radius and theoretical capacity as anodes in lithium ion batteries is listed in **Table 1**. It is surprised to find that alkaline earth metal elements from the same main group of the periodic table bring in un-identical crystal structures and electrochemical properties in terms of cycling performance and operational voltage. Meanwhile, the intrinsic reasons are correspondingly elucidated.

2. Experimental section

2.1 Materials Synthesis

The preparation of calcium terephthalate ($\text{CaC}_8\text{H}_4\text{O}_4$, also named as CaTPA), strontium terephthalate ($\text{SrC}_8\text{H}_4\text{O}_4$, namely SrTPA) and barium terephthalate ($\text{BaC}_8\text{H}_4\text{O}_4$, denoted as BaTPA) are based on chemical displacement reactions of dilithium terephthalate ($\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$, namely Li_2TPA) with corresponding metal chlorides as shown in **Scheme 2**. Firstly, 0.02 mol $\text{LiOH}\cdot\text{H}_2\text{O}$ and 0.01 mol terephthalic acid ($\text{C}_8\text{H}_6\text{O}_4$) were dissolved in 100 ml de-ionized water under continuously stirring for 6 hours. Subsequently, stoichiometric amount of metal chlorides (CaCl_2 , SrCl_2 , and BaCl_2) was dissolved in water to form 0.1 mol/L solution, which was gently added to three bottles of Li_2TPA aqueous solutions under mechanical stirring at 80 °C. The resulting white sediments were filtered and washed for several times by water and ethanol in sequence. For preparing the dehydrate form of the terephthalate salts, the white powders were heated at 250 °C for 6 hours under argon atmosphere. Consequently, the final products of CaTPA, SrTPA, and BaTPA were obtained.

2.2 Materials characterization

The crystal structures of CaTPA, SrTPA, and BaTPA were identified by X-ray diffraction using Cu K α radiation (XRD, $\lambda=1.54056$ Å, X' Pert ProMPD) with a step size of 0.02° (2 θ) in the range from 5° to 70°. The molecular structures were analyzed by a Fourier Transform Infrared Spectrometer system (FTIR, IRrestige-21). A field-emission scanning electron microscope (FE-SEM, Hitachi, S3400N) was used for

morphology characterization. Thermo-gravimetric analysis (TGA) was conducted under nitrogen atmosphere at a heating rate of 10 °C/min from RT to 800 °C using a TA instrument Q500.

2.3 Cell assembling and electrochemical test

The electrodes were prepared by casting slurry of 60 wt% active material, 30 wt% carbon black conducting additive and 10 wt% PVDF binder in N-methyl-2-pyrrolidone (NMP) solution on Cu foil before dried in vacuum at 110 °C for 12 hours. Lithium foil and polypropylene (PP) membrane (Celgard 2400) were used as the counter/reference electrode and the separator, respectively. 1 M LiPF₆ was dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) as the electrolyte. Swagelok-type cells were assembled in an argon-filled glove box and cycled between 1.5 V and 3.0 V using a CT2001A cell test instrument (LAND Electronic Co.). The cyclic voltammetry (CV) curves were recorded at a scan rate of 0.08 mV s⁻¹ using Solartron SI1287 electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements were performed on half-cells at the open circuit voltage state prior to the charge/discharge test using an electrochemical workstation (CH Instruments, CHI660B). The amplitude of the a.c. signal was 5 mV in the frequency range of 10⁻² and 10⁵ Hz. All the measurements were carried out at room temperature. The weight density of the active materials was about 2 mg cm⁻².

3. Results and discussion

X-ray diffraction patterns of CaTPA, SrTPA, and BaTPA were collected as illustrated

