

# Study on the Electrochemical Performance of Graphene Effect on Cadmium Oxide in Lithium Battery

Atef Y. Shenouda, Anton A. Momchilov

**Abstract**—Graphene and CdO with different stoichiometric ratios of Cd(CH<sub>3</sub>COO)<sub>2</sub> and graphene samples were prepared by hydrothermal reaction. The crystalline phases of pure CdO and 3CdO:1graphene were identified by X-ray diffraction (XRD). The particle morphology was studied with SEM. Furthermore, impedance measurements were applied. Galvanostatic measurements for the cells were carried out using potential limits between 0.01 and 3 V vs. Li/Li<sup>+</sup>. The current cycling intensity was 10<sup>-4</sup> A. The specific discharge capacity of 3CdO-1G cell was about 450 Ah.Kg<sup>-1</sup> up to more than 100 cycles.

**Keywords**—CdO, graphene, negative electrode, lithium battery.

## I. INTRODUCTION

THE ever growing demand of the portable electronics industry, the electric vehicle market, and storage for alternative energy sources has put energy storage devices at the forefront of technological investigations [1], [2]. While there may be many ways to store the intermittent power that is from alternative energy resources, the demands and direction of progress of the portable electronic and electric vehicle industries relies heavily on electrochemical storage devices, both batteries and supercapacitors. This dependence on electrochemical storage devices and the need to shift toward higher energy density and low mass devices has specifically focused research attention on lithium ion batteries.

The electrochemical storage of energy and its conversion is of great interest for many practical applications. Electrical energy can be stored through primary and secondary (rechargeable) batteries. The rechargeable lithium ion batteries for portable electronic devices (e.g. PC and laptop computers, wireless and mobile phones, camcorders, etc.) have lately a strong tendency to expansion [3]-[13].

The effect of graphene on tin oxide prepared was studied through hydrothermal preparation [14]. The reversible specific capacity of Li/SnO-graphene (3:1) cell was about 930 Ah.Kg<sup>-1</sup> after 100 cycles. These results indicate that 3 SnO/1 graphene possesses superior cycle performance and high rate capability. The enhanced electrochemical performances with graphene can be attributed to the regulation in the volume change of the

metallic tin through the prevention for the detachment and agglomeration of pulverized tin.

Fine CdO nanoparticles and CdO/Carboxylated multi walled carbon nanotube (CNT) nanocomposites were synthesized via a facile solution method for the first time and characterized by XRD, transmission electron microscopy and electrochemical measurements [15]. As a novel anode material for lithium-ion batteries, the nanosized CdO can deliver an initial capacity as high as 805 Ah.Kg<sup>-1</sup>. However, the capacity retention of pure CdO is poor. By incorporating CNTs and water-soluble sodium alginate binder, the CdO could deliver a reversible capacity of 810 Ah.Kg<sup>-1</sup> up to 100 cycles and a capacity of 720 Ah.Kg<sup>-1</sup> even at the rate of 1500 Ah.Kg<sup>-1</sup>. To better understand the mechanism of the improvements, ex-situ SEM and Energy-dispersive X-ray spectroscopy (EDX) measurements are performed. Our findings would shed light on optimizing the electrochemical performances of other electrodes for lithium-ion batteries and the anodes of Ni-Cd batteries.

Well dispersed CdCO<sub>3</sub>/carboxylated CNTs nanocomposites were synthesized via a facile/CNTs nanocomposites delivered an initial reversible capacity of 876 mAhg<sup>-1</sup> solution method [16]. As a novel anode material for lithium-ion batteries, the CdCO<sub>3</sub> had a better cycle ability. The superior electrochemical performance can be attributed to its unique hierarchy architecture, which facilitates the electron transport and accommodates the large volume change during the alloying/de-alloying reactions.

