

LITHIUM-GRAPHITIC OXIDE CELLS PART IV: INFLUENCE OF ELECTROLYTE AND CATHODE COMPOSITION

M. MERMOUX, R. YAZAMI* and Ph. TOUZAIN

*Science des Surfaces et Matériaux Carbonés, U.A. CNRS 413, E.N.S.
d'Electrochimie et d'Electrometallurgie de Grenoble, I.N.P.G., B.P. 75, 38402 Saint
Martin d'Hères Cédex (France)*

Summary

The behaviour of different lithium-graphitic oxide cells in several electrolytes has been investigated at room temperature. Cell performance has been related both to the quality of the graphite precursor (e.g., natural graphite, high surface area graphite, petroleum coke), and to the electrolyte composition. In terms of performance, the use of 2.5 M LiClO₄ in 1,3-dioxolane is preferred to 1 M LiClO₄ in propylene carbonate. The coulometric titration curve of such a cell has been theoretically examined.

Introduction

Previous studies have shown [1, 2] that graphitic oxide (GO) is a potential cathode material for lithium batteries; energy densities above 2000 W h kg⁻¹ have been obtained [1]. In order to improve on this performance, new studies have been undertaken on the cathode material and on the influence of the electrolyte solvent (propylene carbonate (PC) or 1,3-dioxolane (Diox)).

Work has also been conducted on the experimental OCV-X curve. Armand's model [3] has been fitted to experimental data, and good agreement has been obtained.

Experimental

Preparation of cell materials

Several GO samples were prepared using graphites drawn from different origins and subjected to different oxidization routes, i.e., the Brodie

*Present address: Laboratoire d'Ionique et d'Electrochimie du Solide, U.A. CNRS 1213, ENSEEG, BP 75, 38402 Saint Martin d'Hères, France.

(C + HNO₃ + KClO₃) [4] the Staudenmaier (C + H₂SO₄ + HNO₃ + KClO₃) [5] and Hummers and Offemann's (C + NaNO₃ + KMnO₄ + H₂SO₄) [6] methods were used. The oxidation treatment was twice repeated, except for graphitic oxide prepared from petroleum coke (this reaction is very hazardous).

GO powder as the active cathode material was mixed with 10 wt.% graphite powder in order to improve electronic conductivity, and with 10 wt.% of an organic solid electrolyte consisting of polyethylene oxide (POE) and LiClO₄: (POE)₈ LiClO₄, as a binder. This mixture was then pressed under 1 ton cm⁻² to form a pellet of 4.5 mm dia. and 0.5 - 1 mm thickness. Prior to use, the composite electrode was dehydrated for one day at 80 °C under primary vacuum [7], and then stored under dry argon. The PC and Diox solvents were distilled at reduced pressure (<1 mmHg) with sodium in the still pot, and stored on activated alumina. Lithium perchlorate was heated under vacuum for three days at about 180 °C before dissolution in the solvent. The electrochemical cell has been described elsewhere [8]. In this study, an average formula of C₈O₂(OH)₂ will be used in electrochemical calculations.

Testing of cells

Galvanostatic curves were obtained at a current of 100 μA (*i.e.*, a current density of 630 μA cm⁻²). The cell voltage was plotted against the experimental specific capacity (mA h g⁻¹) and against x , the lithium intercalated amount, following the reaction:



where

$$0 < x < x_{\text{max}} \cong 6$$

The open-circuit voltage (OCV) was measured during discharge of a cell by switching off the current for several hours and allowing the voltage to reach a stable value.

Results and discussion

Discharge characteristics of various GO cathodes

Various GO (thin powder GO (TPGO); high surface GO (HSGO), etc.) synthesized by the method described by Brodie [4] have been evaluated as cathode materials by Yazami *et al.* [2]. Another GO prepared from petroleum coke has been compared here to TPGO and HSGO; 1 M LiClO₄ in Diox is used as the electrolyte. All three GOs exhibit flat voltage curves (Fig. 1). Compared with TPGO and HSGO, the galvanostatic discharge curve of petroleum-coke GO shows higher average voltage and capacity values. To date, no explanation has been found for this phenomenon.

The influence of the oxidation method has also been investigated: no marked differences in the electrochemical characteristics of the cells have been observed.