in **Fig. 1a-c**. To gain detail information, structure refinements with a profile matching mode by a Fullprof-suite software [22-24] were conducted, and the corresponding refinement results are shown in **Fig. 1a-c**. All of these three terephthalate salts are pure phases. Consistent with the results of Mazaj *et al.* [25], the CaTPA can be indexed to space group C2/c, $a=18.833 \text{ \AA}$, $b=5.338 \text{ \AA}$, $c=6.956 \text{ \AA}$, $\beta=87.21^\circ$. SrTPA crystallizes in a monoclinic structure with space group P2₁/c (Lattice parameters: $a=7.260 \text{ \AA}$, $b=5.451 \text{ \AA}$, $c=20.378 \text{ \AA}$, $\beta=108.67^\circ$), as reported by Scholz and coworkers [26]. As for the BaTPA, it is well defined to orthorhombic structure with cell parameters of $a=7.802 \text{ \AA}$, $b=10.400 \text{ \AA}$, $c=18.910 \text{ \AA}$, complying with the previous study [27]. Their corresponding crystallographic structures are shown in **Fig. 1d-f**. It is obvious that these three well-crystallized terephthalate salts do not have analogous structural units, i.e., do not form isostructure. They are typical MOFs with alternating M-O inorganic layer and π -stacking organic terephthalate layer, but the atom packing modes are quite different for each compound. The distances between inorganic layer and organic layer are different, *i.e.* $9.42 \text{ \AA}$, $9.83 \text{ \AA}$, $9.21 \text{ \AA}$ for CaTPA, SrTPA, BaTPA, respectively. And the angles between inorganic plane and organic plane are 87.47° for CaTPA (view along b direction), 83.41° for SrTPA (view along b direction), 79.17° for BaTPA (view along a direction). Moreover, both Ca and Sr atoms form octahedrons with six neighbor oxygen atoms, while Ba atoms have decahedral coordination geometry with eight neighbor oxygen atoms. Note that the distortions in these polyhedrons are still un-identical as demonstrated in **Fig. 1g-i**. We ascribe the distinction on the crystallographic structure to the electrostatic interactions between

the cations and the terephthalate anions as Kaduk *et al.* found the similar phenomena in determining the crystal structures of alkaline metal terephthalates ($\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$, $\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$, $\text{K}_2\text{C}_8\text{H}_4\text{O}_4$) [28].

Based on the crystallographic structures of CaTPA, SrTPA, and BaTPA, their corresponding molecular structures with bond lengths are displayed in **Fig. 2a-c**. It can be seen that Ca^{2+} with smaller ionic radius has a stronger interaction with the carboxylate group, which results in the electron localized within two un-identical bonds of $-\text{COO}$ group (C=O double bond length is 1.19 Å and C-O single bond length is 1.38 Å). As a contrast, Sr^{2+} and Ba^{2+} with larger ionic radius can lead to the appearance of the resonant bonding in $-\text{COO}$ group, where both bond lengths of C=O and C-O are equal to 1.26~1.27 Å. The difference in bond length reflects that the coordination of Ca^{2+} toward $-\text{COO}$ ligand yields more likely ionic bond behavior compared with those almost covalent bond effect of Sr^{2+} and Ba^{2+} .

The molecular structures determine the vibrations of functional groups. Here the infrared spectra and characteristic vibration bands of MTPA are accordingly presented in **Fig. 2d** and **Table 2**, respectively. Neither compound shows the broad band of water molecule between 3200 and 3400 cm^{-1} (not shown here), confirming that no crystal water exists in our obtained phases [11]. Meanwhile, we observe no characteristic absorption peaks of terephthalic acid ($\text{C}_8\text{H}_6\text{O}_4$) (at 1671 cm^{-1} and 1420 cm^{-1}) and Li_2TPA (at 1569 cm^{-1} and 1390 cm^{-1}), demonstrating a complete chemical reaction has been done to produce pure phases of the desired compounds in our synthesis procedure. This is in line with our XRD results. The asymmetric stretching

vibrations of the carboxylate group $\nu_{\text{as-COO}}$ are located at $\sim 1550 \text{ cm}^{-1}$. It is found that the wave numbers for $\nu_{\text{as-COO}}$ have red shifts toward lower frequency side as the ionic radius of the cation is increased. This tendency is interpreted by a less conjugated behavior with similar bond lengths in the -COO group by the increased ionic radius in cations as demonstrated in the molecular structures of **Fig. 2a-c**. Vibration peaks at $\sim 510 \text{ cm}^{-1}$ give bending information between metal to neighbor oxygen atoms, denoted as $\delta_{\text{M-O}}$. It is no doubt that Ca-O bond has a higher electrostatic interaction than Sr-O and Ba-O due to the same charge but smaller radius and lighter atomic mass of the metal elements, consequently leading to $\delta_{\text{Ca-O}}$ (at 530 cm^{-1}) $>$ $\delta_{\text{Sr-O}}$ (507 cm^{-1}) $>$ $\delta_{\text{Ba-O}}$ (506 cm^{-1}).

