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ARTICLE TYPE

Influence of electrolyte additives on the cobalt oxide-based anode's electrochemical performance and their action mechanism

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To further illustrate the influence of different additives on the electrochemical performance of CoO composite-based anodes in lithium-ion batteries, a CoO/carbon nanofiber composite-based electrode has been constructed and its electrochemical performances are investigated in detail in 1 M LiPF₆-EC/DMC (1:1, v/v) electrolyte with different additives, *i.e.*, vinylene carbonate, ethylene sulfite, lithium bisoxalato-borate, Li₂CO₃ and K₂CO₃, respectively. The results show that additional electrolyte additives have great effect on the initial efficiency and capacity retention of CoO-based anodes. For example, it produces better cyclic performance in the presence of vinylene carbonate. The addition of Li₂CO₃ can accelerate the conductivity of lithium-ions, and improve greatly the initial efficiency, charge/discharge capacity and cycling performance as well. With adding Li₂CO₃, the initial efficiency increases from 75.1% to 81% and its reversible capacity can keep at 850 mAh g⁻¹ stably even after 100 cycles. The action mechanism of SEI film between Li₂CO₃ additive and CoO composite anodes has been confirmed too.

1. Introduction

Owing to their low theoretical capacity of 372 mAh g⁻¹, graphite-based anode materials, a kind of materials being widely applied in commercial lithium-ion batteries (LIBs), could not any more satisfy the energy density requirement for electric vehicles.^{1,2} To find some alternative anode materials with high volumetric and gravimetric capacity has been attracted considerable attention.³⁻⁶ Among all the anode materials identified, transition metal oxides, *i.e.*, cobalt oxide-based composites are particularly promising due to their high specific capacities about three times larger than those of graphite.⁷⁻¹² Different cobalt oxide-based composite anodes with controllable structures, morphologies, particle sizes, and components were designed to improve the mechanical stability and cyclability, and to buffer the mechanical stress caused by volume changes during Li⁺ insertion and extraction. For example, cobalt oxide nanotubes,^{9,13} nanowire arrays^{14,15} and platelets¹⁶⁻¹⁹ based anodes had been confirmed to possess large reversible capacity and excellent cycleability. Our group also reported platelike CoO, Co₃O₄, CoO/CNF composites and applied them as electrode materials for LIBs, exhibiting superior Li-battery performance with high capacity, good cycle life and high rate capability due to their appropriate porosity, short and facile diffusion paths.¹⁶⁻¹⁸ However, for their further practical applications, there are still lots of challenges to be resolved, such as irreversible capacity loss (*ca.* 32%) and low cyclability.^{8-10, 20}

Recently, it has been found that a complete solid electrolyte interphase (SEI) film could be formed on the electrode surface during the initial electrochemical lithiation of cobalt oxides.²¹⁻²³ Surface analyses showed that the SEI film formed on CoO anode

always contain the corresponding organic or inorganic electrolyte reduction/decomposition products, *i.e.*, LiF, Li₂CO₃ and alkylcarbonate lithium salts, which will result in an irreversible capacity loss during the first discharging process.^{22,23} A SEI film with proper components can protect the electrode from side reactions and allow a stable lithium insertion/extraction process. Therefore, the components of SEI films will have critical influences on the performance of anodes for lithium-ion batteries. Various electrolyte additives, *e.g.*, vinylene carbonate, Li₂CO₃ and K₂CO₃, have been employed to control the formation of SEI film to affect the anode performance.²⁴⁻³⁰ It has been confirmed that vinylene carbonate can prompt to form a smooth and uniform SEI film on Si anode and so enhance its cycle performance and efficiency. For graphite anodes, to form a thin and dense SEI film on electrode surface, a little Li₂CO₃ additive can reduce the amount of hydrocarbons, the reductate of electrolyte, and so improve the initial efficiency.^{27,28} Similarly, K₂CO₃ additive can also increase the electrode cyclic performance by the formation of SEI films.³⁰ However, how the electrolyte additives affect the electrochemical performance of cobalt oxide-based anode is rarely reported as far as we know.

