Solvents adjusted pure phase CoCO_3 as anodes for high cycle stability

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Abstract: CoCO_3 with high theoretical capacity has been considered as a candidate anode for the next generation of lithium-ion batteries (LIBs). However, the electrochemical performance of CoCO_3 itself, especially the cyclic stability at high current density, hinders its application. Herein, pure phase CoCO_3 particles with different particle and pore sizes were prepared by adjusting the solvents (diethylene glycol, ethylene glycol, and deionized water). Among them, CoCO_3 synthesized with diethylene glycol (DG-CC) as the solvent shows the best electrochemical performance owing to the smaller particle size and abundant mesoporous structure to maintain robust structural stability. A high specific capacity of 690.7 mAh/g after 1000 cycles was achieved, and an excellent capacity retention was presented. The capacity was contributed by diverse electrochemical reactions and the impedance of DG-CC under different cycles was further compared. Those results provide an important reference for the structural design and stable cycle performance of pure CoCO_3 .

Keywords: lithium ion battery (LIB); cobalt carbonate; solvothermal method; morphological control; solvent; pure phase

1 Introduction

Out of the concern for energy and environment, lithium-ion batteries (LIBs) have been widely studied because of their high energy density, low pollution, and compatibility with existing equipment [1–4]. In the

aspect of anode material, it is expected that the commercially used graphite can be replaced because of its rather low specific capacity (372 mAh/g) and the hidden danger of lithium dendrite in the process of charge and discharge [5]. The conversion reaction materials [6], such as transition metal oxides (TMOs) and transition metal carbonates (TMCs), have attracted wide attentions due to their higher specific capacity [7–9] and better security than intercalation type anodes [10–12]. Moreover, TMCs show two obvious advantages

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over TMOs: (1) easier preparation technology (carbonate is often used as the precursor of oxides, which means that the utilization of carbonates can bring about shortening technological process and cost reduction); (2) improved properties (TMCs have even higher specific capacity owing to an additional step of lithium storage reaction provided by CO_3^{2-} [13–16]). Among the carbonates, CoCO_3 has a high theoretical capacity (1577 mAh/g) and the electrochemical reaction process of CoCO_3 can be described by the following two-step chemical reactions [17]:

In addition, some additional structural designs based on cobalt carbonate as the main active material have been carried out to further improve the electrochemical properties [18–22]. Common strategies include: (1) preparing composites with carbon material or conductive polymer [17,23,24]; (2) controlling the shape of CoCO_3 particles by morphology directing agent [25]; and (3) doping of other elements in CoCO_3 [26]. However, these strategies such as doping and compounding themselves create additional problems. Since overmuch carbon materials in the composites might lower tap density, the energy density of the overall composites is whittled down. In addition, these strategies inevitably lead to additional raw materials and tedious process procedures, thus increasing manufacturing costs [27–29]. In a nutshell, the particle structure is considered to be one of the key factors to determine the performance of an anode [30]. Du *et al.* [31] reported the shape control of CoCO_3 crystals by switching the volume ratio of ethylene glycol and water in the mixed solvent, leading to the morphological change from cantaloupe-like patterns to microcubes. Furthermore, Zhao *et al.* [25] compared the electrochemical performance of CoCO_3 with bulk rhombohedra shape and dumbbell shape, which were synthesized in the absence or presence of ascorbic acid, respectively. With high specific surface area, low charge transport resistance, and stable structure, the dumbbell-like CoCO_3 exhibited higher capacity and better cycling performance. Other structural design of carbonates, such as rambutan-like FeCO_3 hollow microspheres [32], submicron peanut-like MnCO_3 also exhibited good electrochemical performance [33]. At present, almost all the preparation of cobalt carbonate

are involved with hydrothermal or solvothermal method, which suggests that solvent plays an important role on controlling the structure of cobalt carbonates. However, the detailed study on the influence of solvent has been reported barely.

Herein, a facile solvothermal route with different solvents was achieved, and thus three kinds of bare CoCO_3 particles with generally consistent structure but different particle and pore sizes were prepared. Corresponding to the applied solvents of diethylene glycol, ethylene glycol, and deionized water, the products are respectively named as DG-CC, EG-CC, and DW-CC. As a result, the cobalt carbonate prepared from diethylene glycol (DG-CC) has a high specific capacity of 690.7 mAh/g at 1 A/g after 1000 cycles, and a high capacity retention with 92.45%. In fact, it is very rare for a pure cobalt carbonate electrode to have such a stable capacity after 1000 cycles, which is attributed to the structure of the particles adjusted by solvents. Such an example in our work can provide an important reference for the structural design of various anode materials in LIBs.

