

LITHIUM GRAPHITIC OXIDE CELLS. PART V. AN ALL-SOLID-STATE BATTERY USING GRAPHITE OXIDE AS ACTIVE CATHODIC MATERIAL

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Summary

The behaviour of an all-solid-state battery using the $\text{POE}_8\text{-LiClO}_4$ complex as an electrolyte and graphite oxide as the active material has been assessed at 90 °C. Experimental cells show high material utilization up to 0.1 mA cm². Practical performances for an ~ 150 A h kg⁻¹ cell have been presented in terms of energy density and power density. Furthermore, the lithium diffusion coefficient in the graphite oxide structure has been determined either by cyclic voltammetry or by analysis of the discharge curves. A value close to 5×10^{-12} cm² s⁻¹ has been found, reinforcing the use of graphite oxide powder of small particle size.

Introduction

The lithium/graphite oxide battery has evolved from recent research carried out in our laboratory. Graphite oxide has been selected as one of the most promising materials on account of its performance, its price, and its complete compatibility with a number of organic electrolytes over a wide range of discharge rates. Discharge experiments have shown that graphite oxide compares well with graphite fluoride as a cathodic material for lithium batteries in terms of capacity, energy, and power density.

A previous paper [1] has pointed out the solvent dependence of the cell performance. This can be ascribed to the swelling properties of graphite oxide when it is in contact with polar media. The formation of the binary compound solvent/graphite oxide leads, in all cases, to an increase in the interlayer spacing of about 3.3 Å. Average voltages may be directly related to electrolyte solvent donicities.

The use of a solvent-free polymer electrolyte therefore appears to be very attractive in the study of non-solvated lithium intercalation in the graphite oxide structure. As the alternative to conventional lithium/graphite

oxide cells using organic electrolytes, we consider the properties of an all-solid-state battery using the poly(ethylene oxide)-lithium perchlorate complex as the electrolyte. Experimental results are reported at 90 °C.

Experimental

Graphite oxide (G.O.) is prepared from a small particle size natural Madagascar graphite (~10 μm) using a modified Brodie method [2, 3]. Dehydration is carried out for two hours at 80 °C under vacuum [3]. The resulting yellow powder has a chemical composition close to C₈O₄H₂, in agreement with formulae previously reported [4].

The positive electrode consists of an intimate mixture of the G.O. powder (40 - 50 vol%), the electrolyte material: commercial 0.9 M poly(ethylene oxide) and LiClO₄, with an O/Li ratio = 8, (30 - 40 vol%), and acetylene black (10 vol%). Acetonitrile is added to this mixture to make a slurry that is spread onto a stainless steel current collector. The solvent is allowed to evaporate, and the deposit is dried for several hours under vacuum at 80 °C. The electrolyte (POE₈-LiClO₄ membrane) is prepared from the well known ex-solvent procedure [5], with commercial 5 M POE. The anodes were cut from 100 μm lithium foils.

Experimental cells were assembled in argon-filled glove boxes (H₂O ≤ 1 ppm). For intensiostatic discharge experiments, 1.75 cm² cells were stacked from the three components. A three electrode cell was used for voltammetric studies. All measurements were performed under vacuum, to prevent atmospheric contamination, at 90 °C.

In this study, an average formula of C₈O₂(OH)₂ will be used in electrochemical calculations. Under this assumption, the theoretical capacity of the positive electrode and the practical energy has been determined from the coulometric titration curves (see ref. 1) in 1 M LiClO₄-dioxolane media. Values close to 990 A h kg⁻¹ and 2365 W h kg⁻¹ have been obtained.

Results and discussion

Basic hypothesis

The postulated reaction during discharge is:



for which the calculated theoretical capacity is effectively 990 A h kg⁻¹. Such a disproportionation reaction would yield a coulometric titration curve whose potential is independent of the state of discharge. In fact, the observed equilibrium potential decreases gradually with the amount of intercalated lithium. This led us to propose the following discharge mechanism:



The rate at which the binary (or ternary if we consider the solvent) compound decomposes to carbon, lithium oxide, and hydroxide is probably a complex function of the solvent used and the discharge rate imposed on the cell. Note that such a discharge mechanism is generally accepted for lithium/graphite fluoride cells. Finally, X-ray analysis of the discharge products effectively shows the carbon lines, but neither LiOH nor Li₂O has been clearly identified. Another hypothesis, which is somewhat questionable, is to consider that the host substance is electronically conductive.