In order to further verify the effect of different organic and inorganic additives on the electrochemical performance of anodes in lithium-ion batteries, CoO/carbon nanofiber (CNF) composite electrodes were constructed in this paper, based on our work reported before.¹⁸ Their electrochemical behaviors in 1 M LiPF₆-EC/DMC (1:1, v/v) with different organic and inorganic additives, *i.e.*, vinylene carbonate (VC), ethylene sulfite (ES), lithium bisoxalato-borate (LiBOB), Li₂CO₃ and K₂CO₃, are investigated respectively, by means of charge/discharge test, electrochemical

impedance spectrum (EIS) and scanning electron microscopy (SEM). And the action mechanisms of SEI film between Li_2CO_3 additive and CoO composite anodes were discussed and presented too.

2. Experimental

All the reagents are analytic grade and directly used without further treatment except that vinylene carbonate (VC), ethylene sulfite (ES), lithium bisoxalato borate (LiBOB), Li_2CO_3 and K_2CO_3 were dried under vacuum at 80°C for 24 h. CoO/CNF composite was prepared according to our work reported before.¹⁸

The standard electrolyte was made from 1M LiPF_6 dissolved in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). The dried VC, ES and LiBOB were added into 1 M LiPF_6 - EC/DMC (1:1, v/v) with 2% by weight, respectively. Li_2CO_3 and K_2CO_3 were added into the standard electrolyte under the condition of stirring for a week to obtain a saturated solution, respectively. All electrolytes above were prepared in a glove box contained less than 5 ppm of H_2O and O_2 . Electrodes in the experiments were made from 80 wt% CoO composite material, 20 wt% polyvinylidene fluoride (PVDF) binder, and 10 wt% acetylene black. After their being mixed in N-methyl-2-pyrrolidinone, the slurry was coated on a copper foil and dried under vacuum at 120°C over 6 hours. A typical electrode disk was made with $1.0\text{--}2.0\text{ mg}\cdot\text{cm}^{-2}$ active material.

Morphologies of the prepared samples were observed by scanning electron microscopy (SEM). The corresponding samples were dispersed in ethanol under sonication and then were dropped on an aluminum sheet. After the solvent evaporation and gold sputtering treated, SEM micrographs were recorded with a JEOL FE-SEM (JSM-7401F) and TESCAN FE-SEM (MIRA3-XM) with an energy dispersive X-ray spectroscopy (EDS). XRD spectra were recorded on a Rigaku diffractometer D/MAX-2200/PC at a scanning rate of 4° min^{-1} with a 2θ ranging from 15 to 80° , using $\text{Cu K}\alpha$ radiation (1.5406 \AA). Electrochemical performance of the CoO composite was evaluated using CR2016 coin cells with lithium metal counter electrode and Celgard 2700 membrane separator. The electrochemical impedance spectroscopy was recorded from 0.1 to 10 kHz frequency range using a Solartron SI 1287 electrochemical interface and a Solartron SI 1260 frequency response analyzer. A small ac voltage of 5 mV amplitude was used as the perturbation of the system throughout the tests. The impedances obtained were fitted using Zview software. Galvanostatic charge (de-lithiation) and discharge (lithiation) was cycled between 3 and 0.01 V versus Li^+/Li on LAND CT2001A cyler at a current density of $100\text{ mA}\cdot\text{g}^{-1}$ at 25°C . Solid and hollow symbols represented lithium insertion and extraction respectively in all the following figures.

3. Results and Discussion

3.1 Effect of organic additives on the electrochemical performance

It is well known that the cyclic performance and charge/discharge capacity are particular important for the electrode materials in lithium-ion batteries, which plays a key role in their practical application. Here the charge/discharge capacity and cyclic

performance of CoO composite electrode in electrolyte with some organic additives were recorded first.

As shown in Fig. 1a, the charge/discharge capacity and cyclic performance of CoO composite electrode in electrolyte with 2wt% VC were similar to these in standard electrolyte. But the initial efficiency in the electrolyte with 2wt% VC was 72.3% lower than that in standard electrolyte. The reason maybe results from VC decomposition on the CoO composite electrode surface. However, the CoO composite electrode in the electrolyte with 2wt% ES showed quite a low initial efficiency of only 56.4%, hinting a large irreversible capacity loss in the first cycle. Obviously, the main differences between VC and ES shown in Fig. 1b were the discharge profile from 2.0 V to 1.5 V with a small plateau for ES attributed to ES reduction on the electrode surface at higher reduction potential.³¹ All above suggest that VC additive makes the CoO composite electrode cyclic performance better than ES, but they both could not improve the electrochemical performance comparing with the standard electrolyte. The reason may be that ES can help to form an SEI film, but the SEI film formed in the first cycle is not stable enough to prevent side reaction from electrode surface.