2 Experimental

2.1 Synthesis of DG-CC, EG-CC, and DW-CC

Three cobalt carbonate samples (DG-CC, EG-CC, and DW-CC) were obtained by solvothermal method with different solvents (diethylene glycol, ethylene glycol, and deionized water, respectively). Typically, 1 mmol $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and 10 mmol NH_4HCO_3 were dissolved in a total of 30 mL of solvent at room temperature. By applying repeated ultrasound and agitation, the solute can be dissolved as soon as possible. After the reactants were completely dissolved, the red solution was transferred to a 45 mL Teflon-lined stainless-steel autoclave and maintained at 200 °C for 15 h. All solvothermal products were washed by centrifugation with deionized water and ethanol three times to remove impurities. After dried at 60 °C, DG-CC, EG-CC, and DW-CC were prepared.

2.2 Material characterization

X-ray diffraction (XRD) patterns of three cobalt carbonate samples were obtained by a D&A25ADVANCE using $\text{Cu K}\alpha$ radiation. The morphologies of as-prepared CoCO_3 samples were examined with a FEI Quanta

200F and a JEM-2100. The thermogravimetric analysis (TGA) was performed on a DTG-60H thermal analyzer under air flow at a rate of 10 °C/min. Chemical state information was studied by using the X-ray photoelectron spectroscopy (XPS) measurement performed on an ESCALAB 250Xi. The specific surface area and pore size distribution were determined based on Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda model, respectively.

2.3 Electrochemical characterization

The CoCO_3 electrodes were prepared by laminating the mixed slurry composed of 80 wt% CoCO_3 , 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride. After the slurry was mixed evenly, it was coated on copper foils, and these foils were cut into discs of 14 mm in diameter. After dried in a vacuum oven at 110 °C overnight, the loading density of these electrodes is around 1.5 mg/cm². The electrodes were assembled into CR2032 coin-cells in an argon filled glovebox, with Li foil as the counter electrode and a microporous polyethylene film (Celgard 2400) as the separator. The electrolyte was 1 M LiPF_6 dissolved in a 1:1:1 mixture of ethylene carbonate, diethyl carbonate, and dimethyl carbonate. The assembled cells were charged and discharged with a voltage range of 0.01–3 V using a cell test system (LAND CT2001A). Cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) data were measured on a CHI760E electrochemical workstation operated in the voltage range of 0.01–3 V at a scan rate of 1×10^{-4} V/s and in the frequency range of 0.01–100 kHz, respectively.

3 Results and discussion

XRD patterns are shown in Fig. 1, in which DG-CC, EG-CC, and DW-CC show the same diffraction peaks. All the diffraction peaks are matched to the standard peaks of CoCO_3 (JCPDS No. 11-0692). The diffraction peaks at 25.1°, 32.6°, 38.6°, 42.7°, 46.5°, 53.8°, 66.1°, and 69.9° correspond to the (012), (104), (110), (113), (202), (116), (214), and (300) reflections of the rhombohedral CoCO_3 phase, respectively, and none impurity phase is observed in these samples [34]. Moreover, based on the Debye–Scherrer equation, the grain size of the obtained CoCO_3 particles prepared in the DG, EG, and DW solutions is 43.1, 19.25, and 227 nm, respectively. TGA curves (Fig. S1 in the

Fig. 1 XRD patterns of DG-CC, EG-CC, and DW-CC.

Electronic Supplementary Material (ESM)) demonstrated the thermal behaviors of the CoCO_3 samples. The curves first undergo a slow decline, corresponding to the evaporation of water in these materials. In the period of 250–400 °C, all of the CoCO_3 samples lost ~33.0% mass, which is consistent with the following chemical reaction:

XPS spectra of DG-CC, EG-CC, and DW-CC are displayed in Fig. S2 in the ESM. Because DG-CC, EG-CC, and DW-CC are the same phase, DG-CC was selected as a typical sample for XPS analysis. In the survey XPS spectrum (Fig. S2(a) in the ESM), the peaks of O 1s, C 1s, and Co 2p are clearly observed, revealing the coexistence of O, C, and Co elements. The Co 2p_{1/2} and Co 2p_{3/2} peaks located at 797.9 and 782.5 eV with two prominent shake-up satellite peaks at 802.7 and 787.4 eV (Fig. S2(d) in the ESM), respectively. A spin-orbital splitting of 15.4 eV between the Co 2p_{1/2} and Co 2p_{3/2} peaks is the characteristic feature for the presence of Co^{2+} .

