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# Cr<sub>2</sub>O<sub>3</sub>/carbon nanosheet composite with enhanced performance for lithium ion batteries

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A Cr<sub>2</sub>O<sub>3</sub>/carbon nanosheet composite is directly synthesized by solution combustion synthesis using chromium nitrate as the chromium source and glucose as the carbon source. The Cr<sub>2</sub>O<sub>3</sub>/carbon nanosheet composite serving as an anode material for lithium ion batteries has been studied, exhibiting higher cycling and rate performance than pure Cr<sub>2</sub>O<sub>3</sub>. The carbon in the composite not only inhibits the growth of Cr<sub>2</sub>O<sub>3</sub> particles, but also improves the electrical conductivity of Cr<sub>2</sub>O<sub>3</sub> and buffers the volume change during the lithium ion insertion/extraction process, which enhances the electrochemical performance.

## 1. Introduction

Due to their superior properties such as high energy density, long cycle life, no memory effect and environmental friendliness, lithium ion batteries (LIBs) have been widely used in portable electronic devices (*e.g.*, laptops and mobile phones), hybrid vehicles and clean energy storage.<sup>1–4</sup> In order to search for new electrode materials with high-capacity and rate capability for LIBs, several transition metal oxides have been intensively studied, such as Co<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>, NiO, MnO<sub>2</sub> and SnO<sub>2</sub>.<sup>5–11</sup> The theoretical specific capacities of metal oxides usually range from 700 to 1000 mA h g<sup>-1</sup> between 0.001 and 3.0 V vs. Li/Li<sup>+</sup>, which is much higher than that of commercial graphite (370 mA h g<sup>-1</sup>). Among various transition metal oxides that are prospective electrodes for LIBs, Cr<sub>2</sub>O<sub>3</sub> has attracted considerable attention due to its low cost, high theoretical capacity (~1058 mA h g<sup>-1</sup>) and relatively low lithium insertion potential (1.085 V).<sup>12–15</sup> Unfortunately, the practical application of Cr<sub>2</sub>O<sub>3</sub> in LIBs is still hindered with problems of low electrical conductivity and severe volume change during cycles, which result in a rapid capacity fading and the end of cycle life.<sup>16,17</sup> Many strategies have been used to solve these problems, including the preparation of nano-materials, mesoporous materials, and carbon composites.<sup>18–22</sup> Among these strategies, carbon composites has been widely studied since carbon could not only cushion the stress from volume change of active materials and maintain the structure integrity of electrode during cycles, but also prevent the agglomeration metal oxide nanoparticles. Ya Fu *et al.*<sup>23</sup> have prepared Cr<sub>2</sub>O<sub>3</sub>/carbon nanocomposites by directly carbonizing the glycine–CrCl<sub>3</sub> gel precursor and the prepared Cr<sub>2</sub>O<sub>3</sub> nanoparticles were embedded in carbon sheets which exhibit superior cycling and rate performances than pure Cr<sub>2</sub>O<sub>3</sub> as lithium-ion

battery anode materials. Syed Mustansar Abbas *et al.*<sup>24</sup> synthesized chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) nanoparticles and carbon nanotubes (CNTs) by *in situ* chemical co-precipitation method and this study offers a possibility of improving lithium ion storage of Cr<sub>2</sub>O<sub>3</sub> nanoparticles by using CNTs buffering matrix. Ling-Yan Jiang *et al.*<sup>25</sup> synthesized Cr<sub>2</sub>O<sub>3</sub>–C composite nanospheres by a facile soft-template assisted method and indicated that the carbon in the composite can improve the lithium storage capacity dramatically. Therefore, Cr<sub>2</sub>O<sub>3</sub> and carbon composite can be expected to show enhanced performance for LIBs.

