Graphite electrodes with tailored porosity for rechargeable ion-transfer batteries

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Abstract

A correlation between porosity and electrochemical behavior of thin graphite electrodes has been found. To enlarge the electrode/electrolyte interface area and thus to enhance the maximum current density, LiCl and NH_4HCO_3 were used as pore-forming additives during the preparation of graphite electrodes. By adjusting the porosity, the electrochemical performance of graphite electrodes was improved. The porosity optimization led to ~500 μm thick graphite electrodes. Up to 30 cycles at 1.5 mA/cm^2 (about 50 μA/mg C) have been performed on a number of these electrodes, confirming that a stable specific charge of > 300 Ah/kg (with respect to the graphite mass) can be achieved. Moreover, the irreversible charge loss in the first cycle was moderate, typically only ~20% of the charge for lithium de-intercalation. © 1997 Elsevier Science S.A.

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1. Introduction

In rechargeable lithium ion-transfer batteries, the use of graphite-based negative electrodes (LiC_6) is favored since graphite combines high specific charge with considerable cell safety and cycling behavior [1]. The drawback of graphite electrodes is their only moderate rate capability as well as their strong tendency to co-intercalate solvent molecules, leading in many cases to increased irreversible charge consumption due to extensive film formation between the graphene layers [2,3].

There are two major strategies for improving the electrochemical properties of graphite electrodes: (i) improving the quality of the Li^+-permeable surface films formed on LiC_6 to minimize the irreversible capacity loss related to solvent co-intercalation, and (ii) enlarging the electrode/electrolyte interface area to improve the electrode rate capability. The latter strategy is the object of this work. The microscopic interfacial area depends strongly on the porosity and the pore distribution of the electrode. On very thin electrodes (50–100 μm), Manev et al. [4,5] demonstrated recently the significance of optimum porosity for the performance of graphite electrodes. In this paper we study the relation between the porosity and the electrochemical performance of very thin electrodes. However, the principal aim of our paper is to show

simple but effective methods of tailoring the electrode porosity, allowing the preparation of significantly thicker electrodes (~500 μm) providing acceptable current densities. For an identical cell hardware, thicker electrodes take advantage of higher specific energies of the entire cell.

2. Experimental

100–150 μm thick electrodes of 1.3 cm^2 geometrical area, containing ~15 mg of graphite were prepared from graphite TIMREX KS 44 (TIMCAL AG, Sins, Switzerland) and 4 wt.% poly(vinylidene fluoride) (PVDF) binder. A graphite slurry prepared from a solution of PVDF in 1-methyl-2-pyrrolidinone was spread on a current collector, dried, pressed at various pressures, and then vacuum-dried for about 8 h at 150 °C. Hereafter, these electrodes are designated as 'thin'.

About 500 μm thick electrodes of 1.3 cm^2 geometrical area, hereafter named 'thick', containing about 40 mg of graphite were prepared from graphite KS 44 and either 4 wt.% PVDF or 1.5 wt.% poly(tetrafluoroethylene) (PTFE) binder. The blend of graphite and binder was dried, then dry-mixed with various amounts of NH_4HCO_3 (20–80 wt.%), pressed at various pressures (0.2–8 t/cm^2), and finally vacuum-dried at 150 °C for 24 h. Porous electrodes resulted from the complete decomposition of NH_4HCO_3. Alternatively, porous electrodes were prepared also by mixing the graphite/

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binder blend with 50 wt.% LiCl, pressing the mixture at 4 t/ cm², and extracting the LiCl with water in a Soxhlet extractor over a period of several days. For comparison, some thick electrodes were prepared analogously but without pore-forming additives.

The pore size distribution of the electrodes was calculated from intrusion curves obtained with a mercury porosimeter (Micromeritics Pore Sizer 9320).

Electrochemical data were measured in three-electrode cells with Li counter and Li reference electrodes. Hermetically sealed cells were used in which the working and counter electrodes were permanently pressed (~ 2 kg/cm²) together against a separator soaked with an electrolyte, 1 M $LiN(SO_2CF_3)_2$ in ethylene carbonate/dimethyl carbonate (1:2 by volume). The internal arrangement of the cell components resembled that of button cells [6]. Typically, three preliminary charge/discharge cycles were performed between +0.005 and +1.8 V versus Li/Li^+. Thereafter, charged electrodes were discharged at +5 μA/mg C for 60 min, and a measurement of the polarization curve (cf. Figs. 1 and 5) followed, starting with +10 μA/mg C (about $C/40$) for 60 s and then keeping the electrode at open circuit for 300 s. Then, the experiment was repeated with +20 μA/mg C for 60 s and 300 s open circuit, etc., up to +1280 μA/mg C (about $3C$), the potentials being read immediately before switching the current off. The whole procedure consumed < 13% of the total charge.