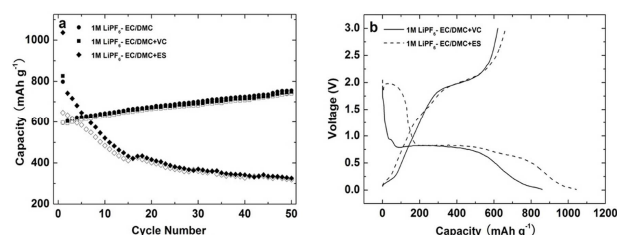


Fig. 1 (a) cycling performance and (b) first discharge and charge curves of CoO composite electrodes in 1 M LiPF_6 - EC/DMC (1:1, v/v) with and without VC or ES, respectively.

To gain more information about the SEI film morphology of CoO anodes, SEMs in combination with EDS were recorded after first full lithiation in electrolyte with and without VC or ES shown in Fig. 2. After first full lithiation, the SEI film formed in electrolyte without additives was rather ambiguous, and all nanoparticles were clearly visible on the surface of CoO platelet (Fig. 2a). While in the presence of VC, the SEI film formed was smooth and the nano-particles could not be seen any more on the CoO surface. Although the SEI film in electrolyte with ES was and smooth, however, some obvious cracks could be found. Both VC and ES can help to form a dense SEI film on the CoO electrode surface. From the EDS analyses (Right in Fig. 2), it is easy to find that the chemical components in the resultant SEI films were different each other, excepting trace S in the presence of ES. The Al peak resulted from the Al sheet and the Au peak was from gold sputtering. There were no peaks for Li, P, C and F for the original CoO electrode, the trace Li, P, F, C and O might be from the SEI film on CoO surface, which was in consistent with the reduction products of electrolytes, such as LiF , Li_2CO_3 and alkylcarbonate lithium salts.^{22,23} The slight differences of SEI film morphology and components, VC and ES in electrolyte might result in different electrochemical property for CoO electrode during the following cycles.

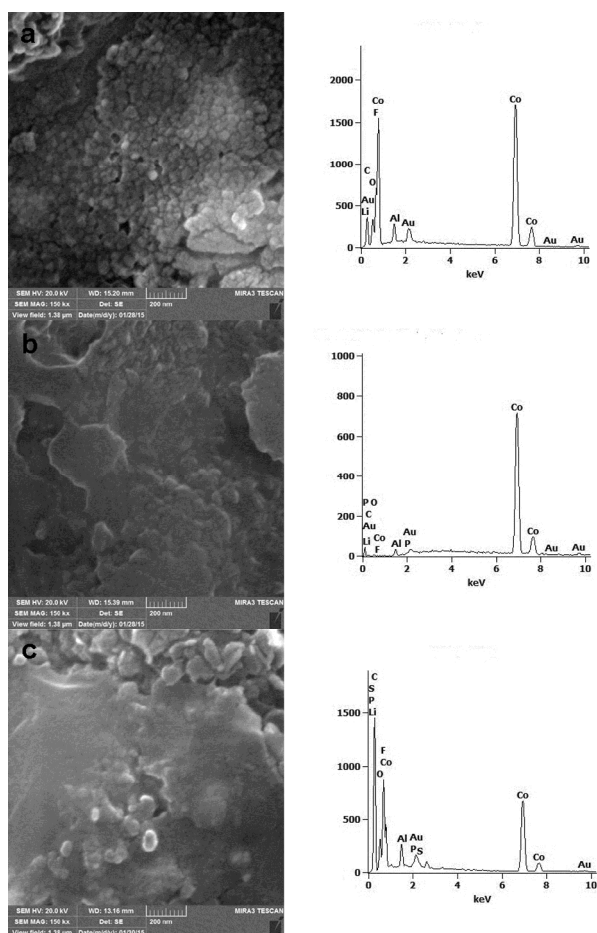


Fig. 2 SEM and EDS data of CoO anode after first lithiation (a) in 1M LiPF₆-EC/DMC (1:1, v/v), (b) in 1M LiPF₆-EC/DMC (1:1, v/v) with VC and (c) in 1M LiPF₆-EC/DMC (1:1, v/v) with ES

As the electrochemical impedance spectroscopy (EIS) technique is an efficient method to investigate the reaction mechanism of the electrode for lithium-ion batteries,³²⁻³⁵ the EIS of the CoO composite electrode was investigated using ac impedance measurements in the presence of ES and VC, respectively. The resultant Nyquist plots of CoO electrode in 1 M LiPF₆-EC/DMC (1:1, v/v) with different additives before and after first lithiation were illustrated in **Fig. 3**.