Herein, this work describe a novel strategy for the preparation of Cr<sub>2</sub>O<sub>3</sub>/carbon nanosheet composite by solution combustion synthesis (SCS). Solution combustion synthesis is typically a redox based reaction that takes place in a homogeneous aqueous solution of oxidizing (*e.g.*, metal nitrates) and reducing agents (fuels).<sup>26–29</sup> In this work, the oxidizing agent is chromium nitrate and the reducing agents is glycine. In order to induce the carbon into the products, the glucose is used as carbon source. This method is very facile and effective for preparing Cr<sub>2</sub>O<sub>3</sub>/carbon nanosheet composite in high yield. On the basis of the crystal structure, morphology and the comparative of the Cr<sub>2</sub>O<sub>3</sub> is also presented and discussed. The electrochemical properties of the as-prepared Cr<sub>2</sub>O<sub>3</sub>/carbon nanosheet composite as LIBs anode materials are also investigated.

## 2. Experimental

### 2.1 Synthesis

The products were prepared by solution combustion synthesis. All the chemicals (analytical reagent grade) used for solution combustion synthesis were commercially purchased. The carbon/Cr<sub>2</sub>O<sub>3</sub> nanosheet composite was prepared by using chromium nitrate [Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O], glycine [NH<sub>2</sub>CH<sub>2</sub>COOH] and glucose [C<sub>6</sub>H<sub>12</sub>O·H<sub>2</sub>O] as starting materials. Briefly, chromium nitrate (10 g), glycine (7.5 g) and glucose (5 g) were

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dissolved in 150 mL deionized water under stirring to obtain a redox mixture. The mixture was filled in a 500 mL glass, and was heated in air on an electrical furnace whose temperature could be controlled. And the temperature was controlled at 300 °C. It took about 10 minutes to take place the redox reaction. The pure Cr<sub>2</sub>O<sub>3</sub> particles were also prepared for comparison. Briefly, chromium nitrate (10 g) and glycine (7.5 g) were dissolved in 150 mL deionized water under stirring to obtain a redox mixture. The experimental phenomenon were similar with the previous reports.<sup>13,30</sup> All of the products were directly synthesized by the solution combustion synthesis without any further process.

## 2.2 Characterization

The products were analyzed by X-ray diffractometer using Cu-K<sub>α</sub> radiation ( $\lambda = 0.1542$  nm, Rigaku D/max-RB12). The X-ray photoelectron spectroscopy (XPS) analysis was carried out using AXIS Ultra DLD spectrometer equipped with an Al K<sub>α</sub> X-ray source and electrostatic hemispherical electron analyzer. The differential scanning calorimetry (DSC) were performed from ambient temperature to 800 °C in air at a heating rate of 10 °C min<sup>-1</sup> using a TGA/DSC type instrument (MettlerToledo, Switzerland). The morphology and particle size of products were observed by scanning electron microscopy (SEM, JSM-5600) and transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN).

## 2.3 Electrochemical measurements

Electrochemical of the electrode material was performed using Cr<sub>2</sub>O<sub>3</sub>/carbon nanosheet composite as a working electrode and lithium metal as a counter electrode. The working electrode was fabricated by mixing the active materials with acetylene black (AB) and a binder, poly(vinylidene fluoride) (PVDF), at weight ratios of 40 : 40 : 20. The mixture was dispersed in the NMP solvent to form slurry and uniformly pasted on the Cu foil with a blade. A non-aqueous solution of 1 M LiPF<sub>6</sub> was dissolved in a 1 : 1 (volume/volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The cells were charged and discharged on a land test system (Land CT2001A) in a voltage window of 0.01–3 V at 25 °C. For the high rate testing, the charge/discharge current gradually increased from 0.1 to 0.2, 0.5, 1, 2, 5 and 10C, and then decreased to 1C and 0.1C, step by step. Electrochemical impedance spectroscopy (EIS) were tested by an electrochemistry workstation (CHI618D) at a scanning rate of 0.5 mV s<sup>-1</sup>. EIS were measured by applying an AC voltage of 10 mV amplitude over the frequency range between 100 kHz and 10 mHz at room temperature.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of products prepared by SCS. All the peaks can be index the eskolaite structure (JCPDS no. 38-1479) with the lattice parameters:  $a = 4.959$  Å,  $b = 4.959$  Å,  $c = 13.594$  Å. No impurity phase is detected either in Cr<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>/carbon, indicating the carbon in the Cr<sub>2</sub>O<sub>3</sub>/carbon composite is amorphous. According to the Scherrer's