Figure 2 shows the morphologies of three CoCO_3 samples at different scales. Scanning electron microscopy (SEM) pictures are displayed in Figs. 2(a)–2(c), in which CoCO_3 particles are all ellipsoidal with angular surfaces. According to the statistical data in Figs. 2(g)–2(i) and S3 in the ESM, the average particle sizes of DG-CC, EG-CC, and DW-CC are 0.85, 1.67, and 3.48 μm, respectively. Moreover, the particle size distribution of DG-CC is relatively concentrated, in comparison with DW-CC. Further observation shows that these CoCO_3 particles appear to be assembled by smaller particles, which is further confirmed by the transmission electron microscopy (TEM) pictures (Figs. 2(d) and 2(e)). The sizes of primary particles in DG-CC, EG-CC, and DW-CC are about 20, 100, and

Fig. 2 SEM and TEM images in detail and particle size distribution of (a, d, g) DG-CC, (b, e, h) EG-CC, and (c, f, i) DW-CC.

300 nm, respectively, which have the similar size relationship with the secondary particles. The specific surface areas of DG-CC, EG-CC, and DW-CC measured by BET are also different (Fig. S4(a) in the ESM), which are 51.37, 45.71, and 29.58 m²/g, respectively. In addition, the secondary particles of DG-CC, EG-CC, and DW-CC possess mesopore structure with average pore diameters of 4.2, 4.6, and 22.7 nm, respectively (Fig. S4(b) in the ESM). These large specific surface and mesoporous structures are conducive to the penetration of electrolyte and the shortening of ion transport path. For the above results, from preparation to product morphology, a schematic diagram of summary is shown in Fig. 3. As the only variate in the preparation process, these differences among the three CoCO₃ samples should be attributed to the different nature of the solvents. Specifically, the value of permittivity could reflect the polarity of solvent, which are 31.8, 41.4, and 80.1 F/m for DG, EG, and DW, respectively. Meanwhile, the viscosity values of DG, EG, and DW are 30.2, 16.1, and 0.89 mPa·s, respectively. High viscosity is unfavorable for the migration of ions in the solvent, thus decreasing the

growth rate of particles [31]. Thus, the lower polarity and higher viscosity of solvent may lead to slower ion diffusion rate and reaction kinetics, which are favorable for the generation of more crystal nucleus and simultaneously inhibit the rapid growth of particles. The value of permittivities can reflect polarity of solvent, and permittivity of DG, EG, and DW are increased in turn. Meanwhile, the viscosity values of DG, EG, and DW are decreased in turn. As a result, DG-CC prepared from the solvent with the lowest polarity and the highest viscosity among the three possesses the smallest primary and secondary particles. In addition, due to the slow chemical reaction rate, the particles of DG-CC are more uniform and smaller, inducing a larger specific surface area. By contrast, DW-CC has a high speed to generate, so the particle size is very uneven. The above standpoint is also confirmed by the phenomenon in the preparation process. The time for dissolution of solutes (Co(Ac)₂ and NH₄HCO₃) in DG-CC, EG-CC, and DW-CC are increased in turn. Besides, the time required for the reaction to produce the phase of cobalt carbonate is 8 h, 2 h, and 15 min for DG-CC, EG-CC, and DW-CC,

respectively. Below this time, no product can be collected in the autoclaves (Fig. S5 in the ESM). These results imply that although solvents are not generally considered as reactants, they actually affect the process of solvothermal reaction and bring about obvious differences in morphology, which eventually lead to

different electrochemical performance.

CV is often used to observe the electrochemical reaction potential and speculate the species change during the reaction. CV curves of the first five cycles of DG-CC, EG-CC, and DW-CC are shown in Figs. 4(a)–4(c), in which the three kinds of cobalt

Fig. 3 Schematic illustration of the as-synthesized DG-CC, EG-CC, and DW-CC.