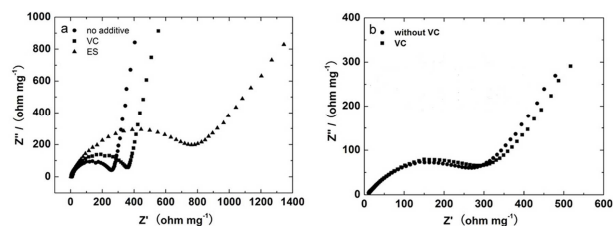


Fig. 3 Electrochemical impedance spectra for CoO composite electrodes measured with VC or ES in 1 M LiPF₆-EC/DMC (1:1, v/v) (a) at the initial open-circuit potential, (b) at the fully de-lithiated state after 50 charge-discharge cycles.

The shape of all EIS curves at the open circuit potential (before lithiation shown in Fig. 3a) were quite similar each other, *i.e.*, a small high-frequency semicircle and an arc in low frequency

region. The high-frequency semicircle is attributed to the contact problems, and the low-frequency arc reflects the retardance of the electrode.^{33,34} The additions of VC and ES both possess larger high-frequency semicircles, hinting that the contact resistance and conductivity of CoO composite electrodes are not improved. The contact resistance increases from 270 Ω in standard electrolyte to 400 Ω with the addition of VC and further to 820 Ω in the presence of ES. As shown in Fig. 3b, even after 50 cycles, the high-frequency impedance of SEI film formed in the presence of VC is still equivalent to that in the standard electrolyte, hinting that a stable SEI film was constructed on the surface of CoO electrode in the electrolyte with VC, which was consistent with their cycling performance shown in Fig. 1a.

3.2 Effect of inorganic additives on the electrochemical performance

The effect of some inorganic additives on the electrochemical performance of the CoO composite electrode, *i.e.*, LiBOB, Li₂CO₃ and K₂CO₃, was also investigated. The cyclic performance of the CoO composite electrode in 1 M LiPF₆-EC/DMC (1:1, v/v) containing 2wt% LiBOB and saturated Li₂CO₃, K₂CO₃ were shown in **Fig. 4**, respectively. The charge/discharge capacities of CoO electrodes were improved greatly with the initial efficiency increasing from 75.1% in standard electrolyte to 79% and 81% in the presence of saturated K₂CO₃ and Li₂CO₃, respectively. However, with the addition of 2wt% LiBOB, the initial efficiency was only 66.4% with a low specific capacity, meaning a large irreversible capacity loss in the first cycle. Both Li₂CO₃ and K₂CO₃ could produce better cyclic performance than LiBOB, which may be attributed to the different properties of the SEI films formed during initial cycling.

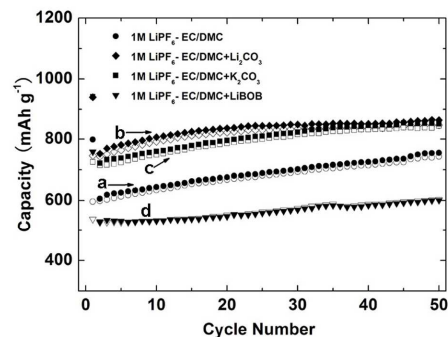


Fig. 4 Cycling performance of the CoO composite electrode using different inorganic additives in 1 M LiPF₆-EC/DMC (1:1, v/v) solutions: (a) 1 M LiPF₆-EC/DMC (1:1, v/v), (b) 1 M LiPF₆-EC/DMC (1:1, v/v)+Li₂CO₃, (c) 1 M LiPF₆-EC/DMC (1:1, v/v)+K₂CO₃ and (d) 1 M LiPF₆-EC/DMC (1:1, v/v)+2wt%LiBOB.