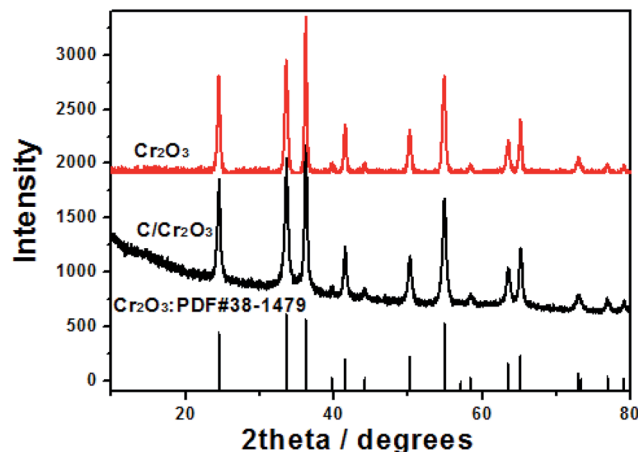


Fig. 1 XRD patterns of Cr<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>/carbon.

formula:<sup>31,32</sup>  $\beta = k\lambda/L \cos \theta$ , where  $\lambda$  is the X-ray wavelength ( $k = 0.154$  nm),  $L$  is the average crystallite size,  $k$  is the shape factor,  $\beta$  is the full width at half maximum, and  $\theta$  is Bragg angle in degree, the average crystalline size of Cr<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>/carbon composites sample is calculated to be about 23.4 and 19.0 nm, respectively. The results imply the carbon in the composite would hinder the particle to growth. Many researches have been indicated that the carbon in the products prepared by SCS can inhibit the growth of nano-oxides.<sup>33,34</sup> The composition of the Cr<sub>2</sub>O<sub>3</sub>/carbon is further characterized by XPS and the results are shown in Fig. 2. In the survey scan XPS spectrum of the Cr<sub>2</sub>O<sub>3</sub>/carbon composites, the peaks of Cr 2p, O 1s, N 1s and C 1s are observed, implying the existence of Cr, O, N and C elements in the composite. The weight content of the Cr, O, N and C elements evaluated by the XPS are 25.2%, 44.1%, 3.96% and 26.8%, respectively. In Fig. 2b, the peaks located at 586.4 and 576.9 eV are assigned to Cr 2p<sub>1/2</sub> and Cr 2p<sub>3/2</sub>, respectively.<sup>35</sup> In Fig. 2c, the deconvoluted C 1s peaks at 288.9, 287.6, 286.5, 284.7 eV are correspond to the O–C=O, C=C, C–O and C–C groups, respectively.<sup>36</sup> In Fig. 2d, the N 1s peak could be divided into four peaks located at 401, 399, 398.0 eV, which correspond to the –NH–, –NO– and –N= groups, respectively.<sup>37,38</sup> Research has confirmed that the N-doped carbon composite was favorable to improvement of the electrochemical performance.<sup>39</sup> The content of carbon in the products were further calculated by TG curves. The experiments were carried out from room temperature to 800 °C at a heating rate of 10 °C min<sup>-1</sup> in air. As shown in Fig. 3, the content of carbon is ~7.2% for Cr<sub>2</sub>O<sub>3</sub> and ~27.6% for Cr<sub>2</sub>O<sub>3</sub>/carbon, respectively, which was consistent with the XPS results. The carbon in the Cr<sub>2</sub>O<sub>3</sub> is due to the decomposed of some glycine. The addition carbon in the Cr<sub>2</sub>O<sub>3</sub>/carbon is attribute to the carbon derived form the glucose.

