LITHIUM–GRAPHITIC OXIDE CELLS
PART II: HIGH SPECIFIC SURFACE AREA GRAPHITIC OXIDE AS CATHODE MATERIAL FOR LITHIUM BATTERIES

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Summary

A high surface area, chemically-prepared graphitic oxide, $C_8O_4H_2$, has been used as cathodic material in lithium batteries. Good performances have been obtained (2000 W h/kg energy density) because of its physico-chemical and electrochemical properties. Industrial applications can be envisaged.

1. Introduction

There has been a considerable and increasing interest in recent years in research into, and development of, new cathode materials for organic lithium batteries. Such electrodes must satisfy many severe conditions which are rarely met by any one compound, and so few candidates could reach industrial applications [1].

Graphite intercalation compounds (GICs) have been widely studied for their electrochemical applications [2 - 17] and the best performances in the lithium batteries range have been found with graphitic fluorides (CF and C_2F) with a maximum energy density of $D = 2110$ W h/kg for the Li/CF system [2].

Graphitic oxide (G.O.) is like CF a covalent GIC. Its structure and stoichiometry have not been, till now, well defined. However, since its discovery in 1855 by Brodie [18], many authors have studied methods for its preparation [19], and also its chemical and physical properties [20], and have shown the presence of carboxyl and hydroxyl groups with the possible occurrence of keto and epoxide or peroxide groups [21]. Its average formula can be written $C_8O_2(OH)_2$, so the equivalent weight based on 6 electrons per mole is 27 g/eq, lower than that of CF (31 g/eq).

Brown and Storey [22] used G.O. as an MnO_2 substitute in a Leclanché-like battery and Jedlika [23] studied it in an acid secondary battery. More

recently, Hunger and Heymach [4] have shown some discharge tests for a lithium/G.O. battery with a 26% energy efficiency. Besenhard et al. [10 - 11] succeeded in preparing G.O. by electrochemical graphite oxidization in $HClO_4$ media.

Reversibility tests on this material give a 100% faradaic efficiency, but this performance decreases with the number of charge–discharge cycles and with current density [11, 24]. When used in a lithium battery, this electro-chemical G.O. showed relatively good characteristics (33% energy efficiency based on the formula $C_{6.4}O_2H_{1.1}$) [10].

The G.O. we present in this study is obtained from a special original graphite which permits higher lithium battery performance.

2. Experimental

(i) Materials

LiClO$_4$ (Fluka, >99% purity). Propylene carbonate (P.C.) (Fluka, >99%) distilled under vacuum at 180 °C and stored under nitrogen. The electrolyte was 1M $LiClO_4$–P.C. solution.

(ii) Electrodes

Negative: Lithium (Foote Mineral Co., >99% purity) cut into 12 mm dia. discs.

Positive: graphitic oxide (G.O.).

The original graphite is a high specific area (>160 m^2/g), and low gra-nulometry (<5 μm) powder, obtained as vacuum dust during graphite grind-ing (Department of Chemistry, the City University, London).

Graphitic oxide is obtained by the Brodie method, as described in a previous publication [25]. Its chemical analysis before dehydration gives $C_8O_{4.7 \pm 0.4}H_{3.2 \pm 0.4}$ as the average G.O. composition, so the faradaic capacity (electron/carbon) is 0.78 ± 0.10. In this study we have taken $C_8O_2(OH)_2$ as the general formula for the electrochemical calculations (0.75 e/C).

Before use, the compound was dehydrated at 80 °C under vacuum for 10 h and stored under a dry nitrogen atmosphere.

X-ray analysis revealed that the interlayer spacing varied from 7.4 Å for a G.O. exposed to air humidity at room temperature, to the theoretical 6.1 ± 0.2 for dried powder [25].

The N_2-adsorption isotherm curves at 77.3 K gave 50 - 80 m^2/g as the G.O. specific area, depending on that of the original graphite. G.O. is a highly porous electrode with about 50 mm^3/g pore volume.