In the following text the reversible (C_{rev}) and irreversible (C_{irrev}) specific charge of graphite is discussed. Both are expressed in Ah/kg with respect to the graphite mass. The reversible specific charge is related to Li^+ de-intercalation and the irreversible specific charge is defined as the difference between the charge consumed and released in a charge/ discharge cycle.

3. Results and discussion

3.1. 'Thin' graphite electrodes

The electrochemical performance of 'thin' electrodes depends on the pressure used in their preparation. Table 1
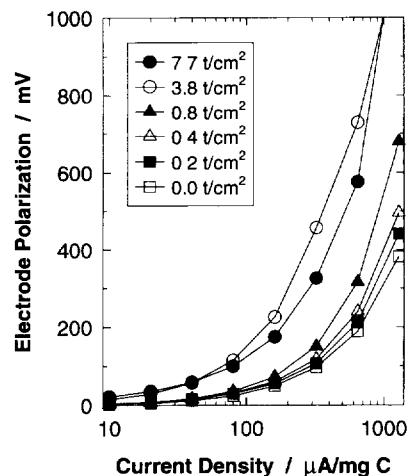

Fig. 1. Typical polarization curves of 'thin' graphite electrodes (TIMREX KS 44) as a function of the preparation pressure.

and Fig. 1 show that increasing the preparation pressure reduces both the reversible and irreversible specific charges and increases the electrode polarization. The reversible specific charge is much more affected by the preparation pressure than the irreversible one. The electrochemical behavior correlates well with porosimetry results. The porosity and the median pore diameter are reduced with increasing preparation pressure (Fig. 2 and Table 1). These results are consistent with the data of Manev et al. [4].

From the perspective of reversible specific charge and electrode rate capability, insufficient porosity and low median pore diameter (due to high preparation pressure) are detrimental to the electrode performance. We attribute this fact to insufficient wetting of the bulk electrode with the electrolyte. Electrodes fabricated at high pressures show a gradual increase in their reversible specific charge with increasing cycle number. Repeated intercalation/de-intercalation of Li^+ causes periodic expansion and contraction of the graphite particles in the composite electrode [7,8]. These periodic changes obviously cause gradual expansion of the entire composite electrode which creates new pores, thus improving the wetting of the electrode by the electrolyte.

Table 1

Reversible (C_{rev}) and irreversible (C_{irrev}) specific charge (in Ah/kg with respect to the graphite mass) as well as porosity and median pore diameters of, (i) 'thin' graphite electrodes as a function of preparation pressure (typical values), and (ii) 'thick' porous graphite electrodes prepared using various preparation pressures and two binders (mean values)

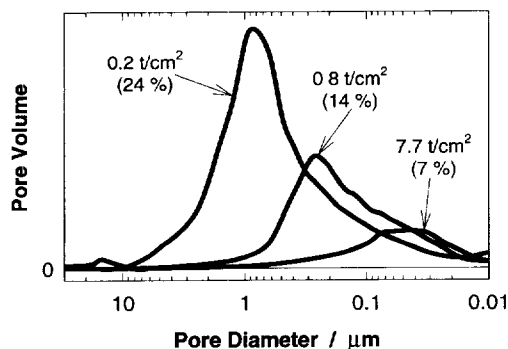| Electrode	C_{rev} 1st cycle	C_{rev} 2nd cycle	C_{rev} 3rd cycle	C_{irrev} 1st cycle	C_{irrev} 2nd cycle	C_{irrev} 3rd cycle	Porosity (%)	Median pore diameter (μm)
'Thin', 7 7 t/cm², PVDF	127	146	182	73	10	15	7	0 06
'Thin', 3.8 t/cm², PVDF	177	214	246	94	15	15	7	0 07
'Thin', 0.8 t/cm², PVDF	248	272	284	84	11	8	14	0.3
'Thin', 0.4 t/cm², PVDF	328	338	345	91	13	7	18	0.6
'Thin', 0 2 t/cm², PVDF	351	355	357	88	12	6	24	0.9
'Thin', 0.0 t/cm², PVDF	365	363	361	106	12	8	63	2 6
'Thick', PVDF	~320	~330	~330	~60	~11	~9	~60	~5
'Thick', PTFE	~340	~355	~355	~70	~10	~5	~60	~5