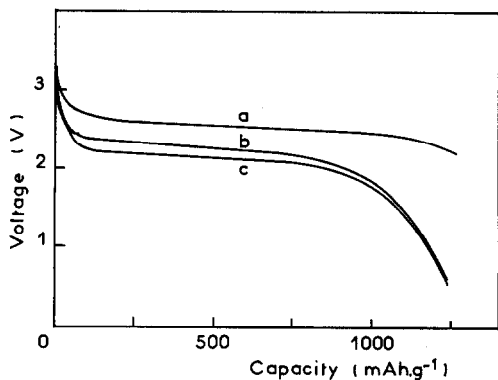


Fig. 1. Effect of graphite origin on galvanostatic discharge curves. (a) Petroleum coke GO; (b) TPGO; (c) HSGO.

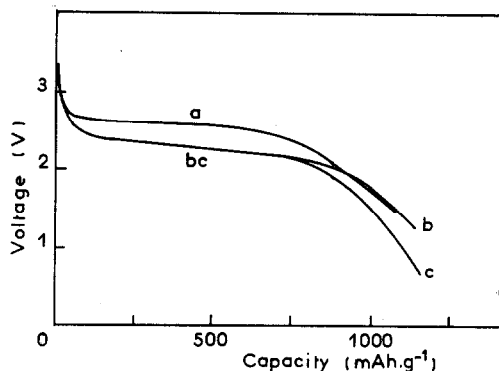


Fig. 2. Effect of electrolyte on galvanostatic discharge curves (TPGO as cathode). (a) 2.5 M LiClO_4 in Diox; (b) 1 M LiClO_4 in Diox; (c) 1 M LiClO_4 in PC.

Electrolyte influence

Both PC and Diox have been employed as the solvent for the electrolyte. LiClO_4 has been mainly used as the lithium salt because of its high solubility in organic solvents. Figure 2 presents galvanostatic discharge curves obtained in various electrolytes. It is of interest to note that 2.5 M LiClO_4 in Diox is effective in improving the discharge performance. This may result from co-intercalation of the Diox within the GO sheets (note, Diox does not intercalate in pure graphite). Expansion of the c axis parameter of GO when the latter is wetted by pure Diox is reported in Table 1 (note, pure PC does not intercalate between GO sheets).

Such co-intercalation does not cause any significant destruction of the cathode material. The formation of the ternary compounds $\text{Li}_x(\text{Diox})\text{GO}$ and $\text{Li}_x(\text{PC})\text{GO}$ leads to an increase of the interlayer spacing to 9.4 Å and 14 Å, respectively. Thus, it can be concluded that the use of a solvent (S) which does not solvate lithium ions as strongly as PC, e.g., Diox, results in an improvement in the discharge characteristics of Li-GO cells.

TABLE 1
c-axis expansion in GO

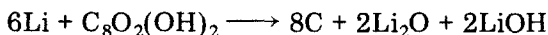
GO sample	d_1^1 (Å)	d_1^2 (Å)
HSGO	6.15	9.4
TPGO	6.15	9.4
Petroleum Coke GO	6.65	9.67

d_1^1 : lattice parameter of dry GO.

d_1^2 : lattice parameter of diox wetted GO.

Coulometric titration curve

The initial OCV of the Li-GO battery is usually between 3.2 and 3.6 V. This value of the OCV may result from the formation of an intermediate non-stoichiometric compound, $\text{Li}_x\text{S GO}$, rather than from the formation of Li_2O and LiOH as given by:



According to the insertion models developed by Armand [3] and by Atlung *et al.* [9], the equilibrium potential, E , of the GO electrode can be separated into three terms: a standard electrode potential E° , a configurational term accounting for the distribution over ideal equivalent sites, and a term $E_{\text{int}}(x)$ representing the interaction of lithium ions with each other or between ions and the host lattice, *i.e.*,

$$E = E^\circ + \frac{RT}{F} \ln\left(\frac{x_{\text{max}} - x}{x}\right) + E_{\text{int}}(x) \quad (1)$$

If the reaction parameter is given relative to its saturation value (x_{max}), *i.e.*, $X = x/x_{\text{max}}$ (with $x_{\text{max}} = 6$), then the potential of the GO electrode assumes the following form:

$$E = E^\circ + \frac{RT}{F} \ln\left(\frac{1 - X}{X}\right) + E_{\text{int}}(X) \quad (2)$$