The thermo-stability of CaTPA, SrTPA, and BaTPA was evaluated from RT to 800 °C under inert atmosphere (**Fig. 2e**). No noticeable weight loss is observed under 500 °C, which is an indication of the formation of dehydration compounds and pure phase for the as-synthesized metal terephthalate. The decomposition temperatures for CaTPA, SrTPA, and BaTPA are 550 °C, 590 °C, and 605 °C, respectively, which mean an increase in the decomposition temperature induced by the heavier metal elements. That is to say, the stronger interaction between the metal atom and the oxygen atom in -COO group does not make the higher thermal stability. It is well known that thermal decomposition is a process of breaking the chemical bonds of the target material, where the weakest bonding interaction determines the occurrence temperature of the decomposition process. Although Ca-O bond is stronger than Sr-O and Ba-O bonds according to FTIR data, the wavenumber difference between $\nu_{\text{as-COO}}$ and $\nu_{\text{s-COO}}$ is in

the sequence of $\Delta v_{\text{CaTPA}} > \Delta v_{\text{SrTPA}} > \Delta v_{\text{BaTPA}}$, where the peak position of $\nu_{\text{s-COO}}$ moves toward high frequency side slowly in the order of CaTPA, SrTPA and BaTPA as shown in Fig. 2d. These evidences suggest that $-\text{COO}$ group of CaTPA in the symmetric vibration mode might be relatively unstable with respect to that of SrTPA and BaTPA [29-30]. Supposing the bonding condition of benzene ring is same for all three compounds, the interaction variation concerning $-\text{COO}$ group can well explain the thermal stability tendency observed for MTPA ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$). Moreover, compared with the conventional organic electrodes [20], these three electroactive materials have a relative high decomposition temperature and provide more possibility to build safe batteries.

Fig. 3 shows the surface morphologies of CaTPA, SrTPA, and BaTPA by SEM imaging with different magnifications. They are plate shape particles with sizes of 5-30 μm , where a number of cracks are observed in the plates. According to our previous studies on MgTPA [31], CaTPA [32] and the recently reported CuTPA [33], we know that terephthalate salt easily leads to hydration form with the crystal structure different from that of the preliminarily synthesized one. That is to say, dehydration process triggers structural transformation and concomitantly brings in volume contraction/expansion with thus appearance of micro-cracks in the particles.

The electrochemical performances of CaTPA, SrTPA, and BaTPA were systematically studied. **Fig. 4a** depicts the typical galvanostatic discharge/charge curves for the first two cycles in voltage window 0.5 -2.8 V for CaTPA. In the discharge process, the CaTPA reveals a flat plateau at ~ 0.8 V vs. Li/Li^+ followed by a

two-phase reaction: $\text{CaC}_8\text{H}_4\text{O}_4 + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{CaC}_8\text{H}_4\text{O}_4$. While for the charge process, the capacity-voltage curves are asymmetric, delivering a sloppy curve. This phenomenon suggests that the charge process might not follow a conventional two-phase reaction to directly transform the fully lithiated $\text{Li}_2\text{CaC}_8\text{H}_4\text{O}_4$ into the completely delithiated $\text{CaC}_8\text{H}_4\text{O}_4$, where an intermediate crystalline phase such as $\text{LiCaC}_8\text{H}_4\text{O}_4$ might be formed. However, there are no two voltage plateaus observed. As a part of future work, further experimental evidence is required to gain deep insight into the lithiation/delithiation mechanism. In fact, Armand [11] and other researchers [16, 34-35] observed similar cases in the electrochemical tests of $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$, $\text{NaC}_8\text{H}_4\text{O}_4$, $\text{Li}_2\text{C}_{18}\text{O}_8\text{H}_{12} \cdot 4\text{H}_2\text{O}$, and so on. Chen and coworkers ascribe this to be appearance of an intermediate phase that consists of alternating layers of occupied lithium and un-occupied lithium ion in the inserted structure by dispersion-corrected density functional theory method [16]. As for the initial coulombic efficiency of CaTPA, it is only 35%, which is a typical value for the organic electrodes [7, 36], although the electrolyte decomposition and/or formation of solid electrolyte interphase (SEI) film are not severe in this voltage window. The defects in crystal structure and formation of dangling bonds on the particle surface in the synthesis procedures as well as electrochemical kinetics limitations fruiting lithium-trapped in the active material could be the routes.

