Graphite–metal oxide composites as anode for Li-ion batteries

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Abstract

To improve the rate capability and cyclability of carbon anode for Li-ion batteries, graphite was modified by forming a graphite–metal oxide (G–MO) composite. Structure analyses and electrochemical characteristics were performed. An insertion mechanism is proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Li-ion batteries; Graphite–metal oxide composites; Anode materials; Rate capability; Insertion mechanism; Activation

1. Introduction

Graphite used as the anode for Li-ion batteries is advantageous over other kinds of carbons in terms of high lithium intercalation capacity and flat intercalation potential. The main disadvantage of graphite is the low discharge rate capability limiting it in a wide field of applications. In order to improve this rate performance, various additives were added, among which metals and soft carbons were used [1,2]. Recently, graphite–metal oxide (G–MO) composites were prepared in our laboratory and the electrochemical performances were studied in detail [3]. Considering the abundance, low cost, electronic conductivity, and stability towards lithium, research has been focused on the G–CuO composite.

2. Experimental aspects

Graphite oxide (GO) powders were obtained by dispersing graphite powders in a $KMnO_4$ solution with suitable pH at $70^{\circ}C$ for a certain time. Due to the layered structure and high content of oxygen-containing groups at the edge of carbon layers, GO is able to adsorb large amounts of metal ions. G–MO composite (M = Cu, Fe, Ni, Pb, etc.) composites were prepared by dispersing metal oxide particles in GO coarse suspension and subsequently dried at $150^{\circ}C$ in air.

X-ray diffractormeter (XRD) was performed using a Phillips PW1840 with Cu Kα radiation. FTIR spectra were recorded on a Perkin-Elmer FTIR Spectrometer 1000. The discharge/charge measurements were controlled and recorded automatically on a MACCOR battery tester while the cyclic voltammetry measurements were performed with an AUTOLAB electrochemical device.

3. Results and discussions

XRD patterns indicates that G–CuO is mainly a mixture of graphite and copper oxide. A similar result was obtained with FTIR where vibration bands at 500 and 600 cm^{-1} were found, which can be attributed to CuO and Cu_2O, respectively. Besides, a new vibration band at 420 cm^{-1} was observed that can be explained by copper carbonate or cupric acetate [4], alike the bondings between copper and carboxylic group. This further leads to the decrease of the relative intensity at 1640 cm^{-1} corresponding to the carboxylic content on the surface of graphite. Hence, these results indicate the occurrence of an interaction in G–CuO between graphite, especially the carboxylic groups on the surface, and copper oxide. When G–CuO was reduced in H_2 at $380^{\circ}C$ for 5 h, it changed into a mixture of graphite and copper (G–Cu).

Fig. 1 presents the first and the third discharge/charge profiles of the cells with G–MO as the working electrode, 1 M $LiPF_6$–EC–EMC as the electrolyte, and Li as the counter electrode. A significant irreversibility was observed in the first cycle for all the four composites. This can be

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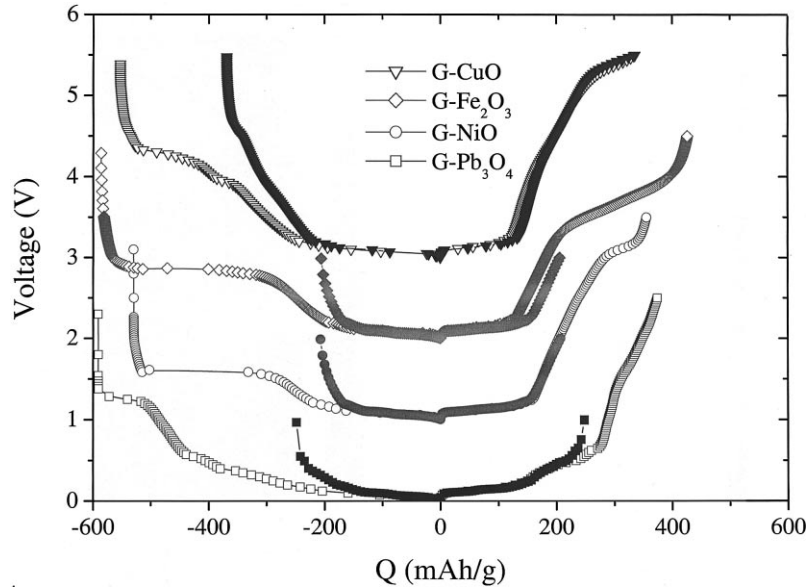*E-mail address*: h.huang@tnw.tudelft.nl (H. Huang).