Fig. 4a shows the SEM images of the Cr<sub>2</sub>O<sub>3</sub>/carbon composite. It is obvious that the products has sheet structure. The sheet structure is attribute to the glucose which can lead to the formation of nanosheet microstructure.<sup>40</sup> The energy dispersive spectra (EDS) elemental mapping of the selected area obtained on SEM results (Fig. 4b–d) clearly reveal that a uniform distribution Cr, O and C elements. The magnification of the



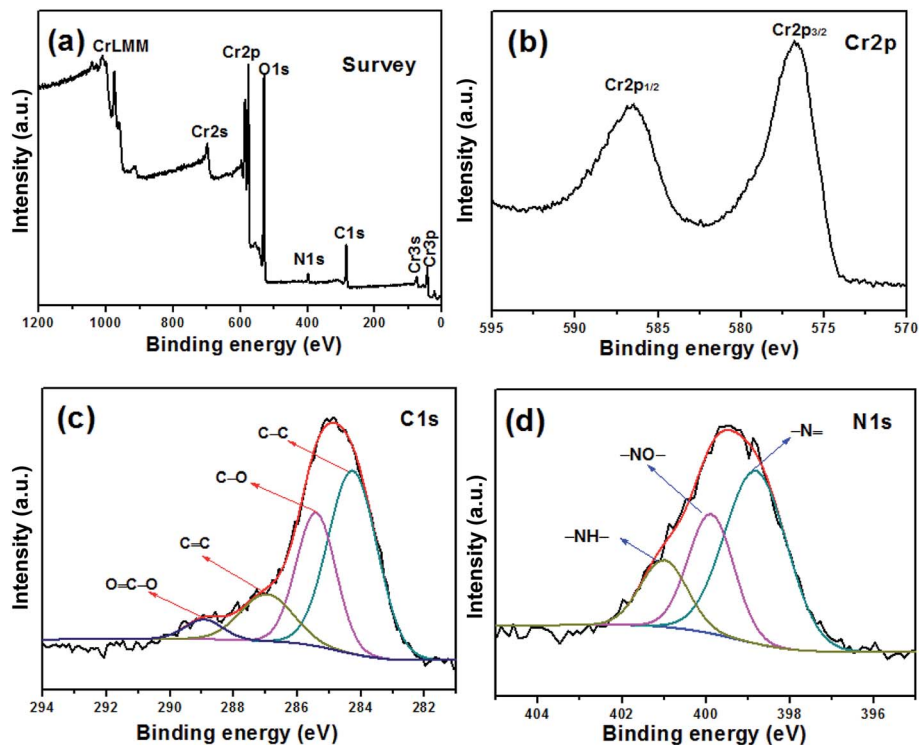


Fig. 2 XPS spectra of  $\text{Cr}_2\text{O}_3/\text{carbon}$ : (a) survey scan, (b–d) high resolution spectra of Cr 2p, C 1s and N 1s.

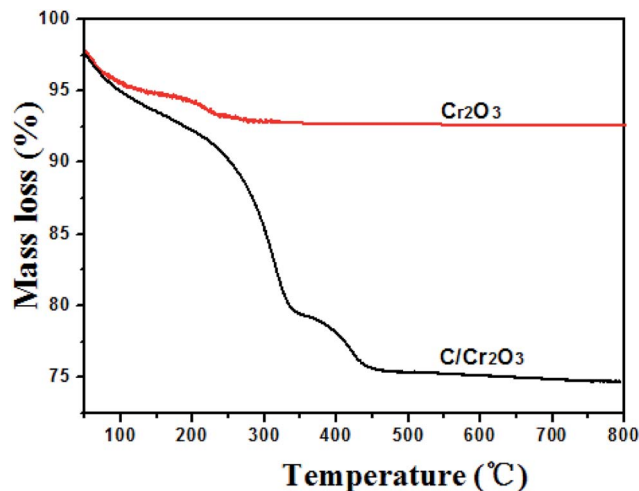


Fig. 3 TG curves of  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3/\text{carbon}$ .