The typical cyclic voltammetry test at the same scan rate of 0.08 mV s^{-1} is performed for MTPA (**Fig. 4b**). A sharp cathodic peak and a broader anodic peak confirm the asymmetric redox process. In terms of the operation voltage, a lower

operational voltage vs. Li/Li^+ could theoretically reflect the existence of the stronger electrostatic interaction between M^+ and -COO^- as it is more difficult to break the C=O bond and regroup the electrons into a set of new π -bonds. It is interesting to find that this hypothesis is complying with our experimental CV results. Actually, the introduction of longer organic ligand units and making full use of the isomeric effect to modify the electronic structure thus to tune the operational voltage have been proven to be effective ways [20-21].

The cyclic performance with a function of cycling number was recorded and the results are shown in **Fig. 4c**. In the first several cycles, the capacity for all the three materials decays a lot because of an activation process and dissolution of active materials in electrolytes. While in all, the CaTPA has the best cycling performance with the highest discharge capacity, from 170 mAh g^{-1} at the 5th cycle to 155 mAh.g^{-1} at the 50th cycle with a capacity fading rate of 0.19% per cycle. Regarding SrTPA, the discharge capacity of 122 mAh g^{-1} at the 5th cycle decreases to 91 mAh g^{-1} after 45 cycles with a capacity fading rate of 0.56% per cycle. In terms of the BaTPA, its fading rate is 0.26% per cycle from 149 mAh g^{-1} (5th) to 131 mAh g^{-1} (50th cycle). According to our Inductively Coupled Plasma Mass Spectrometry (ICP-MS) study, the solubility of CaTPA, SrTPA, and BaTPA in EC-DMC solvents for one month at 45 °C are 13.3 mg L^{-1} , 40.5 mg L^{-1} , 1.10 mg L^{-1} . The high solubility of SrTPA partly accounts for its bad capacity retention behavior especially at the early stage. On the other hand, the rate performances of MTPA were also tested (**Fig. 4d**). A rise in the current rate depresses the discharge capacities mainly due to the kinetic limitation,

where as the capacities can be recovered when the current goes back to a lower value (*i.e.* 13.7 mA g⁻¹ in our case). Among these three materials, CaTPA delivers the best rate performance and SrTPA presents the worst. According to the theoretical calculations, the discharge capacity of SrTPA (213 mAh g⁻¹) is supposed to be between CaTPA (263 mAh g⁻¹) and BaTPA (178 mAh g⁻¹), while in the real case, SrTPA has a lower discharge capacity especially at high current density than both CaTPA and BaTPA. From the electrochemical impedance spectroscopy at open circuit voltage 3.0 V (**Fig. 4e**), the SrTPA has the largest charge transfer resistance and the BaTPA has the smallest one. The charge-transfer resistance provides the information of electron transfer rate between the electrolyte and electrode, revealing kinetic information of Li⁺ ion storage/release, which can be well explained by rate performance of MTPA electrode. In all, besides the difference in charge/discharge capacity caused by the variable molecular weights of these MTPA compounds, the variation in electrochemical properties including cycling performance and rate performance are mainly owing to their dissolution in electrolytes and the kinetic limitations. As the kinetic limitations are mainly from the intrinsic properties of the organic matters (lithium ion diffusivity, the band gap, etc.), we believe that the designing/modifying of advanced organic electrode materials with novel molecular/crystal structure are quite intriguing under the guidance of theoretical simulation. On the other hand, it needs to be mentioned here that the electrochemical performance of these organic electrode materials can be optimized by minimizing the particle sizes for shortening lithium ion diffusion routes and/or adding conducting

additives (e.g. graphite [37], carbon [38], silver metal particles) for better kinetics and preventing direct contact with the electrolyte for prolonged cyclic lifetime.