To investigate the surface morphology and component of CoO electrode after first full lithiation in electrolyte with different inorganic additives, SEMs and EDS data of CoO electrode were recorded shown in **Fig. 5**. After first full lithiation, the SEI films formed in electrolyte with Li₂CO₃ (Fig. 5a) and K₂CO₃ (Fig. 5b) were quite thinner and smoother than that with LiBOB (Fig. 5c). The uneven SEI might result in further reaction of the active surface with solution species to make the SEI thicker to increase the electrode's impedance, which was consistent with the charge/discharge results. The EDS analyses revealed that all SEI films were mainly composed of F, P, C, O and trace Li except that trace B was found in the SEI film on CoO surface in

electrolyte with LiBOB.

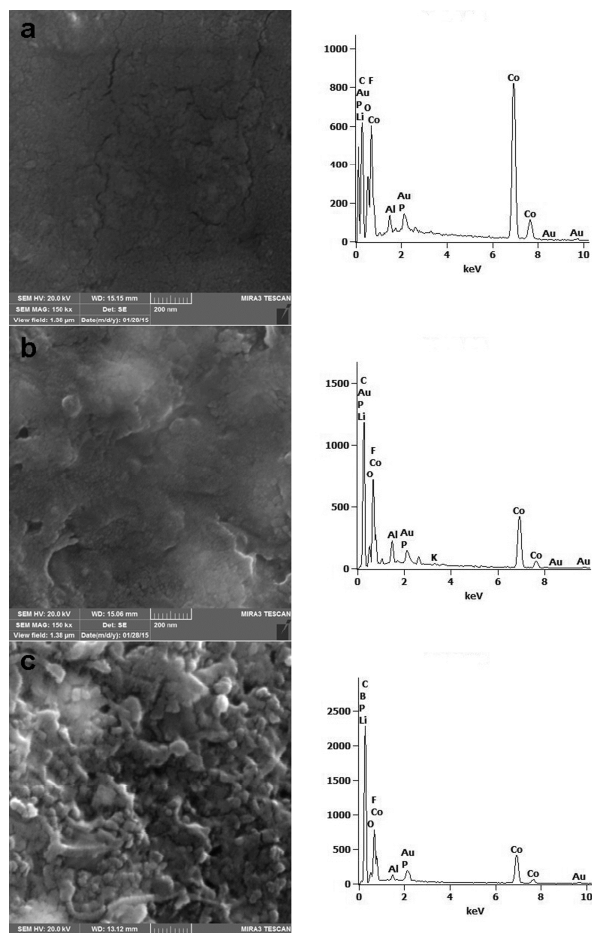


Fig. 5 SEM and EDS data of CoO anode after first lithiation (a) in 1M LiPF₆-EC/DMC (1:1, v/v) with Li₂CO₃, (b) in 1M LiPF₆-EC/DMC (1:1, v/v) with K₂CO₃ and (c) in 1M LiPF₆-EC/DMC (1:1, v/v) with LiBOB.

It has been reported that the SEI film is resulted from the reaction between electrode materials and electrolyte.^{36,37} The resultant SEI film can prevent further electrolyte reduction and keep lithium-ion continuous insertion, so side-reactions are efficiently reduced during following cycling procedures. Electrochemical impedance is a common method to detect Li⁺ conductivity in the SEI film. The lower impedance value means the faster Li⁺ transport through the SEI film.

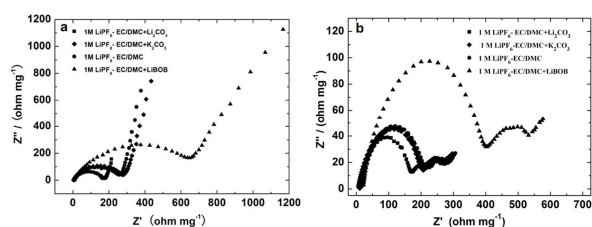


Fig. 6 Electrochemical impedance spectra for CoO composite electrodes measured with different organic additives in 1 M LiPF₆-EC/DMC (a) at the initial open-circuit potential, (b) at the full lithiation state for the first cycle.