It was reported that a compound such as CdO, which can react with Li via both of alloying-de-alloying and conversion reactions would be a good choice for investigation. CdO is an important semiconductor with a density of 8.15 Kg m<sup>-3</sup> and relatively low cost. It has been used as the anode for Ni-Cd batteries due to its reversible Cd↔CdO conversion reaction. Moreover, the Cd can alloy with 3 mol lithium to form Li<sub>3</sub>Cd, the total reaction CdO + 5Li↔Li<sub>3</sub>Cd + Li<sub>2</sub>O can deliver a high theoretical capacity of 1046 Ah.Kg<sup>-1</sup> with 5 mol lithium ion consumption [17].

The main challenge of anode materials is the huge volume change during the reversible conversion and alloying process which will lead to pulverization and loss of electrical contact within an electrode and thus to capacity fading [18]-[21]. Intense attempts have been made to address the volume change issues with incremental improvements by minimizing the particle size or incorporating inert buffers to alleviate the fracture and pulverization. Carbon and carbon derivatives such

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as graphene beside CNTs are well-known due to its special 3D structure, superior electronic conductivity, large activated surface area and flexibility. Incorporation transition metal oxides with CNTs have been considered to be a promising method to improve their electrochemical performance. The CNTs serves not only as a conductive agent, but also as an inactive confining buffer to accommodate the volume change during electric cycling [22]-[24].

The aim of this work is to study the effect of graphene on CdO as anode material for lithium batteries as we found a few articles deal with the effect of carbon on CdO.

## II. EXPERIMENTAL SECTION

### A. CdO and Graphene Preparation and Characterization Steps

Graphene and CdO with ratios: 0:1, 1:1, 1:2, 1:3, 1:4 and 1:5 samples were prepared by hydrothermal reaction using stoichiometric ratios weights from  $\text{Cd}(\text{CH}_3\text{COO})_2$ , ammonia solution and graphene. The solution mixture was stirred and heated firstly, at about 15 °C using hot plate to form  $\text{Cd}(\text{OH})_2$ . Finally, the active mixture was transferred into an autoclave and heated at 250 °C for 24 h. The crystalline phases of pure CdO and 3CdO:1graphene were characterized by XRD using Cu- $K_\alpha$  ( $\lambda = 1.5406$  nm) radiation. The particles morphology was studied with a scanning electron microscope (JEOL, model JSM-5040).

### B. Electrochemical Cell Assemble Process

The working electrode (WE) was prepared from slurry (200 mg) of the 70% active material, 15% C- black and 15% binder (polyvinylidene difluoride: PVDF). The slurry was pasted with some drops of N-methyl pyrrolidone (NMP) to form the active material. Copper disk substrate was coated with some of the active material to form the WE. The WE was dried in vacuum oven at 100 °C. A Teflon cell was used to house the lithium foil metal that acts as counter and reference electrode, separator of Celgrad (micro-porous poly propylene). The electrolyte was 1M  $\text{LiClO}_4$  dissolved in propylene carbonate (PC).

### C. Electrochemical Measurements

Galvanostatic charging and discharging cycling of the cells were achieved with potentials windows between 0.01 and 3V vs.  $\text{Li/Li}^+$  using charging and discharging current intensity of  $10^{-4}$  A. Furthermore, impedance measurements were applied using frequency range between  $10^6$  and  $10^{-2}$  Hz using amplitude of 10 mV using Parastat 4000, Princeton, USA.

## III. RESULTS AND DISCUSSION

The XRD pattern is shown in Fig. 1 for CdO nanoparticles, the diffraction peaks are absorbed at  $2\theta$  values. All the intense XRD patterns can be indexed to a pure face centered cubic phase structure CdO. The synthesis of graphene and its characterization was reported in a previous work [14].