4. Conclusions

We have synthesized pure phases of alkaline metal earth terephthalates CaTPA, SrTPA, and BaTPA *via* eco-friendly and facile displacement reactions. Their lithium storage behaviors are unveiled. The electrostatic interactions between the metal cations and terephthalate anions are the main factors to different crystallography and molecular structures as well as different electrochemical properties in terms of capacity, operational voltage, cyclic lifetime and rate performance. This study provides a better understanding of the correlation among composition-structure-electrochemical properties, which will shed light on the design of new organic material with advanced performance. It is no doubt that a variety of organic compounds can be applied to fabricate flexible/stretchable battery and/or transparent battery for driving wearable intelligent device in the future. Alternatively, taking into account of its cheaper price and low volume energy density, organic battery might be suitable for large scale energy storage such as stationary power station.

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References

- [1] H. Li, Z. Wang, L. Chen, X. Huang, Research on advanced materials for Li-ion batteries, *Adv Mater* 21 (2009) 4593.
- [2] A.K. Padhi, K. Nanjundaswamy, J. Goodenough, Phospho - olivines as positive - electrode materials for rechargeable lithium batteries, *J Electrochem Soc* 144 (1997) 1188-1194.
- [3] J.B. Goodenough, Y. Kim, Challenges for rechargeable Li batteries, *Chem Mater* 22 (2009) 587-603.
- [4] K. Zaghib, M. Simoneau, M. Armand, M. Gauthier, Electrochemical study of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as negative electrode for Li-ion polymer rechargeable batteries, *J Power Sources* 81 (1999) 300-305.
- [5] H.Q. Zhang, Q.J. Deng, C.X. Mou, Z.L. Huang, Y. Wang, A.J. Zhou, J.Z. Li, Surface structure and high-rate performance of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated with N-doped carbon as anode material for lithium-ion batteries, *J Power Sources* 239 (2013) 538-545.
- [6] Z. Song, Y. Qian, T. Zhang, M. Otani, H. Zhou, Poly(benzoquinonyl sulfide) as a High-Energy Organic Cathode for Rechargeable Li and Na Batteries, *Adv Sci* 2 (2015).
- [7] B. Häupler, A. Wild, U.S. Schubert, Carbonyls: Powerful Organic Materials for Secondary Batteries, *Adv Energy Mater* 5 (2015) 1402034.
- [8] Z. Song, H. Zhou, Towards sustainable and versatile energy storage devices: an overview of organic electrode materials, *Energy Environ Sci* 6 (2013) 2280-2301.
- [9] Y. Liang, Z. Tao, J. Chen, Organic electrode materials for rechargeable lithium batteries, *Adv Energy Mater* 2 (2012) 742-769.
- [10] L.P. Wang, H.Q. Zhang, C.X. Mou, Q.L. Cui, Q.J. Deng, J. Xue, X.Y. Dai, J.Z. Li, Dicarboxylate $\text{CaC}_8\text{H}_4\text{O}_4$ as a high-performance anode for Li-ion batteries, *Nano Res* 8 (2015) 523-532.
- [11] M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribiere, P. Poizot, J.M. Tarascon, Conjugated dicarboxylate anodes for Li-ion batteries, *Nat Mater* 8