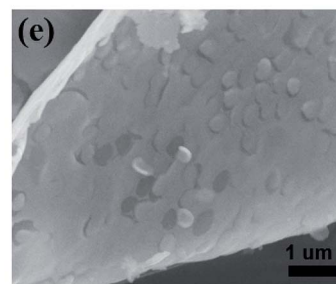
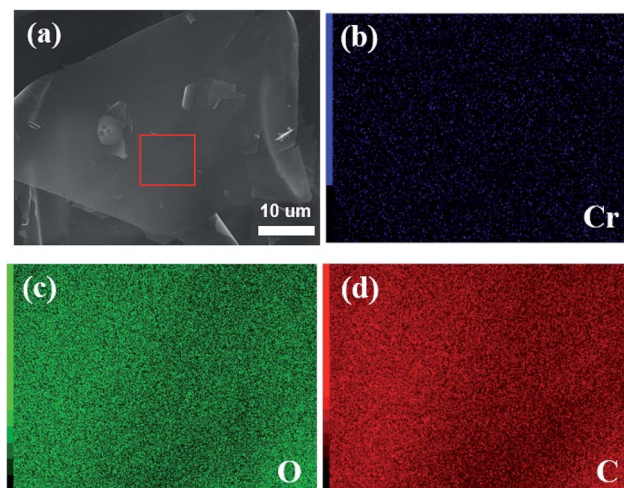


Fig. 4 (a) SEM micrographics of  $\text{Cr}_2\text{O}_3/\text{carbon}$ ; (b–d) EDS element mapping data of precursor; (e) SEM micrographics of precursor.

SEM shown in Fig. 4e exhibits some pores in the sheet which is formed by the gases liberated during the reactions.

The  $\text{Cr}_2\text{O}_3/\text{carbon}$  composite was further characterized by TEM. As shown in Fig. 5a and b, the  $\text{Cr}_2\text{O}_3$  particles with size less than 20 nm was uniformly embedded on the carbon sheet. In the HRTEM image (Fig. 5c, the typical lattice fringe spacing are measured to be 0.36 and 0.26 nm, corresponding to the (012) and (104) crystal plane of  $\text{Cr}_2\text{O}_3$ . The carbon sheet form interconnected and continuous network with  $\text{Cr}_2\text{O}_3$  particles, which is a special feature of the composites. This is essential to





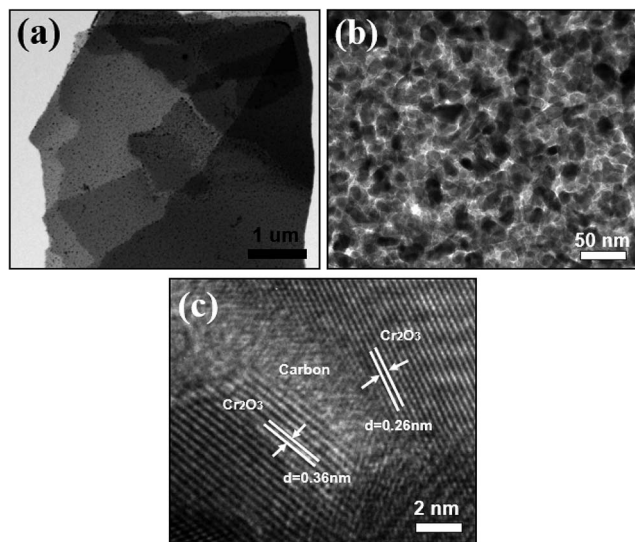


Fig. 5 (a and b) TEM images of  $\text{Cr}_2\text{O}_3/\text{carbon}$ ; (c) HRTEM images of  $\text{Cr}_2\text{O}_3/\text{carbon}$ .