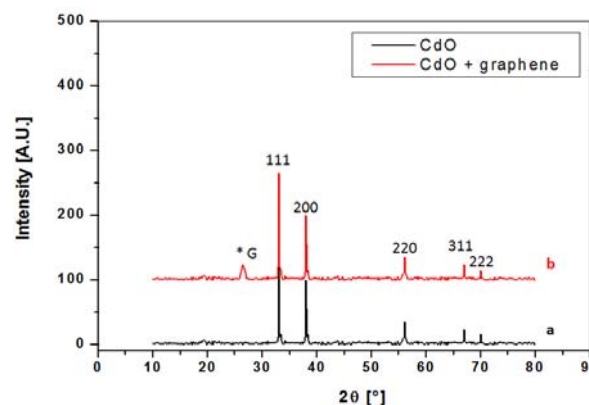


Fig. 1 XRD spectra of CdO (a) and 3 CdO/graphene (b)

The main peak has been used to estimate the grain size of sample with the help of Scherrer equation [7]:

$$x = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where  $\lambda$  is the wavelength ( $\lambda = 1.5418$  Å) ( $\text{Cu } K_\alpha$ ),  $\beta$  is the full width at the half-maximum of the line and  $\theta$  is the diffraction angle. The grain size estimated using the relative intensity peak (111) at  $33.04^\circ$  for CdO particles was found to be 60.3 nm. The (111), (200), (220), (311) and (222) reflections are clearly seen and closely match the reference patterns for CdO (Joint Committee for Powder Diffraction Studies JCPDS No. 78-0653) [15]. Also, the XRD pattern of CdO with graphene is similar to CdO one besides the peak of graphene at  $26^\circ$ . The crystallite size of CdO with graphene particles was about 29.83 nm, which explains the effect of graphene in reducing the particle size. This is similar to previous results of influence of carbon nano tubes on CdO [15].

The morphology of the samples was investigated by SEM as shown in Fig. 2. The pure CdO is displayed as prismatic particles with the particle size of 1–2  $\mu\text{m}$  (Fig. 2 (a)). However, it can be seen that the CdO/graphene (Fig. 2 (b)) is composed of fine CdO nanoparticles covered with graphene layers. The diameter of CdO nanoparticles is about 1  $\mu\text{m}$ .

Electrochemical impedance spectroscopy (EIS) is considered an important technique for the study of the electrode and electrolyte/interface behavior due to surface interchanges [7]. The electrochemical impedance spectra of the cells, as presented in Fig. 3, show  $R_e$  at high frequency.

The charge transfer resistance,  $R_{ct}$ , is equal to the semicircle. The plot of the real part of the impedance,  $Z_{re}$ , versus the reciprocal root square of the lower angular frequencies is displayed in Fig. 4.

There are straight lines in the low frequencies that are attributed to the diffusion of the lithium ions into the bulk of the electrode material, or the so-called Warburg diffusion. This relation is governed by (2).

It is observed that the Warburg impedance coefficient,  $\sigma_w$ , is  $515 \Omega \cdot \text{s}^{0.5}$  for the Li/3CdO-1G cell, and it has the lowest value in comparison with the other cells. The parameters of

the equivalent circuit are presented in Table I. Also, the diffusion coefficient values of the lithium ions for diffusion

into the bulk electrode materials have been calculated using (3) and are recorded in Table I.