- (2009) 120-125.
- [12] N. Ogihara, T. Yasuda, Y. Kishida, T. Ohsuna, K. Miyamoto, N. Ohba, Organic Dicarboxylate Negative Electrode Materials with Remarkably Small Strain for High- Voltage Bipolar Batteries, *Angew Chem Int Edit* 53 (2014) 11467-11472.
- [13] H. Kim, D.-H. Seo, G. Yoon, W.A. Goddard, III, Y.S. Lee, W.-S. Yoon, K. Kang, The reaction mechanism and capacity degradation model in lithium insertion organic cathodes, $\text{Li}_2\text{C}_6\text{O}_6$, using combined experimental and first principle studies, *J Phys Chem Lett* 5 (2014) 3086-3092.
- [14] D. Banerjee, J.B. Parise, Recent Advances in s-Block Metal Carboxylate Networks, *Crystal Growth & Design* 11 (2011) 4704-4720.
- [15] K. Hernandez-Burgos, S.E. Burkhardt, G.G. Rodriguez-Calero, R.G. Hennig, H.D. Abruna, Theoretical Studies of Carbonyl-Based Organic Molecules for Energy Storage Applications: The Heteroatom and Substituent Effect, *J Phys Chem C* 118 (2014) 6046-6051.
- [16] Y. Chen, Z. Wu, S. Sun, First-principles study of an ethoxycarbonyl-based organic electrode material of lithium battery, *The Journal of Physical Chemistry C* 118 (2014) 21813-21818.
- [17] H.H. Lee, Y. Park, S.H. Kim, S.-H. Yeon, S.K. Kwak, K.T. Lee, S.Y. Hong, Mechanistic Studies of Transition Metal-Terephthalate Coordination Complexes upon Electrochemical Lithiation and Delithiation, *Adv Funct Mater* 25 (2015) 4859-4866.
- [18] B. Zhang, X. Wang, H. Li, X. Huang, Electrochemical performances of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ with high Mn content, *J Power Sources* 196 (2011) 6992-6996.
- [19] F. Wang, S.-W. Kim, D.-H. Seo, K. Kang, L. Wang, D. Su, J.J. Vajo, J. Wang, J. Graetz, Ternary metal fluorides as high-energy cathodes with low cycling hysteresis, *Nat Commun* 6 (2015).
- [20] S. Gottis, A.L. Barres, F. Dolhem, P. Poizot, Voltage gain in lithiated enolate-based organic cathode materials by isomeric effect, *Acs Appl Mater Inter* 6 (2014) 10870-10876.
- [21] A. Shimizu, H. Kuramoto, Y. Tsujii, T. Nokami, Y. Inatomi, N. Hojo, H. Suzuki, J.

- Yoshida, Introduction of two lithiooxycarbonyl groups enhances cyclability of lithium batteries with organic cathode materials, *J Power Sources* 260 (2014) 211-217.
- [22] L.P. Wang, H. Li, X.J. Huang, E. Baudrin, A comparative study of Fd-3m and P4332 “ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ”, *Solid State Ionics* 193 (2011) 32-38.
- [23] L.P. Wang, H. Li, M. Courty, X.J. Huang, E. Baudrin, Preparation and characterization of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ thin films taking advantage of correlations with powder samples behavior, *J Power Sources* 232 (2013) 165-172.
- [24] L.P. Wang, H.Q. Zhang, Q.J. Deng, Z.L. Huang, A.J. Zhou, J.Z. Li, Superior rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2/\text{C}/\text{CNTs}$ composites via microemulsion-assisted method as anodes for lithium ion battery, *Electrochim Acta* 142 (2014) 202-207.
- [25] M. Mazaj, G. Mali, M. Rangus, E. Zunkovic, V. Kaucic, N.Z. Logar, Spectroscopic studies of structural dynamics induced by heating and hydration: a case of calcium-terephthalate metal-organic framework, *J Phys Chem C* 117 (2013) 7552-7564.
- [26] G. Scholz, F. Emmerling, M. Dreger, E. Kemnitz, Mechanochemical synthesis and characterization of hydrated and dehydrated crystalline strontium terephthalates, *Z Anorg Allg Chem* 639 (2013) 689-693.
- [27] S. Lo, S. Chui, I. Williams, Barium terephthalate, a three-dimensional coordination polymer with 7: 7 cation–anion connectivity, *Acta Crystallogr C* 54 (1998) 1846-1848.
- [28] J.A. Kaduk, Terephthalate salts: salts of monovalent cations, *Acta Crystallogr B* 56 (2000) 474-485.
- [29] G.P. Panasyuk, L.A. Azarova, M. Khaddaj, G.P. Budova, I.L. Voroshilov, T.V. Grusha, A.D. Izotov, Preparation and properties of sodium, potassium, magnesium, calcium, and aluminum terephthalates, *Inorg Mater* 39 (2003) 1292-1297.
- [30] P. Larkin, *Infrared and Raman spectroscopy - principles and spectral interpretation*, Elsevier, Amsterdam, 2011.
- [31] Z.L. Huang, L.P. Wwang, C.X. Mou, J.Z. Li, Magnesium terephthalate as an organic anode material for Sodium ion batteries, *Acta Phys-Chim Sin* 30 (2014)

1787-1793.

