



# Different solid electrolyte interface and anode performance of $\text{CoCO}_3$ microspheres due to graphene modification and $\text{LiCoO}_2||\text{CoCO}_3@\text{rGO}$ full cell study

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## ABSTRACTS

Hollow and urchin-like  $\text{CoCO}_3$  dumbbell microspheres (HCCM) and  $\text{CoCO}_3$ @reduced graphene oxide composite microspheres (CC@rGO) were synthesized by one-step solvothermal methods. RGO modification significantly improves the cycling stability of  $\text{CoCO}_3$  microsphere anodes at low current densities. CC@rGO delivers 1067 and 997 mAh/g after 50 cycles at 0.1 C and 100 cycles at 0.2 C, respectively. Interestingly, HCCM shows rising cycling stability with increased rates while CC@rGO exhibits slight and continuous capacity fading at almost all rates thus declining advantage with rising rates. A competition theory between “protective force” mainly from solid electrolyte interface (SEI) or rGO layer and “destructive force” from volume swing applied on the microspheres was raised to clarify this phenomenon. The changing volume swing degree and SEI formation rate with increased rates, as well as different protective effects of HCCM and CC@rGO's SEI film or rGO layer, determined various competition results of the two forces at each rate thus various structural stability and cycling performance of the two samples. Furthermore, the application prospect of  $\text{CoCO}_3$  anodes in lithium ion full cells has been explored and the assembled  $\text{LiCoO}_2||\text{CC@rGO}$  exhibits an initial coulombic efficiency of 92.9%, a discharge mid-voltage of 2.3 V and stable cycling performance.

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## 1. Introduction

As the portable electronic devices continuously develop towards miniaturization and long standby time, and kinds of electric vehicles are widely enabled, Li-ion batteries are facing increasingly high demands on their portability and energy density, which can't be satisfied with the current graphite anodes. Researchers turned to alloy and conversion-type anode material to solve this problem. Although the alloy-type ones such as silicon and tin show high capacity [1–4], security risk caused by huge volume swing strictly

limits their contents in Li-ion batteries [5], whose energy density thus can't be improved significantly.

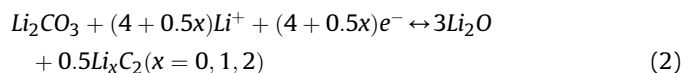
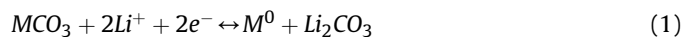
Due to much higher capacity than graphite and much smaller volume swing than alloy ones, conversion-type anode materials show good application prospect in Li-ion batteries [6]. Previous research on conversion anodes mainly focused on transition metal oxides [7,8]. The metal carbonates usually appear as their precursors. Since Tirado first reported better performance of  $\text{MnCO}_3$  than  $\text{MnO}$  [9], lithium storage performance of various metal carbonates has been reported, including the single ones of  $\text{MnCO}_3$  [10–14],  $\text{CoCO}_3$  [15–19],  $\text{FeCO}_3$  [20–23] and  $\text{CdCO}_3$  [24], the binary ones of  $\text{Mn}_{1-x}\text{Co}_x\text{CO}_3$  [25],  $\text{Co}_x\text{Fe}_{1-x}\text{CO}_3$  [26] and  $\text{Zn}_{0.12}\text{Co}_{0.88}\text{CO}_3$  [27], as well as the ternary ones of  $\text{Cd}_{1/3}\text{Co}_{1/3}\text{Zn}_{1/3}\text{CO}_3$  [28] and  $\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}(\text{CO}_3)_{0.8}$  [29]. It was proved that transition metal carbonates show comparable even better electrochemical activity than oxides [9,17,18]. Their specific capacities were increased from the initial 466 [9] to around 1800 mAh/g [16]. Accordingly, their

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lithium storage mechanism has been developed from the initial one-pot conversion between  $\text{MCO}_3$  and  $\text{Li}_2\text{CO}_3$  to the current two-order ones, as shown in eqn (1) [9] and 2 [16]. Furthermore, the reversible transition of  $\text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O}$  was confirmed by Fourier transform infrared spectroscopy [16] and the production of  $\text{C}^0$  or  $\text{Li}_2\text{C}_2$  during discharge and recovery of  $\text{Li}_2\text{CO}_3$  with charge was verified by X-ray photoelectron spectroscopy, transmission electron microscopy and Raman spectra evidences [15,30].



Among the numerous carbonates,  $\text{CoCO}_3$  shows optimal lithium storage activity. Like other conversion-type anode material, it requires specific structural design or modification to overcome the capacity fading caused by volume swing. Now only a few works about  $\text{CoCO}_3$  anodes display capacity retention up to 85% after 80 cycles at low rates [16,17,19]. The dumbbell-shaped nano-architectures of  $\text{CoCO}_3$  prepared by Shen et al. could show a value of only 86.8% after 100 cycles at 200 mA/g [19]. Kim et al. modified  $\text{CoCO}_3$  with graphene and achieved a capacity retention of 93.5% after 80 cycles at 100 mA/g [17]. But  $\text{CoCO}_3$  accounts for only 35.1 wt% in the  $\text{CoCO}_3$ /graphene composite. Too much graphene would sacrifice its volume capacity and rate performance, as evidenced by the obvious capacity fading at 1 A/g. When the  $\text{CoCO}_3$  was modified with polypyrrole (PPy), the composite maintained 1070 mAh/g after 100 cycles at 100 mA/g, showing a capacity retention of 91.5%. However, the capacities during the 100 cycles showed obvious fluctuation [16]. And, the preparation of  $\text{CoCO}_3$ @PPy related to a hydrothermal and the subsequent PPy coating process, which required precise controlling of temperature and pH value, being complex and time consuming. Therefore, it is necessary and important to develop a simple and controllable preparation method to realize subtle structure design of  $\text{CoCO}_3$ -based anode material, making them achieve stable low-rate performance without sacrificing the tap density and rate performance.