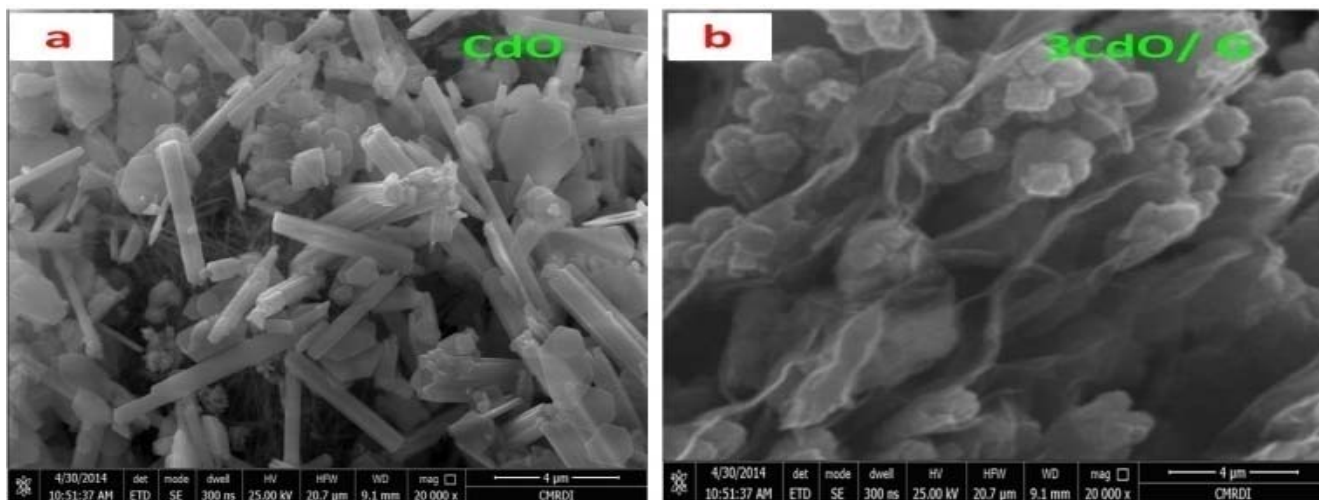


Fig. 2 FESEM of CdO and 3CdO/graphene

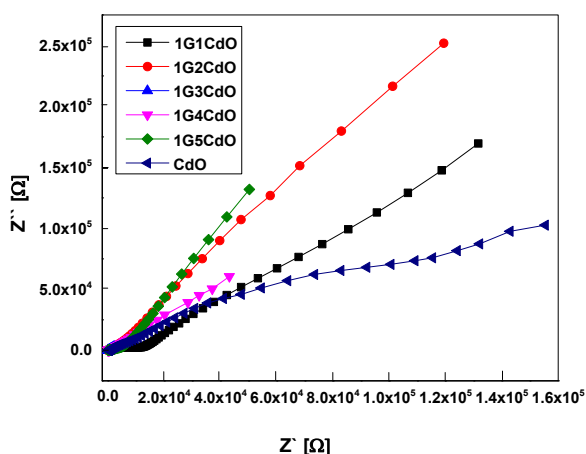


Fig. 3 EIS measurements of CdO and different ratios of CdO/graphene

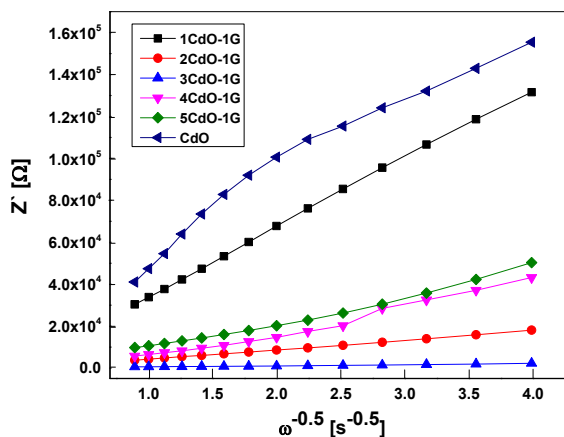


Fig. 4 The plot of real impedance vs. reciprocal root square of angular frequency for the difference cells

$$Z_{re} = R_c + R_{ct} + \sigma_w \cdot \omega^{-0.5} \quad (2)$$

$$D = 0.5 \left( \frac{RT}{A F^2 \sigma_w C} \right)^2 \quad (3)$$

$$Z_{re} = R_c + R_{ct} + 2\sigma_w \cdot C_{dl} \quad (4)$$

The double layer capacitance is given by:

$$\omega = \frac{1}{R_{ct} C_{dl}} \quad (5)$$

where  $R_{ct}$ : charge transfer resistance,  $R_c$ : electrolyte resistance,  $\omega$ : angular frequency in low frequency region,  $D$ : diffusion coefficient,  $R$ : the gas constant,  $T$ : the absolute temperature,  $F$ : Faraday's constant,  $A$ : the area of electrode surface, and  $C$ : molar concentration of  $Li^+$  ions [13], [25].