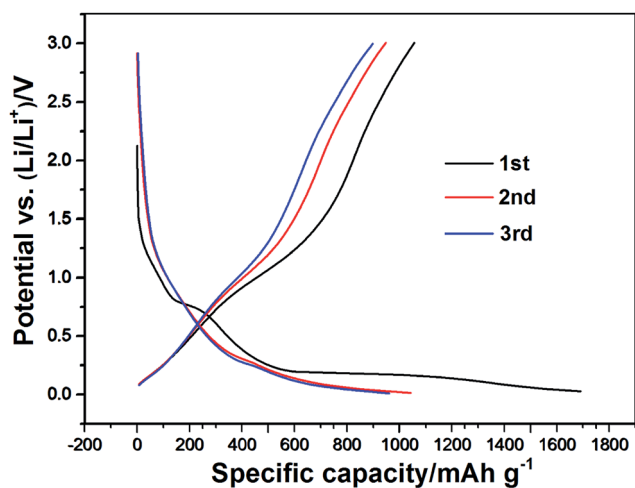


Fig. 6 The first three charge/discharge curves of  $\text{Cr}_2\text{O}_3/\text{carbon}$  at a current density of  $100 \text{ mA g}^{-1}$ , in the  $0.01\text{--}3.0 \text{ V}$  voltage range.

maintain the internal electronic contact of particles during the charging and discharging process, especially for insulating electrode materials with high capacity.

The charge/discharge curves of the  $\text{Cr}_2\text{O}_3/\text{carbon}$  for the first three cycles obtained at the current density of  $100 \text{ mA h g}^{-1}$  in the voltage window of  $0.01\text{--}3.0 \text{ V}$  (vs.  $\text{Li}/\text{Li}^+$ ) are presented in Fig. 6. It can be seen that the first and second specific discharge capacity of the mesoporous  $\text{Cr}_2\text{O}_3$  nanoparticles is as high as  $1680 \text{ mA h g}^{-1}$  and  $1042 \text{ mA h g}^{-1}$ , respectively. The first discharge capacity is larger than the theoretical capacity of  $1058 \text{ mA h g}^{-1}$ , which can be due to the SEI (solid electrolyte interphase) layer forming by the decomposed electrolyte at low voltage and further lithium insertion *via* interfacial charging at the metal/ $\text{Li}_2\text{O}$  interfaces.<sup>41,42</sup> Moreover, there is a plateau at  $0.7 \text{ V}$  only for the initial discharge capacities. It is assigned to the irreversible reductive decomposition of the electrolyte forming the SEI layer. The overlap of the second and the third discharge curves shows that the  $\text{Cr}_2\text{O}_3$  sheet structure electrode is stable during these cycles.

Fig. 7a shows the cycle performance of  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3/\text{carbon}$  evaluated at  $0.1\text{C}$ . Without the carbon as substrate, the capacity of  $\text{Cr}_2\text{O}_3$  decreased rapidly to  $500 \text{ mA h g}^{-1}$  after 20 cycles. On the contrary,  $\text{Cr}_2\text{O}_3/\text{carbon}$  shows better cycling stability and higher specific capacity retention than  $\text{Cr}_2\text{O}_3$ . Even after 55 cycles, the reversible capacity of  $\text{Cr}_2\text{O}_3/\text{carbon}$  is stable and still retains at  $710 \text{ mA h g}^{-1}$ . Fig. 7b shows the cycle performance of  $\text{Cr}_2\text{O}_3/\text{carbon}$  evaluated at  $0.5\text{C}$  and  $1\text{C}$ . The reversible capacity of  $\text{Cr}_2\text{O}_3/\text{carbon}$  is  $410 \text{ mA h g}^{-1}$  and  $360 \text{ mA h g}^{-1}$ , respectively.