Fig. 6a showed the electrochemical impedance spectra of CoO/CNF composite electrodes with the above inorganic

additives at the initial open-circuit potential. The lithium-ion battery containing Li₂CO₃ additive in the electrolyte had the smallest high-frequency semicircle, *i.e.*, the best contact resistance and conductivity. The contact resistance decreased from 240 Ω in standard electrolyte to 180 Ω in the electrolyte containing saturated Li₂CO₃. In the electrochemical impedance spectra during the full lithiation range (Fig. 6b), all EIS curves had similar outlines consisting of 3 parts, namely high-frequency arc (HFA), middle-frequency arc (MFA) and a sloping line in low frequency region. HFA is attributed to the process of Li⁺ migrating through the SEI film, MFA is to charge transfer process at electrolyte-electrode interface and the sloping line at low frequency region is resulted in Li⁺ solid-state diffusion within anode composite electrode.^{27, 28} Considering the truth that there is an initial semicircle in the high frequency region before lithiation, the HFA in full lithiation should be related to both the contact problems and the migration of Li⁺ through the SEI film. As shown in Fig. 6b, the lithium-ion battery containing Li₂CO₃ additive in the electrolyte possesses the smallest high-frequency semicircle among the standard electrolyte and other additives. So the contact resistance and conductivity of the CoO composite electrode in the electrolyte with Li₂CO₃ was the best. All the results above confirm that the addition of Li₂CO₃ to electrolyte solution will be an efficient method to improve the electronic properties of CoO composite electrode for lithium-ion batteries.

To rationalize the conclusion above, the impedance spectra of the CoO composite electrode during the first lithiation process was fitted to an equivalent circuit as shown in **Fig. 7**. In this equivalent circuit, R_s , R_{SEI} and R_{ct} represent the ohmic resistance, the resistance of the SEI film and the charge transfer resistance, respectively. Due to the depressed arc, constant phase element (Q) is used to replace double layer capacitance. Q_{SEI} represents the space charge capacitance of the SEI layer, and Q_{dl} is double layer capacitance at the electrode surface. Z_w was Warburg impedance, which was connected in series to R_{ct} .^{34, 38} Based on this equivalent circuit, a typical fitting result was shown in **Fig. 8** compared with the experimental EIS data at 0.01 V in the first discharge process in 1 M LiPF₆-EC/DMC (1:1, v/v) with saturated Li₂CO₃. The values for all the related parameters were fitted very well accordingly.

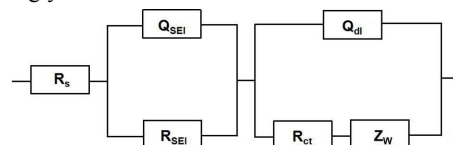


Fig. 7 Equivalent circuit of CoO composite electrodes measured at 0.01 V during the course of first lithiation.

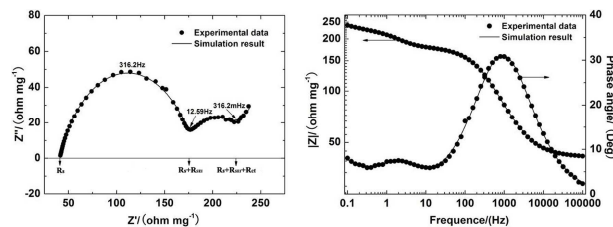


Fig. 8 The typical Nyquist plots and Bode plots of CoO composite electrode measured at 0.01V during the course of first lithiation in 1M LiPF₆-EC/DMC (1:1, v/v) with saturated Li₂CO₃.

The effect of Li_2CO_3 additive on the reversible capacity and cycleability of CoO composite anode in lithium-ion battery was investigated too. The cycling performance and coulombic efficiency of the CoO composite electrode in 1M $\text{LiPF}_6\text{-EC/DMC}$ (1:1, v/v) with Li_2CO_3 additive was shown in Fig. 9a. The coulombic efficiency increased rapidly from 81% in the first cycle to 99% in the second one, and then remained quite a constant efficiency of ca. 98% during the following cycles. Even after 100 cycles, the reversible capacity of CoO composites anode in the electrolyte with Li_2CO_3 was still 850 mAh g^{-1} , which was much higher than 700 mAh g^{-1} in the standard electrolyte. The shape of the charge and discharge curves of CoO composite with or without Li_2CO_3 additive were shown in Fig. 9b, which were quite similar each other with a little improvement for the charge/discharge voltage hysteresis, resulted from the internal polarization processes of lithium conversion.²¹ The influence of charge and discharge rate on the capacity retention was illustrated in Fig. 9c. With the enhanced current rate, the capacity decreases regularly. However, the capacity still kept 630 mAh g^{-1} at 2C, higher than 580 mAh g^{-1} in the standard electrolyte.¹³ Therefore, the capacity can be completely recovered when the discharge rate ranged from 10C to 0.2C rate, indicating that CoO composite with Li_2CO_3 additive had good electrochemical reversibility and structural integrity.