TABLE I  
EIS OF LI/CDO-GRAPHENE CELLS

Cell	$R_{ct}$ [Ω]	$\sigma_w$ [Ω s <sup>0.5</sup> ]	$D$ [m <sup>2</sup> /s]	$i^0$ [Am <sup>-2</sup> ]	$C_{dl}$ [F]
1CdO-1G	9792	32727	3.31E-19	2.62E-05	1.625E-09
2CdO-1G	442	4632	1.65E-17	5.81E-04	3.60E-07
3CdO-1G	363	515	1.33E-15	7.08E-04	4.38E-06
4CdO-1G	598	11693	2.59E-17	4.30E-04	2.66E-07
5CdO-1G	935	12502	2.26E-17	2.75E-04	2.69E-08
CdO	115432	38293	2.41E-19	2.23E-06	1.37E-10

The obtained diffusion coefficient ( $1.33 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ ) for the Li/3CdO-1G cell explains the higher mobility for  $Li^+$  ion diffusion than in the other cell. Furthermore, the exchange current density is given by:

$$i^0 = RT/nFR_{ct} \quad (6)$$

where  $n$  is the number of electron involved in the electrochemical reaction. Therefore, the charge-transfer reaction of 3CdO-1G electrode is stronger than in the other electrodes.

Fig. 5 shows the curves of the discharge capacity vs. the

cycle number of the samples. The specific discharge capacity of 3CdO-1G cell delivered about 450 Ah.Kg<sup>-1</sup> up to more than 100 cycles. Also, this cell has a higher specific discharge capacity rather than the other cells.

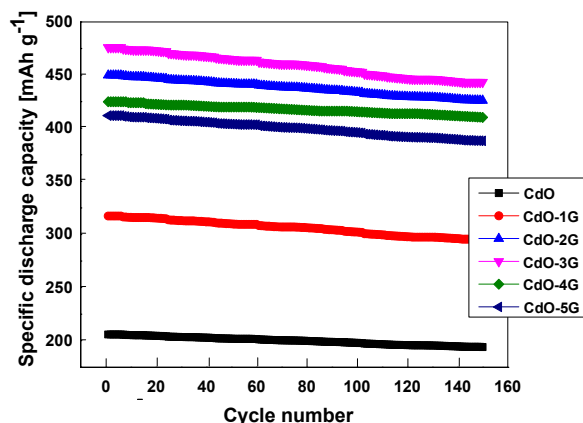


Fig. 5 The cycle life performance of Li / CdO-graphene cells

#### IV. CONCLUSION

All the intense XRD patterns can be indexed to a pure face centered cubic phase structure CdO. The grain size estimated using the relative intensity peak for CdO particles was found to be 60.3 nm. Also, the XRD pattern of CdO with graphene is similar to CdO one beside the peak of graphene at 26°. The crystallite size of CdO with graphene particles was about 29.83 nm, which explains the effect of graphene in reducing the particle size. The morphology of CdO is displayed as prismatic particles with the particle size of 1–2 μm. However, it can be seen that the CdO/graphene is composed of fine CdO nanoparticles covered with graphene layers. The diameter of CdO nanoparticles is about 1 μm. EIS measurements revealed that the Warburg impedance coefficient,  $\sigma_w$ , is 515 Ω.s<sup>0.5</sup> for the Li/3CdO-1G cell, and it has the lowest value in comparison with the other cells. The obtained diffusion coefficient ( $1.33 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ ) for the Li/3CdO-1G cell explains the higher mobility for Li<sup>+</sup> ion diffusion than in the other cell. The specific discharge capacity of 3CdO-1G cell is about 450 Ah.Kg<sup>-1</sup> up to more than 100 cycles.

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