As expected, the cycle performance of the  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3/\text{carbon}$  with varied current rates are revealed in Fig. 8. The  $\text{Cr}_2\text{O}_3/\text{carbon}$  delivers a reversible capacity of  $705, 560, 439, 358, 290, 215$  and  $169 \text{ mA h g}^{-1}$  at a current rate of  $0.1, 0.2, 0.5, 1, 2, 5$  and  $10\text{C}$ , respectively. When the current rate is returns to  $0.1\text{C}$ , and  $\text{Cr}_2\text{O}_3/\text{carbon}$  still a reversible capacity of  $694 \text{ mA h g}^{-1}$  is obtained. In contrast, the only delivers a reversible capacity of  $582, 441, 331, 305, 225, 155$  and  $121 \text{ mA h g}^{-1}$  at a current rate of  $0.1, 0.2, 0.5, 1, 2, 5$  and  $10\text{C}$  respectively. It is obvious that the  $\text{Cr}_2\text{O}_3/\text{carbon}$  exhibits better rate capability than  $\text{Cr}_2\text{O}_3$ . It is believed that the carbon in the  $\text{Cr}_2\text{O}_3/\text{carbon}$  nanosheet composite favorable to improve the electrical conductivity of between  $\text{Cr}_2\text{O}_3$  nanoparticles which would proved in EIS analysis and finally improve the cycle and rate performances.

Fig. 9 compares the Nyquist plots of  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3/\text{carbon}$  after 5 cycles CV testing. As shown in Fig. 9, both electrodes comprise a depressed semicircle in the high frequency and

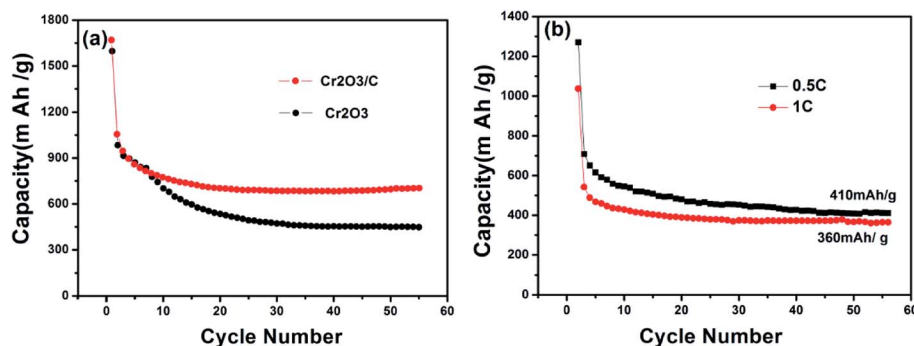


Fig. 7 (a) Cycle performance of  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3/\text{carbon}$  at  $0.1\text{C}$  rate; (b) cycle performances of  $\text{Cr}_2\text{O}_3/\text{carbon}$  at  $0.5\text{C}$  rate and  $1\text{C}$ .



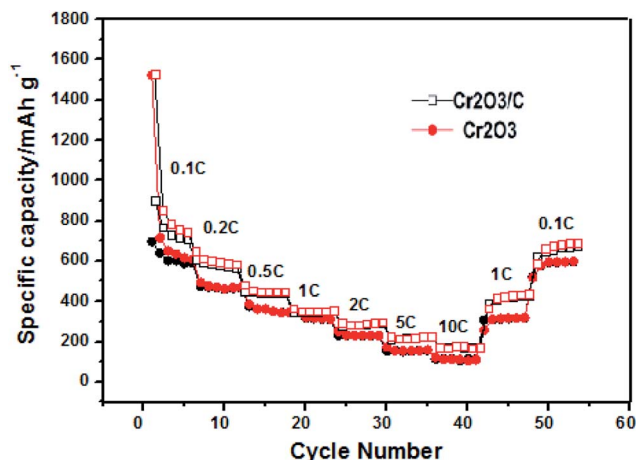


Fig. 8 Rate capability of the  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3/\text{carbon}$  in the potential window between 0.01 and 3 V.