Fig. 1. The discharge/charge profiles of the first (open symbol) and the third (filled symbol) cycle with the cells of Li/LiPF$_6$–EC–EMC/G–MO (MO = CuO, Fe$_2$O$_3$, NiO, and Pb$_3$O$_4$), $I = 0.1$ mA cm^{-2} (for a better resolution, the voltage data of G–NiO, G–Fe$_2$O$_3$, and G–CuO are displayed plus 1–3, respectively).

explained by the following reduction reaction confirmed by XRD data.

$$MO + 2Li \rightarrow M + Li_2O$$
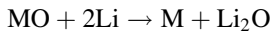
During charging, only a small amount of the formed metal can be oxidized again thus, reflecting the irreversibility. For G–MO (M = Ni, Fe, and Pb) composites, the electrochemical reduction/oxidation process showed poor reversibility upon cycling in the voltage range of 5 mV to 2.5 V. Therefore, further studies used the charge cut-off voltage at 1.2 V. Under this condition, the electrode changed into a graphite–metal (G–M) composite as no oxidation reaction occurs below 1.2 V. Conversely, for G–CuO composite the above electrochemical reduction/oxidation processes presented a good reversibility upon cycling, which is beneficial for the improvement of the rate capability. Details will be discussed below.

The discharge capacities at 0.1 and 1 mA cm^{-2} are listed in Table 1. A decrease of the capacity was observed with increasing discharge current density for all the samples. However, the improvement of G–M composites compared to

the non-modified graphite is obvious. G–Cu, G–Fe, and G–Ni composites showed similar rate properties, however, the G–Pb composite showed less improvement possibly due to Li–Pb alloying/de-alloying processes which usually reveal poor cycling performance. A strong improvement was found for the G–CuO composite. Even at a 2C-rate about 60% of the power can be utilized. Fig. 2 presents the absolute discharge capacity as a function of discharge current density (Q–I_d). Usually at a low current, lithium can be intercalated into graphite step by step and the phase transitions corresponding to 1′→4, 4→3, 3→2L, 2L→2, and 2→1 can be clearly distinguished [5]. In contrast, at a high discharge rate, i.e. $I = 1$ mA cm^{-2}, some plateaus disappeared or were mixed indicating that the corresponding phase transition processes were not completed or occurred separately due to the existing polarization and low intercalation rate. For G–M, the polarization can be expected to decrease in the presence of metallic particles. From ac electrochemical impedance analyses and dc polarization measurements, the internal resistance of the cells was evaluated and a decrease of the internal resistance with the G–M