Two mathematical models will be used for the determination of the lithium diffusion coefficient in the graphite oxide structure. Unlike conventional transient techniques, the two methods applied here yield only integral information, *i.e.*, to the determination of an average value of the diffusion coefficient.

Effect of cathode thickness

Due to the low conductivity of the polymer electrolyte, only a thin film technology can be used [6]. As shown in Fig. 1, the Faradaic efficiency decreases with cathode loading. It is worth noting that electrolyte limitations in the cathodic deposit are very sensitive to cathode loadings higher than 1.5 mA h cm⁻² (corresponding approximately to a 100 μm deposit thickness). Later, results will only be given for thin deposits for which kinetics are limited only by diffusion in the cathode material.

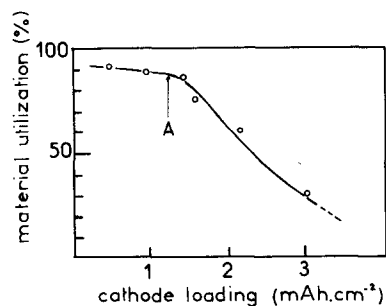


Fig. 1. Plot of material utilization vs. cathode loading.

Cyclic voltammetry

Typical cyclic voltammograms of Li/G.O. cells can be seen in Fig. 2. They are characterized by a unique reduction peak, suggesting that all carbon-oxygen functions are reduced in a one step procedure. In spite of the presence of a reoxidation peak, the second and the third scans (not presented here) tend to show that charge injection leads to an irreversible cleavage of the C-O bonds. The separation between the anodic and the cathodic peaks is very large, and increases with sweep rate. This indicates an irreversible process. The plot of cathodic peak current *versus* the square root of the sweep rate (Fig. 3) and the plot of peak potential *versus* the log of the sweep

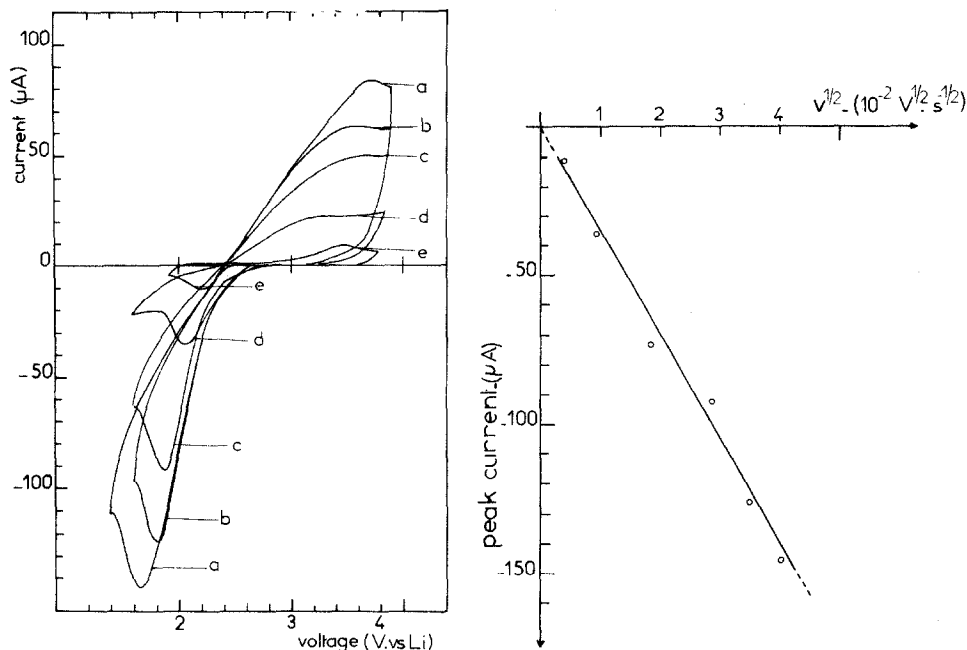


Fig. 2. Cyclic voltammograms of Li/G.O. cells. a, 100 mV/mn; b, 50 mV/mn; c, 20 mV/mn; d, 5 mV/mn; e, 2 mV/mn.