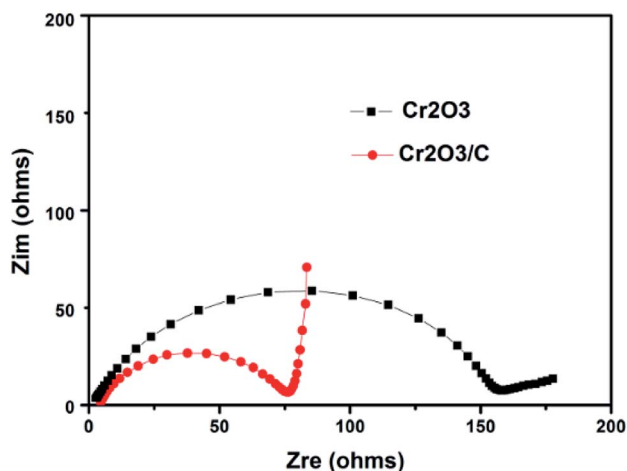


Fig. 9 Nyquist plots of  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3/\text{carbon}$  electrodes after 5 cycles CV testing. Frequency range between 100 kHz and 10 mHz at room temperature.

a sloped straight line in the low frequency. Researches indicated that the diameter of the semicircle is related to the charge transfer process occurring at the electrode and electrolyte interface, and is in direct proportion to the impedance including electrolyte resistance ( $R_e$ ), surface film resistance ( $R_{sf}$ ) and charge transfer resistance ( $R_{ct}$ ).<sup>43</sup> The inclined line low frequency corresponds to the Warburg impedance ( $W$ ) associated with the lithium ion diffusion process inside the electrode, and the straight line is in inverse proportion to the Warburg impedance.<sup>44</sup> It is obvious in Fig. 9 that the diameter of the semicircle for the  $\text{Cr}_2\text{O}_3/\text{carbon}$  is smaller than that of  $\text{Cr}_2\text{O}_3$ , indicating that the carbon in the composites can improve the electrical conductivity and charge transfer at interface of  $\text{Cr}_2\text{O}_3$  nanoparticles. In addition, the  $\text{Cr}_2\text{O}_3/\text{carbon}$  shows larger slope than  $\text{Cr}_2\text{O}_3$  in the low frequency, which suggests that the ion diffusion ability of  $\text{Cr}_2\text{O}_3/\text{carbon}$  is better. The electrochemical impedance spectroscopy results can infer the  $\text{Cr}_2\text{O}_3/\text{carbon}$

exhibits lower impedance (including  $R_e$ ,  $R_{sf}$ ,  $R_{ct}$  and  $W$ ) at the electrode/electrolyte interface and inside the electrode, validating that the introduced carbon to the  $\text{Cr}_2\text{O}_3$  can improve charge transfer and lithium ion diffusion ability, and thereby resulted in the enhanced of the electrochemical performances in LIBs. This is due to that the carbon in the composites not only buffer the strain from the volume variation of  $\text{Cr}_2\text{O}_3$  during lithiation and delithiation process, and also inhibit the aggregation of  $\text{Cr}_2\text{O}_3$  during charge/discharge process.

## 4. Conclusion

$\text{Cr}_2\text{O}_3/\text{carbon}$  nanosheet composite is successfully synthesized by solution combustion synthesis using chromium nitrate, glycine and glucose as raw materials. As anode materials for LIBs, the  $\text{Cr}_2\text{O}_3/\text{carbon}$  nanosheet composite shows superior cycling and rate performance compared with pure  $\text{Cr}_2\text{O}_3$ . The carbon and the special sheet structure play an important role on inhibiting the growth of  $\text{Cr}_2\text{O}_3$  particles, improving the electrical conductivity of  $\text{Cr}_2\text{O}_3$  and acting as a favorable buffer to the volume change during the lithium ion insertion/extraction process, leading to an enhanced electrochemical performance. This facile strategy can offer an effective technique for the preparation of other transition metal oxides and carbon nanosheet composites for energy storage devices.

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