Fig. 2. Pore size distribution (y-axis, arbitrary units) and porosity (in %) of 'thin' graphite electrodes (TIMREX KS 44) as a function of the preparation pressure
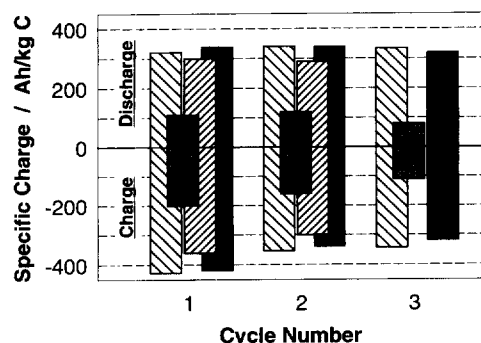

Fig 3. Specific charge [in Ah/kg with respect to the graphite mass; first charging with −10 μA/mg C, then ±50 μA/mg C (about 1.5 mA/cm², ∼C/7) between +0.005 and +1 8 V vs Li/Li⁺] of 'thick' graphite electrodes prepared using the binder PTFE: (▨) without additive, preparation pressure 0.2 t/cm²; (▨) without additive, preparation pressure 3.8 t/cm²; (▧) porous, with 50% LiCl, preparation pressure 3.8 t/cm², H₂O-extracted, (■) porous, with 50% NH₄HCO₃, preparation pressure 3.8 t/cm², thermally decomposed

To achieve an optimum porosity the electrode preparation procedure would have to be optimized at very low preparation pressures. Although their specific charge is acceptable (Fig. 3), electrodes prepared at low pressures show, unfortunately, inferior mechanical stability for practical applications. Hence, to combine mechanical stability with the most favorable porosity, electrode preparation using pore-forming additives has been tested.

3.2. 'Thick' graphite electrodes

The porosity of the 'thick'-type electrodes was regulated by the amount of pore-forming additives (LiCl or NH₄HCO₃) dispersed in the electrode mass during the preparation process. As a result of this preparation procedure the electrode porosity was almost independent of the preparation pressure.

The pore-forming process using LiCl yielded a porosity of ∼60%, the pore diameters vary from 2 to 8 μm. As intended, the charge/discharge performance of porous graphite electrodes improved dramatically in comparison with thick

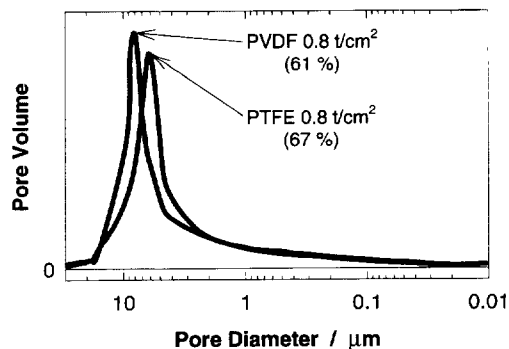Fig. 4. Pore size distribution (y-axis arbitrary units) and porosity (in %) of 'thick' graphite electrodes (TIMREX KS 44 with 50% NH₄HCO₃, thermally decomposed) prepared by using the binder PTFE or PVDF and a preparation pressure of 0.8 t/cm².

compact ones prepared at high pressures [1] (Fig. 3). The alternative pore-forming method using 50 wt.% of NH₄HCO₃ provided similar results, i.e. a porosity of ∼60% and pore diameters mainly distributed in the region from 1 to 10 μm. Although both pore-forming methods gave similar results, the one using NH₄HCO₃ was preferred in subsequent work because it yielded slightly higher specific charges and was simpler to use.

The effect of various amounts of NH₄HCO₃ and of different binder materials in the electrode mass has been examined in detailed investigations. Typically, porosities ranging from ∼35% (20 wt.% NH₄HCO₃) to ∼70% (80 wt.% NH₄HCO₃) have been measured. The pore diameter distribution was not very much affected by the amount of NH₄HCO₃ and also the type of binder material showed no critical influence on the porosity. Fig. 4 shows two representative pore distribution curves. (Compare with Fig. 2 where pore distribution curves for electrodes prepared without pore-forming additives are shown.)