Fig. 4 CV curves of (a) DG-CC, (b) EG-CC, and (c) DW-CC. (d) Galvanostatic discharge–charge profiles for the first cycle. (e) Cycling performance at 0.1 A/g. (f) Rate performance and (g) Long cycle performance at 1 A/g of the three CoCO_3 samples. (h) Comparison of our DG-CC with previous works.

carbonate have basically similar peaks. In the first cycle, a sharp anode peak at 0.6–0.7 V is observed for the three CoCO_3 samples, corresponding to the formation of the solid electrolyte interface (SEI) and the reduction of Co^{2+} (Reaction (1)). Then, the reduction peak splits into two main peaks centered at around 1.0 and 0.8 V in the following cycles, which are attributed to the reduction of Co^{2+} to Co^0 and C^{4+} to lower valence C in CO_3^{2-} (Reaction (2)), respectively [17]. Two main anodic peaks of the three CoCO_3 samples are observed at around 1.2 and 1.9 V, which are attributed to the oxidation of low-valence C (C^{x-}) and Co^0 , respectively. Moreover, in the larger version of the charging process in Fig. S6 in the ESM, only a small oxidation peak at ~2.6 V in the CV curves of the three CoCO_3 materials can be observed, corresponding to the reversible oxidation of $\text{Co}^{2+}/\text{Co}^{3+}$, coincident with the previous reports [15]. It can be noted that the peaks corresponding to Reaction (2) are relatively inconspicuous for DW-CC, implying insufficient reaction during the electrochemical process.

To further evaluate the lithium storage properties of the DG-CC, EG-CC, and DW-CC, cycling tests of the three CoCO_3 samples are carried out. Discharge–charge profiles in Fig. 4(d) revealed that the initial discharge/charge capacities at 0.1 A/g for DG-CC, EG-CC, and DW-CC are 1478.6/1054.6, 1748.0/1168.5, and 1512.9/1116.9 mAh/g, respectively, and the corresponding initial coulombic efficiencies (ICEs) are 71.32%, 66.84%, and 73.82%. The initial irreversible capacity loss is mainly attributed to the formation of the SEI layer. According to the initial discharge capacity, it can be inferred that 4.7–5.2 Li was involved in per CoCO_3 in the first cycle. In terms of capacity, this value indicates that the typical conversion process involved the $\text{Co}^{2+}/\text{Co}^0$ is not the only reaction contributing capacity, which is consistent with the CV analysis. As shown in Fig. 4(e), the electrochemical properties of the cobalt carbonates are measured at 0.1 A/g for 200 cycles. In the first 20 cycles, the specific capacity of the three materials decreases rapidly due to the structural adjustment and slight volume expansion, and the charge capacities for DG-CC, EG-CC, and DW-CC are 904.3, 861.5, and 612.1 mAh/g, respectively. Then, the curves tend to be stable and the value of coulombic efficiencies (CEs) are close to 100% in the following cycles. Following, the specific capacity of the three materials begin to rise, which may be due to the growth of a polymeric gel-like film originating from

kinetic activation of the electrode [35]. After 200 cycles, the discharge/charge capacities for DG-CC, EG-CC, and DW-CC achieve 960.0/957.2, 857.5/851.9, and 829.6/821.6 mAh/g, respectively. Rate performance of DG-CC, EG-CC, and DW-CC is shown in Fig. 4(f). The sample DG-CC delivers the highest capacity with average specific capacity of 1014, 841, 711, 595, and 476 mAh/g at current densities of 0.1, 0.2, 0.5, 1, and 2 A/g, respectively. When the current density returns to 0.1 A/g, the specific capacity returns to 889 mAh/g. After the rate measurements, the cycling test was conducted at a current density of 0.5 A/g, and the sample DG-CC still exhibits a high reversible capacity of 660 mAh/g. And for the EG-CC and DW-CC, they deliver lower specific capacities than DG-CC with the increased current densities, demonstrating a gradient relationship (DG-CC > EG-CC > DW-CC).