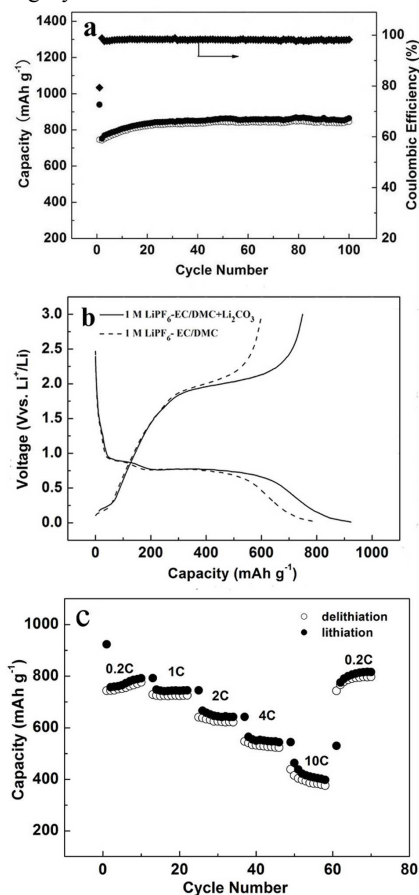


Fig. 9 (a) Cycling performance and coulombic efficiency of CoO composite electrodes using Li_2CO_3 in 1M $\text{LiPF}_6\text{-EC/DMC}$ (1:1, v/v), (b) first discharge and charge curves of CoO composite electrodes in 1M $\text{LiPF}_6\text{-EC/DMC}$ (1:1, v/v) with and without Li_2CO_3 , (c) reversible capacities during continuous cycling at various charge rates.

3.3 The action mechanism

To present a clear action mechanism of SEI film between Li_2CO_3 additive and CoO composite, electrochemical impedance spectra of CoO composite electrode was recorded after different cycle numbers in 1M $\text{LiPF}_6\text{-EC/DMC}$ (1:1, v/v) with saturated Li_2CO_3 .

As shown in Fig. 10a, the diameters of high frequency semicircles increased dramatically with the increasing of the number of cycles at first. But when the number of cycles was more than 50 cycles, the diameter almost was not changed any more (Fig. 10b). The increase in SEI layer impedance may be attributed to the change of SEI layer thickness. For initial cycles, the newborn SEI was quite thin and so the electrolyte can permeate it easily. With new SEI layers formed constantly on the surface of CoO composite electrode during each cycle, the SEI layer thickness increased accordingly. Once the thickness was stable and impermeable to electrolytes, the impedance of SEI film would not change any longer. For CoO composite electrode in 1M $\text{LiPF}_6\text{-EC/DMC}$ (1:1, v/v) with saturated Li_2CO_3 , the impedance of SEI film would be stabilised at ca. $140 \Omega/\text{mg}$ after 50 cycles. It indicated that a stable SEI layer was formed on the surface of CoO composite anode in electrolytes with Li_2CO_3 , which was consistent with the result drawn from Fig. 9.

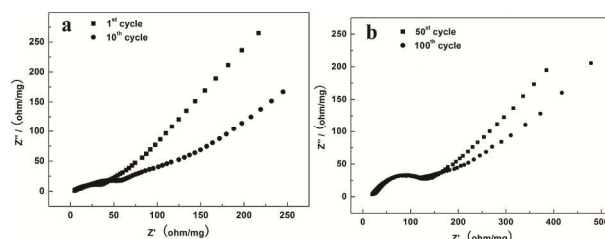


Fig. 10 Electrochemical impedance spectra for CoO composite electrodes measured after different cycle numbers in 1M $\text{LiPF}_6\text{-EC/DMC}$ (1:1, v/v) with saturated Li_2CO_3 .