Electrochemical tests showed that for ≥20 wt.% NH₄HCO₃ the amount of this additive does not influence the available specific charge of graphite significantly but the electrode polarization at high rates. Through optimization of the electrode composition and the conditions of electrode preparation mechanically stable 'thick' electrodes were developed. The electrodes can be fabricated by either pressing or rolling. Their porosity and, therefore, their electrochemical properties (Table 1, Fig. 5) are almost insensitive to the applied preparation pressure. (The two polarization curves for 'thick' electrodes prepared without pore-forming additives shown as dashed lines in Fig. 5 confirm the beneficial effect of the pore-forming additives as discussed above.) Slightly better specific charges were measured when PTFE was used as a binder instead of PVDF (Fig. 6). We suspect that in the case of PVDF, which was applied from a solution, a part of the graphite surface is covered and therefore blocked by a thin PVDF film. This film has been earlier observed in

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[1] Be aware of a strong rate dependence of thick compact electrodes. The use of significantly lower current densities increases naturally the specific charge available from compact non-porous electrodes
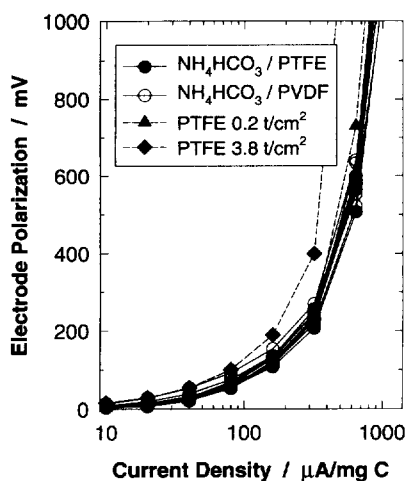
Fig. 5. (——) Polarization curves of 'thick' graphite electrodes (TIMREX KS 44 with 50% NH$_4$HCO$_3$, thermally decomposed) prepared by using the binders (●) PTFE or (○) PVDF and various preparation pressures (0.2–8 t/cm^2). (- - -) Polarization curves of 'thick' graphite electrodes prepared as above but without the NH$_4$HCO$_3$ additive; preparation pressure (▲) 0.2 t/cm^2 and (◆) 3.8 t/cm^2.

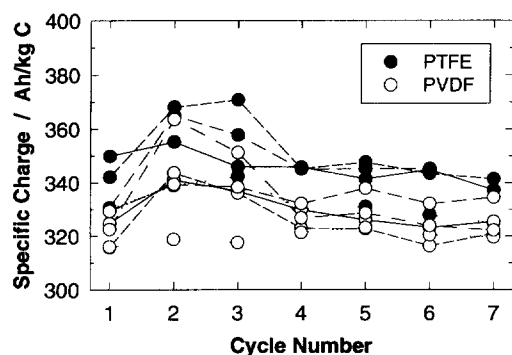Fig. 6. Scattering of specific charge for Li$^+$ de-intercalation (discharge, in Ah/kg with respect to the graphite mass) of 'thick' porous graphite electrodes prepared by using the binders PTFE or PVDF; cycling with about 1.5 mA/cm^2 (~ C/7) between +0.005 and + 1.8 V vs. Li/Li$^+$

our laboratory [9] on petroleum cokes by scanning electron microscopy (SEM). (PTFE in the electrode has a fibrous morphology. It cannot, therefore, block the surface.) In addition, the PVDF has a tendency to swell in organic electrolytes. Swelling of a binder can disintegrate the composite electrode to some extent. Moreover, it is our experience from the preparation of 'thin' electrodes that the casting 'slurry method' is superior to 'pressing methods' in the case of the PVDF binder. We assume that for the preparation of 'thick'-type electrodes the binding properties of PVDF could be also improved by the use of the 'slurry method'.

During the first seven charge/discharge cycles on our optimized porous graphite electrodes shown in Fig. 6, a reproducible (around ± 5%) and stable specific charge of ~ 340 Ah/kg (with respect to the graphite mass) was observed even

at current densities of up to 1.5 mA/cm^2 (about 50 µA/mg C). Moreover, the irreversible charge loss in the first cycle was moderate, typically ~ 20% of the reversible charge. Up to 30 cycles at 1.5 mA/cm^2 have been performed on a number of electrodes confirming that the specific charge of > 300 Ah/kg (with respect to the graphite mass) is stable.

4. Conclusions

A correlation between the porosity and electrochemical behavior of thin graphite electrodes was found, confirming the recent results of Manev et al. [4]. LiCl and NH$_4$HCO$_3$ were used as pore-forming additives during the preparation of graphite electrodes to provide custom-tailored porosity. By adjusting the porosity, the electrochemical performance of graphite electrodes could be improved. Moreover, in comparison to electrodes prepared without additives, the pore size is more uniform and almost independent of the preparation pressure and binder. We expect that our method of electrode preparation is suitable for many kinds of insertion electrode.

The best results were obtained using NH$_4$HCO$_3$ as the pore-forming additive. About 500 µm thick graphite electrodes having stable specific charge of > 300 Ah/kg (with respect to the graphite mass) at current densities of up to 1.5 mA/cm^2 were prepared using the method described.

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