Table. 1
Comparison of the capacity at low and high discharge current densities

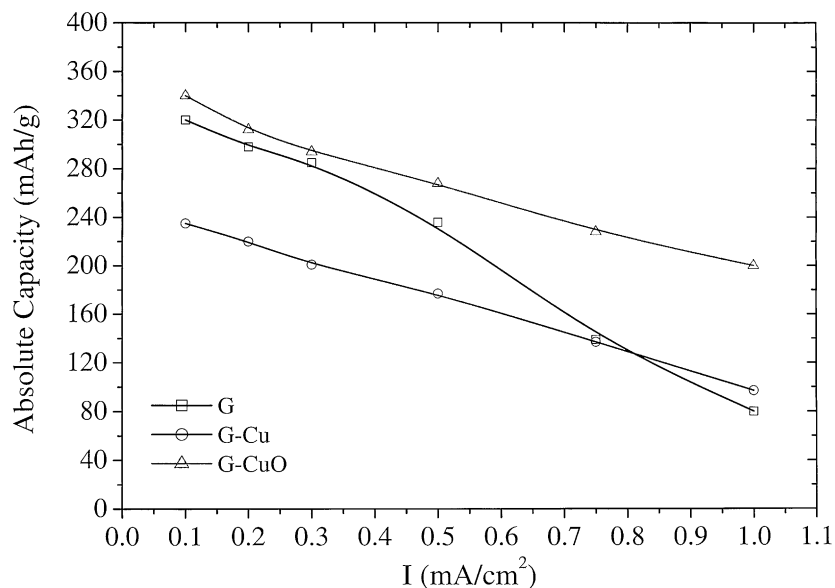| Sample specifications	Q_1 ($I_d = 0.1$ mA cm^{-2})		Q_2 ($I_d = 1$ mA cm^{-2})		Q_2/Q_1 (%)
	Composite (mAh g^{-1})	Graphite (mAh g^{-1})	Composite (mAh g^{-1})	Graphite (mAh g^{-1})	
Graphite	–	330	–	81	25
G–Cu	210	333	88	140	42
G–Fe	206	325	85	134	41
G–Ni	207	324	81	126	40
G–Pb	248	674	95	258	37
G–CuO	347	518	210	313	60

Fig. 2. The reversible capacity as a function of the discharge current density with the non-modified graphite, G–Cu, and G–CuO composites.

composites was found. The difference in rate capabilities between G–CuO and G–M indicates that the improvement is not only due to an increase of the electronic conductance of the electrode. The completion of the transition going from stage-1′ to 4 suggests another improved electrode kinetics.

Cyclic voltammetry experiments were performed on the G–CuO sample. When the scan range was set between 0 and 3 V, one broad peak at 2.2 V and two sharp peaks at 1.2 and 0.8 V appeared during discharging. In the charging process, a broad peak in the potential range of 2.3–2.8 V was obtained. This is consistent with the discharge/charge profiles indicating a reversible reaction between Li and CuO, e.g. Li intercalation into the structure of copper oxide [6] or Li adsorbed on the surface of CuO particles, in the potential
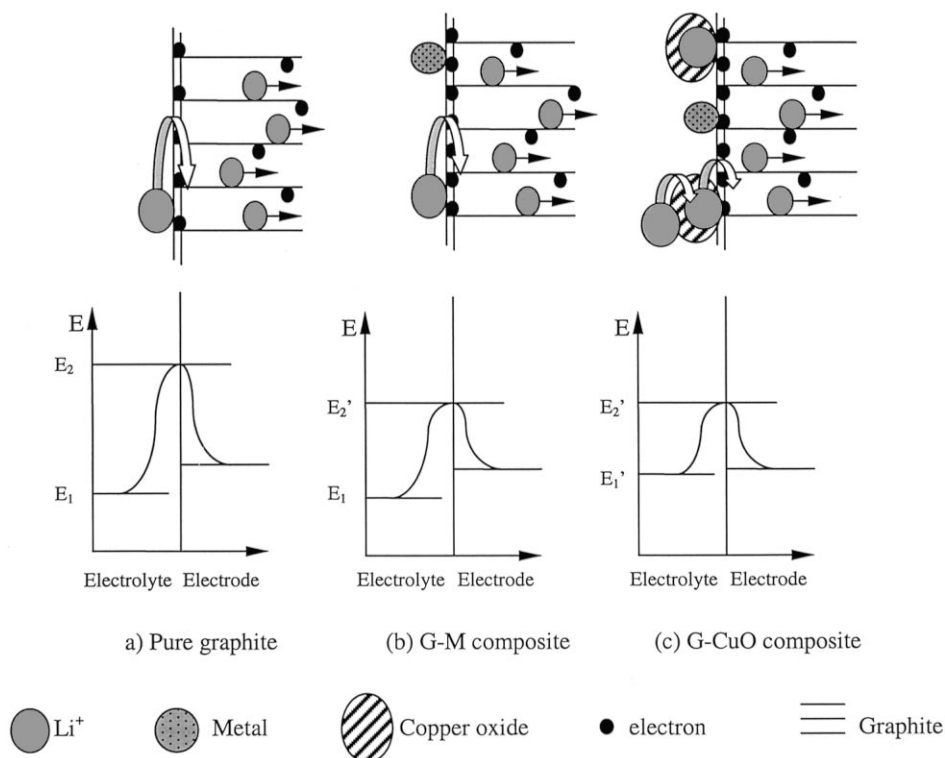