Since it has been shown previously [3, 9] that the degree of intercalation ($E_{\text{int}}(X)$) is linear with respect to potential, eqn. (2) becomes:

$$E = E^\circ + \frac{RT}{F} \ln\left(\frac{1 - X}{X}\right) - fX \quad (3)$$

In Fig. 3, the experimental OCV- X curve of the Li/2.5 M LiClO_4 in Diox/GO cell is compared with Nernstian behaviour, and is fitted using eqn. (3). It can be seen that good agreement is obtained for $E^\circ = 3.129$ V and $f = 0.258$ (giving 4.15 kJ mole $^{-1}$ for the interaction term).

The interaction energy term between two lithium ions, deduced from the Armand model, cannot be determined because the structure of GO is not well known. Nevertheless, this model is adequate to allow electrochemical studies of the GO electrode, *e.g.*, for determination of the diffusion coefficient of Li^+ in GO according to the GITT method of Huggins [10].

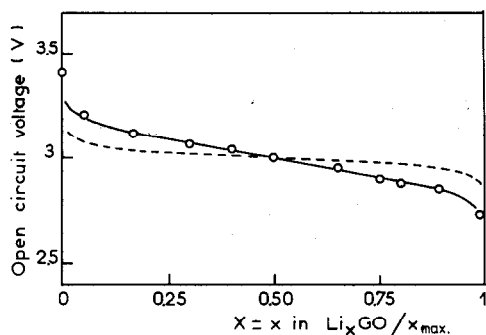


Fig. 3. OCV- X curves. \circ , experimental data; —, $E = 3.129 + RT/F \ln(1 - X/X) - 0.258X$; ---, Nernstian behaviour of GO electrode.

TABLE 2

Performance of Li-GO cells. Graphite oxidation according to method of Brodie [4]

Graphite origin	Fig.	Cell discharge characteristics			
		Electrolyte	Average potential (V)	Capacity (A h kg ⁻¹)	Energy density (W h kg ⁻¹)
TPG	1 (b)	1 M LiClO ₄ in Diox	2.3	990	1825
HSG	1 (c)	1 M LiClO ₄ in Diox	2.25	990	1770
Petroleum coke	1 (a)	1 M LiClO ₄ in Diox	2.5	1150	1970
TPG	2 (c)	1 M LiClO ₄ in PC	2.3	990	1825
TPG	2 (b)	1 M LiClO ₄ in Diox	2.3	990	1825
TPG	2 (a)	2.5 M LiClO ₄ in Diox	2.55	990	2005

Conclusions

A summary of the results obtained for Li-GO cells is given in Table 2. Two main conclusions emerge:

(i) cathode materials using petroleum-coke graphitic oxide exhibit good performance compared with TPGO and HSGO;

(ii) in order to obtain a high energy density, the use of 2.5 M LiClO₄ in Diox as electrolyte rather than 1 M LiClO₄ in PC is required.

For OCV- X curves, an empirical formula has been fitted with experimental data and the total interaction term has been calculated. Further structural studies are necessary to explain this interaction term.

References

- 1 Ph. Touzain, R. Yazami and J. Maire, *J. Power Sources*, 14 (1985) 99.
- 2 R. Yazami and Ph. Touzain, *Synth. Met.*, 12 (1985) 499.

- 3 M. Armand, *Thesis*, Grenoble, 1978.
- 4 B. C. Brodie, *Ann. Chim. Phys.*, 45 (1855) 251; 59 (1860) 466.
- 5 L. Staudenmaier, *Ber. Dsch. Chem. Ges.*, 31 (1899) 1481.
- 6 W. S. Hummers and R. E. Offemann, *J. Am. Chem. Soc.*, 80 (1958) 1339.
- 7 R. Yazami, Ph. Touzain, Y. Chabre, D. Berger and M. Coulon, *Rev. Chim. Miner.*, 22 (1985) 398.
- 8 M. Armand and Ph. Touzain, *Mater. Sci. Eng.*, 31 (1977) 319.
- 9 T. Jacobsen, K. West and S. Atlung, *Electrochim. Acta*, 27 (1982) 1007.
- 10 W. Weppner and R. A. Huggins, *J. Electrochem. Soc.*, 124 (1977) 1569.