(iii) Electrochemical cell

G.O. powder was mixed with 10 wt.% of Celanese graphite powder and with 10 wt.% of an organic polymer as binder (polyethylene oxide P(EO)$_8$–LiClO$_4$, in acetonitrile), and pressed under 1 ton/cm^2 to form a pellet 12 mm in diameter.
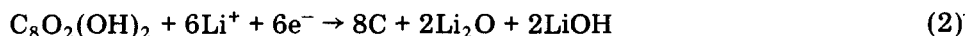
The experimental electrochemical cell can be represented as follows:

$$(-)\text{Li}/\text{LiClO}_4, 1\text{M in P.C.}/\text{C}_8\text{O}_2(\text{OH})_2/\text{C}(+)$$

and the electrode reactions during the battery discharge are:
at the anode:

$$\text{Li} \rightarrow \text{Li}^+ + e^- \tag{1}$$

and at the cathode:

$$\text{C}_8\text{O}_2(\text{OH})_2 + 6\text{Li}^+ + 6e^- \rightarrow 8\text{C} + 2\text{Li}_2\text{O} + 2\text{LiOH} \tag{2}$$

The test cell was of Pyrex glass, as described elsewhere [5].
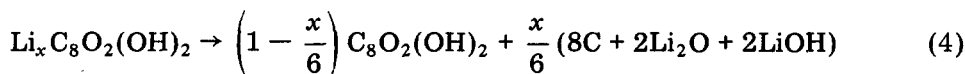
3. Results and discussion

To describe the electrochemical process at the cathode and to calculate the energy density, two battery discharge techniques have been used in this study: galvanostatic with different discharge rates, and voltammetric with cell potential control.

(i) Galvanostatic discharge (chronopotentiometry)

The current density is controlled and the battery potential is followed as a function of time or of x, the amount of lithium intercalated into the G.O. cathode in the reaction:

$$\text{C}_8\text{O}_2(\text{OH})_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C}_8\text{O}_2(\text{OH})_2 \tag{3}$$

Besenhard and co-workers [10, 11] showed that the ternary compound Li–P.C.–G.O. is non-stoichiometric, offering the possibility of Li^+ solvated by P.C. molecules diffusing within the G.O. structure and increasing the interlayer spacing to about 14 Å. This will take place until x reaches a maximum value x_{max}, beyond which a non-reversible electrode decomposition occurs following the scheme:

$$\text{Li}_x\text{C}_8\text{O}_2(\text{OH})_2 \rightarrow \left(1 - \frac{x}{6}\right)\text{C}_8\text{O}_2(\text{OH})_2 + \frac{x}{6}(8\text{C} + 2\text{Li}_2\text{O} + 2\text{LiOH}) \tag{4}$$

Thus, the battery discharge is complete (100% discharge) when $x = 6$.

The discharge curves shown in Fig. 1 correspond to different reaction rates and to the open circuit voltage (O.C.V.) at different stages of utilization. The initial O.C.V. is 3.6 V. In Table 1, we report the most important characteristics of the curves: plateau potential, e, faradaic and energetic yields (ρ_F and ρ_E) and practical energy density (D_{pr}).

The G.O. faradaic capacity Q based on the formula $\text{C}_8\text{O}_2(\text{OH})_2$ can be calculated using the relation:

$$Q = \frac{1}{M_{\text{G.O.}}} \int_{x=0}^{x=6} \frac{F \, dx}{3600} = 990 \text{ A h/kg}$$
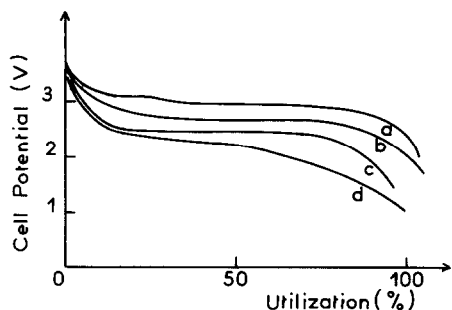
Fig. 1. Li/G.O. cells discharge curves. Li/G.O. cells (a) O.C.V.; (b) i = 25 μA cm^{-2}; (c) i = 100 μA cm^{-2}; (d) i = 630 μA cm^{-2} in 1M LiClO$_4$–P.C. electrolyte.