Fig. 3. The schematics and energy diagrams of the proposed mechanism.

range of 1.5–3 V. Such a reaction probably catalyzes the removal of the anions or solvents from the Li-ions and, hence, promotes Li-ions transport across the electrolyte/electrode interface. It is known that carbon oxidation rate can be significantly enhanced by catalytic agents including many metals and their inorganic salts or oxides. In a commonly accepted mechanism, oxygen from the reactant gas is extracted by the catalyst, which then is supplied in an active form to react with carbon through the zig-zag, arm-chair, or other defect sites on the basal plane. In the present case, copper oxide may act similarly for Li intercalation, i.e. as a catalyst for ionic transfer. Thus, Li-ions are accelerated upon arrival at the surface of the electrode.

According to the present results, Li-ions transport cross the interface between electrode and electrolyte can be considered as an activation process. Li-ions have to overcome a certain energy barrier in order to arrive on the graphite surface. The activation energy, and hence, the rate of such ionic charge transfer process, is determined by electron concentrations and lithium-ion transport process at the interface. Possible mechanisms are presented in Fig. 3.

Comparing the G–M composites with pure graphite, the energy level of electrons at the surface will decrease to some extent due to the changes of surface states by the presence of metal atoms with various work function and electronic conductivity. The increase of the electron concentration will facilitate Li-ion transport across the interface (see Fig. 3(b)). On the other hand, in the G–CuO composite, there exists copper oxide on the surface of graphite which is able to react with Li-ions so as to accelerate the transport process of Li-ions across the interface. Hence, the improved performance is further enhanced as compared with the G–M composite (see Fig. 3(c)). In such a G–CuO composite, CuO and Cu dispersed in the graphite electrode act as a shuttle of Li-ions and electrons between the electrolyte and the graphite, respectively. Therefore, the energy barrier for Li-ion transport across the electrolyte/electrode interface is significantly reduced.

4. Conclusions

G–M composites are able to improve the cyclability and rate capability of graphite. The improvement is due to the increase of electron concentration at the surface. For G–CuO composites, a further improvement has been found. A certain reaction between lithium and copper oxide is probably the main reason to catalyze lithium-ion transport onto graphite surface. It is proposed that the transport of Li-ions onto graphite surface is an activation process and plays a dominant role in the kinetics of the following intercalation reaction. The activation energy is correlated with the electron concentration at the surface of the electrode and Li-ion transport process across the electrolyte/electrode interface. Therefore, improved performance of graphite anode (capacity and rate capability) can be established by: (1) increase the interface electron density via metal additives; and (2) create active surface sites for Li-ion fast transport via a certain metal oxide additives. Both additives can lower the activation energy of the transport process and accelerate Li-ion onto the surface of graphite.

References

[1] H. Morose, H. Honbo, S. Takeuchi, K. Nishimura, T. Horiba, Y. Muranaka, Y. Kozono, K. Miyadera, J. Power Sources 68 (1997) 208.
[2] K. Skine, T. Shimoyamada, R. Takagi, K. Sumiyu, T. Takamura, in: Electrochemical Society Proceedings 97–18, Abstract 126, Paris, France, 1997.
[3] H. Huang, Anode materials for lithium-ion batteries, Ph.D. Thesis, Delft University of Technology, Universal Press, The Netherlands, ISBN 90-9013379-8, 1999.
[4] R.A. Nyquist, R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, New York, 1971.
[5] J.R. Dahn, A.K. Sleigh, H. Shi, B.M. Way, W.J. Weydanz, J.N. Reimers, Q. Zhong, U. von Sacken, in: G. Pistoia (Ed.), Lithium Batteries: New Materials, Development and Perspectives, Elsevier, Amsterdam, 1994.
[6] H. Arai, S. Okada, Y. Sakurai, J. Yamaki, Solid State Ionics 106 (1998) 45.