Most importantly, the three CoCO_3 samples also show excellent cycle stabilities at a high current density. After the activation for initial 3 cycles at 0.1 A/g and then tested at 1 A/g, the specific capacity of all the CoCO_3 samples goes through the process of rising in the beginning and then keeping stable (Fig. 4(g)). The specific discharge/charge capacity of DG-CC, EG-CC, and DW-CC is 692.6/690.7, 383.1/382.8, and 295.6/295.0 mAh/g after 1000 cycles, respectively. Specially, the DG-CC shows the best cycling performance with high retention ratio of 92.45% (based on the stable capacity of 20th cycle). Comparison of our CoCO_3 samples and other previous anode materials in which cobalt carbonate is the main component is summarized in Fig. 4(h) and Table S1 in the ESM. The reference points of green, orange, purple, and blue in Fig. 4(h) correspond to cobalt carbonates of pure, compounding, doped, and both doped/compounding, respectively. The ability of DG-CC to withstand repeated charge and discharge under large current density is better than that of most cobalt carbonate materials, and the capacity of DG-CC at 1 A/g even exceeds the samples compounding with other conductive carbon or doped materials. At the same time, the ICE of the DG-CC (71.32%) prepared in this study is also at the upstream level. All of the above results show the superiority of DG-CC as an anode material for LIB.

To further analyze the performance difference of the three materials, the differential charge vs. voltage plots and corresponding charging curves are conducted to identify the voltage platform and polarization behavior

Fig. 5 (a) Differential charge vs. voltage plots based on 20th and 1000th charging process and (b) their corresponding charge profiles. (c) Capacity contribution and (d) the corresponding ratio of each region in the 20th and 1000th cycle for DG-CC, EG-CC, and DW-CC, respectively.

at 1 A/g. The corresponding dQ/dV curves of the three samples are shown in Fig. 5(a). At the 20th and 1000th cycles, three peaks at ~1.3, ~2.0, and ~2.5 V reveal a three-step electrochemical reaction process which is consistent with the CV curves in Figs. 4(a)–4(c). Therefore, the voltage can be divided into three regions. Region 1 from 0 to 1.63 V corresponds to the oxidation of $\text{C}^{\text{x-}}$, Region 2 from 1.63 to 2.26 V corresponds to the oxidation of Co^0 , and Region 3 from 2.26 to 3 V corresponds to the transition of $\text{Co}^{2+}/\text{Co}^{3+}$ according to the result of CV curves. Based on the charge profiles in Fig. 5(b), different voltage ranges correspond to different capacity contributions. The concrete capacity contribution in different regions of the three materials in different cycles is summarized in Table S2 in the ESM and further expressed as Fig. 5(c). At the beginning of the cycle, little difference between DG-CC and EG-CC in performance could be found, but the difference is obvious when reaching the 1000th cycle. For DG-CC, capacity contributed from the three regions is similar for the 20th and 1000th cycle. However, the capacity provided by these three electrochemical reactions for EG-CC and DW-CC are greatly reduced compared with that of DG-CC, suggesting superior structural stability of DG-CC. Except for the absolute value of capacity, Fig. 5(d) further shows the contribution ratio statistics of different regions. Compared with the case

at the 20th cycle, it is obvious that the main reason for capacity declination at the 1000th cycle is the decrease of capacity contribution of Regions 1 and 2. The decrease in reversibility may be due to the structural instability caused by the repeated volume changes during cycling. Theoretically, Reactions (1) and (2) involve more lithium ions, but the transition of $\text{Co}^{2+}/\text{Co}^{3+}$ in Region 3 only corresponds to 1 equivalent lithium ion. Therefore, the volume effect is more serious in Regions 1 and 2. What is more, once the previous reaction becomes inadequate, the remaining reactants in the subsequent cycle will reduce. This kind of chain effect makes the capacity continue to decline. However, DG-CC shows better stability than EG-CC and DW-CC, which indicate its structural superiority. The particle size and pore size brought by different solvents should be the key to affect the electrochemical performance.

To further confirm the above conjecture, the morphologies of the three kinds of electrodes before and after 1000 cycles are displayed in Figs. 6 and S7 in the ESM. The typical particles are selected as the specimens for analysis, which are shown in the upper-right corners of each images. Particles in fresh electrodes of DG-CC, EG-CC, and DW-CC distribute uniformly across the whole film surfaces (Figs. 6(a)–6(c) and S7(a)–S7(c) in the ESM). The smaller nanoparticles scattered around CoCO_3 should be ascribed

to the conductive agent. After 1000 discharge–charge cycles, apparently, pulverization is observed on EG-CC and DW-CC particles (Figs. 6(e), 6(f), and S7(d)–S7(f) in the ESM). As is known to all, conversion-type anode materials suffer from relatively large volume change ($< 200\%$) during repeated cycles [5]. Nevertheless, the particles of DG-CC maintain the integrity of morphology (Fig. 6(d)), which is attributed to the proper sizes of both primary particles and pore sizes of DG-CC. Small primary particles are beneficial to distributing the strain evenly in all regions of the material. Meanwhile, as shown in Fig. 7, appropriate pore size can accommodate these volume changes, so that the secondary particles will not collapse and effectively reduce the loss of active materials. The structure advantage of DG-CC prevents it from falling into the chain effect mentioned above during a long cycle process, which induced by the initial solvent control.