TABLE 1

High surface graphitic oxide/lithium cells main electrochemical characteristics

$\bar{i}$ (μA/cm^2)	$\langle e \rangle$ (V)	ρ_F (%)	ρ_E (%)	D_{pr} (W h/kg)
0	3.0	—	—	2360
25	2.7	95	85	2020
100	2.5	90	75	1770
630	2.35	85	67	1580

The theoretical energy density, D_{th}, is calculated with 3 V as the maximum average battery potential:

$$D_{th} = 3Q \frac{M_{G.O.}}{M_{G.O.} + 6M_{Li}} = 2360 \text{ W h/kg}$$

ρ_F is defined as: $\rho_F = 100\{x(e = 1.5 \text{ V})/6\}$ and $\rho_E = (\langle e \rangle_i/3)\rho_F$, and $D_{pr} = \rho_E D_{th}$.

(ii) Voltammetric discharge

A slow and linear battery potential decrease of −0.1 mV/min is imposed from 3.6 V (initial potential) to 0.8 V (electrolyte decomposition), and $\bar{i}$, current density, is plotted as a function of e. In Fig. 2 we report two curves obtained under the same conditions: (a) for an Li/G.O. battery, and (b) for an Li/pure graphite system. The first curve shows a peak, A, attributed to the G.O. reduction (reaction (3)) with a maximum rate $\bar{i}$ = 900 μA/cm^2 at 1.5 V. P.C. reduction to propene starts beyond e = 1 V *vs.* Li/Li$^+$ (peak B).

Note that no parasitic reaction from electrode dissolution into the electrolyte has been observed by this voltammetric method.

(iii) X-ray analysis

After complete discharge, the cathode is washed with acetonitrile (to remove P.C. and P(EO)$_8$), then with acidulated water (Li$_2$O, LiOH, Li$_2$CO$_3$,
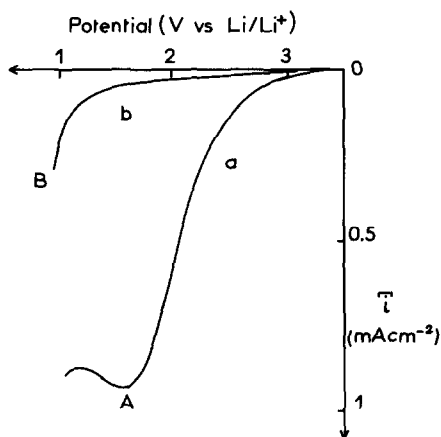
Fig. 2. Voltammetry curves: (a) Li/G.O. system; (b) Li/pure graphite system at 100 μV min^{-1} in 1M LiClO$_4$–P.C. electrolyte.

LiClO$_4$ ...) and dried under vacuum at room temperature. The X-ray diffractogram shows a characteristic pure graphite diagram with 3.35 Å as the strongest line. Thus, as proposed by reaction (4), the G.O. reduction consists of transforming it into graphite.

4. Conclusion

Very good performances have been obtained with this new lithium/high specific surface area G.O. battery. In summary, the most important characteristics of G.O. for application as a cathode are:
  — low equivalent weight giving 990 A h/kg
  — high potential *vs.* lithium anode (3.6 V initial, 3 V O.C.V. plateau)
  — insolubility in the electrolyte
  — good host structure for Li$^+$ diffusion, with a wide, non-stoichiometric range
  — high energy density (>2000 W h/kg).
Other studies [25] have shown that G.O. can be very easily dried and can be stored indefinitely under a dry atmosphere. It is thermally stable up to 150 °C. Industrial applications [26] can be envisaged.

List of symbols

G.I.C.   Graphite Intercalation Compounds
G.O.   Graphitic Oxide
P.C.   Propylene Carbonate
P.E.O.   Polyethylene Oxide

x	Amount of lithium in the G.O. electrode
x_{max}	Maximum reversible x value
i	Cathodic current density (in $\mu A/cm^2$)
$\langle e \rangle_i$	Battery average potential under current i (in V $vs.$ Li/Li$^+$)
D_{th}	Theoretical energy density (in W h/kg)
D_{pr}	Practical energy density (in W h/kg)
ρ_F	Faradaic efficiency under current i (in %)
ρ_E	Energy efficiency under current i (in %)
Q	Faradaic capacity in (mA h/g)
$M_{G.O.}$	G.O. molar mass ($C_8O_2(OH)_2$ = 162 g/mole)
M_{Li}	Lithium molar mass (Li = 7 g/mole)
F	1 Faraday = 96 500 C

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