Fig. 3. Plot of cathodic peak current vs. the square root of the sweep rate.

rate (Fig. 4) are linear, as expected for a diffusion controlled process, considering a semi-infinite diffusion, in the 1 - 100 mV mn⁻¹ range. Following Barral *et al.* [7], and assuming that the formation of the non-stoichiometric compound Li_xG.O. [5] is the limiting step in the reduction process, the diffusion coefficient can be estimated at $6 \pm 3 \times 10^{-12}$ cm² s⁻¹ from theoretical analysis of the voltammograms.

Galvanostatic discharge curves

Figure 5 presents the galvanostatic discharge curves of optimized cells at various rates. As reported by Atlung *et al.* [8], the Faradaic yield only depends on the $T \cdot D/a^2$ constant, where T is the stoichiometric discharge time, a the diffusion length (*i.e.*, the radius of the, assumed, cylindrical particles of G.O.) and D is the diffusion coefficient. Here, D can be estimated from the theoretical analysis of discharge curves as $5 \pm 3 \times 10^{-12}$ cm² s⁻¹, in total agreement with the value obtained by voltammetric measurements.

Performances of Li/G.O. cells

Table 1 shows estimates of the power and energy densities deduced from the present results obtained on experimental Li/G.O. cells. These estimates are based on experimentally determined values such as the

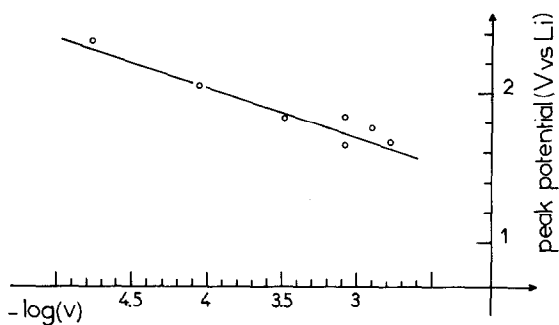


Fig. 4. Plot of the peak potential *vs.* the log of the sweep rate.

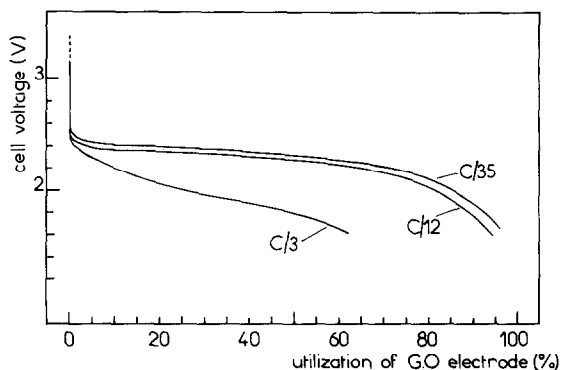


Fig. 5. Galvanostatic discharge curves of optimized cells.

TABLE 1

Practical performances of a 150 A h kg^{-1} optimized cell

	Energy density		Power density	
	W h kg^{-1}	W h l^{-1}	W kg^{-1}	W l^{-1}
C/3	168	203	56	168
C/12	289	350	24	29
C/35	313	379	9	11
C/100	319	386	3	4

Faradaic yield and the electrode thickness. Lithium electrode and electrolyte thicknesses are each assumed to be equal to $50 \mu\text{m}$. Data have been calculated for a 150 mA h g^{-1} experimental cell, corresponding to point A in Fig. 1.

The results are slightly inferior to those obtained with liquid electrolytes [1, 9], probably due to the low conductivity of the electrolyte and the low diffusivity of non-solvated lithium in the G.O. structure.

Conclusion

The present work, although incomplete, suggests the feasibility of an all-solid-state battery using the $\text{POE}_8\text{-LiClO}_4$ complex as the electrolyte and G.O. in a composite positive electrode. Positive results in terms of energy density have been obtained. The lithium diffusivity in the G.O. structure is low compared with the value obtained using the usual inorganic positive materials (10^{-8} - 10^{-10} $\text{cm}^2 \text{s}^{-1}$) but is higher than the value obtained for polyacetylene (10^{-13} $\text{cm}^2 \text{s}^{-1}$). This reinforces the requirement to use G.O. powders of low granular size (a particle size of a few μm is technologically possible) with low discharge rates.

Other experiments, including X-ray *in situ* determinations, ^{13}C and ^7Li NMR measurements, are in progress to obtain a better picture of the reduction process.

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