- [32] L.P. Wang, C.X. Mou, Y. Sun, W. Liu, Q.J. Deng, J.Z. Li, Structure-property of metal organic frameworks calcium terephthalates anodes for lithium-ion batteries, *Electrochim Acta* 173 (2015) 235-241.
- [33] G. Panasyuk, L. Azarova, G. Budova, A. Savost'Yanov, Copper terephthalate and its thermal decomposition products, *Inorg Mater* 43 (2007) 951-955.
- [34] S.W. Wang, L.J. Wang, Z.Q. Zhu, Z. Hu, Q. Zhao, J. Chen, All organic sodium-Ion batteries with $\text{Na}_4\text{C}_8\text{H}_2\text{O}_6$, *Angew Chem Int Edit* 53 (2014) 5892-5896.
- [35] L. Zhao, J. Zhao, Y.-S. Hu, H. Li, Z. Zhou, M. Armand, L. Chen, Disodium Terephthalate ($\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$) as High Performance Anode Material for Low-Cost Room-Temperature Sodium-Ion Battery, *Adv Energy Mater* 2 (2012) 962-965.
- [36] S.W. Wang, L.J. Wang, K. Zhang, Z.Q. Zhu, Z.L. Tao, J. Chen, Organic $\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$ nanosheets for lithium-ion batteries, *Nano Lett* 13 (2013) 4404-4409.
- [37] C.X. Mou, L.P. Wang, Q.J. Deng, Z.L. Huang, J.Z. Li, Calcium terephthalate/graphite composites as anode materials for lithium-ion batteries, *Ionics* 21 (2015) 1893-1899.
- [38] H.Q. Zhang, Q.J. Deng, A.J. Zhou, X.Q. Liu, J.Z. Li, Porous $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$ coated with N-doped carbon by using CVD as an anode material for Li-ion batteries, *J Mater Chem A* 2 (2014) 5696-5702.

Figure Captions

Scheme 1 Lithium storage mechanism of carbonyl-based terephthalates at molecular structure level.

Scheme 2 Synthesis routes for $\text{MC}_8\text{H}_4\text{O}_4$ (M=Ca, Sr, Ba).

Fig. 1 (a-c) XRD patterns and their refinements with observed data points (black points), calculated data (red line), Bragg positions (blue bars), difference (green line) for MTPA, Crystallography structures of CaTPA (d), SrTPA (e), BaTPA (f), (g-i) M (Ca, Sr, Ba)-O polyhedron information in the inorganic layer of $\text{MC}_8\text{H}_4\text{O}_4$.

Fig. 2 Molecular structures with bond length information of CaTPA (a), SrTPA (b) and BaTPA (c), (d) Fourier transform infrared spectra of MTPA, (e) Thermogravimetric analysis of MTPA from RT to 800 °C under argon atmosphere.

Fig. 3 SEM images of (a-b) CaTPA, (c-d) SrTPA and (e-f) BaTPA under different magnifications.

Fig. 4 (a) Galvanostatic charge-discharge curves of CaTPA for the first two cycles, (b) typical cyclic voltammetry curves of MTPA at a scan rate of 0.08 mV/s, cycling performance (c) and rate performance (d) of MTPA, (e) electrochemical impedance spectroscopy of MTPA at open circuit voltage 3.0 V.

Table 1 Basic information of MTPA (M= Ca, Sr, Ba)

Materials	Ionic radius (pm)	Molecular weight	Theoretical capacity/mAhg ⁻¹
CaTPA	Ca ²⁺ (100)	204.13	263
SrTPA	Sr ²⁺ (118)	251.75	213
BaTPA	Ba ²⁺ (135)	301.43	178

Table 2 Characteristic vibration bands of MTPA

Materials	ν_{as}/cm^{-1}	ν_s/cm^{-1}	$\delta(\text{O-M})/\text{cm}^{-1}$
CaTPA	1608	1397/1360	530
SrTPA	1552	1397	507
BaTPA	1532	1397	506