In addition, most research work on conversion anodes is limited to half cells, where the working electrodes are matched with lithium and actually act as cathodes. Aravindan and co-workers reviewed the limited works on full-cell assemblies where conversion anodes are matched with conventional cathodes [31]. The mentioned  $\text{LiFePO}_4|\alpha\text{-Fe}_2\text{O}_3$  [32],  $\text{LiNi}_{0.59}\text{Co}_{0.16}\text{Mn}_{0.25}\text{O}_2|\text{C-Fe}_3\text{O}_4$  [33],  $\text{LiMn}_2\text{O}_4|\text{MnO}_x\text{-C}$  [34] and  $\text{LiCoO}_2|\text{Co}_3\text{O}_4$  [35] exhibit good cycling performance. In addition to the cycling performance, the quality of a full-cell assembly also depends on the initial coulombic efficiency (ICE), the utilization of cathode and anode materials and the feasibility of assembly methods. The above assemblies generally show drawbacks of low ICE and low utilization rate of cathodes and anodes, which are due to the improper lithium pre-supplement amount and cathode/anode capacity ratio. As for carbonates based anodes, there's rare work on their anode performance in full-cell assembly. Zhao and co-workers have combined  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  and  $\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}(\text{CO}_3)_{0.8}$  into a full cell and studied its performance [29]. However, the initial coulombic efficiency (CE) is only 55% and the study only gives capacity within 5 cycles. Also, the discharge cut-off potential of 0.1 V is too low to make sense and there's not any trace of platforms on the potential curves except for the first charge one. So, the Li-ion full cells with conversion anodes should be deeply developed to further improve their performances.

Herein, we prepared dumbbell-shaped  $\text{CoCO}_3$ /reduced graphene oxide composite microspheres (CC@rGO) by a simple one-

step solvothermal method. For comparison, hollow and urchin-dumbbell-like  $\text{CoCO}_3$  microspheres (HCCM) were also prepared without addition of graphene oxide (GO). The rGO component with a content of 11.4 wt% significantly contributed to a better cycling stability of CC@rGO at low rates while keeping relatively stable high-rate capacity. Furthermore, a competition theory between "protective force" from solid electrolyte interface (SEI) film and rGO layer, and "destructive force" from volume change was first put forward to explain the better cycling stability of HCCM with increased rate, and slow and continuous capacity fading of CC@rGO at 0.1–0.2 C. Different SEI states on HCCM and CC@rGO microspheres were evidenced by SEM and TEM images to support this theory. Besides, Li-ion full cells of  $\text{LiCoO}_2|\text{CoCO}_3\text{@rGO}$  were successfully assembled by taking the commercial  $\text{LiCoO}_2$  as cathode material and CC@rGO as anode one. While adopting optimized cathode-anode capacity ratio and electrolyte and pre-supplying lithium on anodes, the full cells achieve an initial CE of 92.9%, a mid-discharge voltage and energy density of 2.3 V and 23.75 Wh/kg, as well as stable cycling performance.

## 2. Experimental

### 2.1. Synthesis of HCCM and CC@rGO

HCCM were prepared by a one-step solvothermal method. Typically,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.7462 g) and PVP (K30, 1.2 g) were dissolved in 60 mL of dimethylformamide (DMF). After magnetic stirring for 10 min, the solution was transferred to an 80 mL teflon-lined stainless-steel autoclave and maintained at 220 °C for 30 h. After cooling down naturally, the product was filtered and successively washed with deionized water and ethanol for several times. Finally, rose-red  $\text{CoCO}_3$  power was obtained by vacuum drying at 60 °C for 4 h. Similarly, CC@rGO could be obtained by replacing DMF with GO/DMF dispersion (1.5 mg/mL) for the solvothermal process. All the chemicals were AR grade and supplied by Sinopharm Chemical Reagent Co. Ltd without further purification.

### 2.2. Material characterization

X-ray diffraction (XRD) patterns of HCCM and CC@rGO were recorded on a Rigaku Dmax 2500 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The morphologies were characterized by field-emission scanning electron microscopy (FESEM; Hitachi S-4800) equipped with energy dispersive X-ray spectroscopy (EDS; Oxford), as well as high-resolution transmission electron microscopy (HRTEM; FEI Tecnai G2, 300 KV). Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 apparatus. The specific surface area and pore size distribution were determined based on Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda model, respectively. Raman spectra were collected using 532 nm excitation from an Ar ion laser on a HORIBA Labram HR spectrometer. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Mettler Toledo thermoanalyzer under air flow at a rate of 10 °C  $\text{min}^{-1}$ .

### 2.3. Electrochemical characterization

#### 2.3.1. Fabrication of the working electrodes

The working electrodes of HCCM and CC@rGO were fabricated by mixing the sample power, carbon black and polyvinylidene fluoride in a weight ratio of 65:20:15 in N-methyl-2-pyrrolidone. The resulting slurry was pasted on the copper foil and vacuum dried at 60 °C for 24 h. The loading density of HCCM and CC@rGO on

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