The superiority of morphology of DG-CC is also reflected in the impedance information. Nyquist plots of freshly assembled cells with the active substances of DG-CC, EG-CC, and DW-CC are shown in Fig. 8(a), and the data fitted by the equivalent circuit is exhibited in Fig. 8(b). R_s represents the ohmic resistance of the battery; R_{ct} and Z_w (Warburg impedances) describe the resistance of charge transfer and mass transfer, respectively. The specific values of these parameters obtained by fitting are also displayed in Table S3 in the ESM. It is observed from Fig. 8(b) that almost no difference in the R_s of the cells was made by the three CoCO_3 samples before cycle. However, DG-CC possesses the lowest R_{ct} , and DW-CC exhibits the highest value, which further confirms the faster reaction kinetics of DG-CC. To further explore the cycling stability of DG-CC, the changes of the impedance for DG-CC electrode during the repeated

Fig. 6 SEM images of the electrodes (a–c) before cycling and (d–f) after 1000 cycles for (a, d) DG-CC, (b, e) EG-CC, and (c, f) DW-CC.

Fig. 7 Schematic diagram of the morphologic change of cobalt carbonate particles during lithiation and delithiation processes.

Fig. 8 (a) Nyquist plots of freshly assembled cells of DG-CC, EG-CC, and DW-CC and (b) their corresponding comparisons of fitting parameters. (c) Nyquist plots of DG-CC after different cycles and (d) the variation of different resistance with cycle number. CPE represents the constant phase element.

cycles were studied. Nyquist plots of DG-CC after the 30th, 90th, 120th, and 200th cycle at 1 A/g are displayed in Fig. 8(c). The variation of impedance is summarized in Fig. 8(d) and Table S4 in the ESM. From the beginning to the 200th cycle, both R_{SEI} (SEI layer resistance) and R_{ct} have an upward trend in the early stage which may be due to the structural instability caused by volume change. Nevertheless, R_{SEI} and R_{ct} decline rapidly after 90 cycles suggesting that the negative effect of electrode structure change disappeared and thus brought about enhanced charge-transport kinetics [8,36]. It is not difficult to recognize that this result is consistent with the phenomenon that the specific capacity decreases first and then increases during the cycle process (Fig. 4(g)).

Therefore, the excellent performance of the DG-CC with high specific capacity and superior cycling stability could be attributed to the several factors as follows: (1) The porous features of the DG-CC induced by the small permittivity and high viscosity of the DG solvents could promote the infiltration of electrolyte and shorten ion diffusion distance, leading to rapid electrochemical reaction kinetics and higher reversible capacity; (2) the appropriate pore structure and large specific surface area of DG-CC endow the electrode with abundant active sites for Li^+ storage, and could

also promote the in-depth reaction of C and Co elements during lithiation/delithiation processes; (3) the porous structure of DG-CC can accommodate the volume expansion and release the strain/stress to avoid the collapse of the nano-micro particles during the cycling process efficiently, which guarantees the ultra-long cycling stability.

4 Conclusions

In summary, three $CoCO_3$ particles with comparable structures were successfully prepared by a facile solvothermal method using different solvents, and the results showed that the solvent had a significant effect on the morphologies of $CoCO_3$. Due to the good matching relationship between particle and pore sizes, DG-CC showed excellent electrochemical performance. When tested at 0.1 A/g, the DG-CC can achieve the capacity of 957.2 mAh/g after 200 cycles. Besides, under the high current density as 1 A/g for 1000 cycles, DG-CC also showed a high specific capacity of 690.7 mAh/g, and corresponding capacity retention could reach 92.45%. The stable particle structure of DG-CC ensured its performance stability in the process of high current circulation. Further analysis showed that the

super electrochemical performance for the DC-CC came from the multi-step electrochemical reactions and the enhanced charge-transport kinetics. The above work shows that reliable cobalt carbonate anode materials can be obtained by simple solvent selection. We hope that our work could provide a reference for further studies in the structural design of CoCO_3 or other anode materials.

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Electronic Supplementary Material

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