The structure of the SEI layer can be characterized directly by its morphology. To do this, the surface of CoO composite electrodes that had been lithiated and delithiated after 100 cycles in the electrolyte with Li_2CO_3 additive was examined by scanning electron microscopy shown in Fig. 11a. By comparison, a typical SEM image of the original CoO and its XRD pattern were also presented in Fig. 11b and 11d. The original CoO indicated a multilayered hexagonal platelet structure with the cubic symmetry of CoO phase (space group $\text{Fm}\bar{3}\text{m}$, JCPDS card no. 48-1719).¹⁸ A smooth thin SEI layer with uniform density was clearly formed on the CoO electrode surface. And the original dimension and morphology of the CoO platelet were still maintained even after 100 cycles. After the CoO composite electrode was taken out, it was washed with DMC and then dried in an argon dry box for XRD analysis. As shown in Fig 11c, only the diffraction peaks of the copper substrate and the CNF can be identified and the diffraction peaks of CoO phase cannot be detected, suggesting that the CoO phase structure becomes amorphous completely after 100 cycles. According to the literatures,^{27,28} saturated Li_2CO_3 in the electrolyte might be deposited on carbon electrode surface before the reduction reaction occurs, which accelerates to form a more conductive SEI film on the surface of the carbon anode. What's more, owing to a more stable SEI film formed, Li_2CO_3 can decrease the initial irreversible capacity and so improve the cycling performance for

the anode. Accordingly, we deduce that the similar reason for Li_2CO_3 additive to form a more stable and compact SEI film to increase the conductivity of CoO composite electrode, and to improve the electrochemical performance.

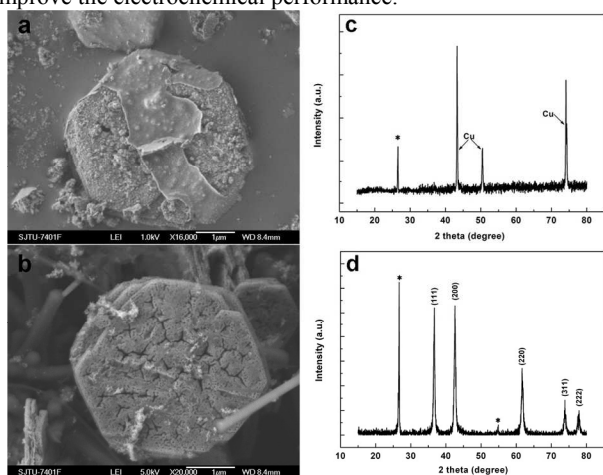


Fig. 11 (a) SEM image and (c) XRD pattern of CoO after 100 cycles in 1M $\text{LiPF}_6\text{-EC/DMC}$ (1:1, v/v) with Li_2CO_3 , (b) SEM image and (d) XRD pattern of CoO before cycling. Asterisks response from CNF.

4. Conclusions

In conclusion, the effect of different organic and inorganic electrolyte additives on the electrochemical performance of CoO/CNF composite anode was investigated by the methods of charge/discharge test, electrochemical impedance spectrum and scanning electron microscopy in 1 M $\text{LiPF}_6\text{-EC/DMC}$ (1:1, v/v). For the organic additives, half-cell testing and EIS results showed that VC additive could result in better cyclic performance than ES, but its initial efficiency was not improved. For inorganic additives, Li_2CO_3 produced the best cyclic performance among K_2CO_3 , LiBOB and Li_2CO_3 . The initial efficiency of CoO composite electrode with saturated Li_2CO_3 was 81%, higher than 75.1% for initial efficiency in standard electrolyte. Even after 100 cycles, the reversible capacity of CoO composite electrode in the electrolyte with Li_2CO_3 was still kept at 850 mAh g^{-1} , much higher than 700 mAh g^{-1} in the standard electrolyte. All these favorable effects will provide a novel insight to select ideal additives to improve the performance of cobalt oxide-based anodes in lithium-ion batteries in the future.

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Notes and references

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Influence of electrolyte additives on the cobalt oxide-based anode's electrochemical performance and their action mechanism

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Abstract: A CoO/carbon nanofiber composite-based electrode was constructed and its electrochemical performances were investigated in detail in 1 M LiPF₆-EC/DMC (1:1, v/v) with different additives, *i.e.*, vinylene carbonate, ethylene sulfite, lithium bisoxalato borate, Li₂CO₃ and K₂CO₃, respectively. The action mechanism of SEI films between additives and CoO composites were confirmed too.

