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Determination of the absolute and relative extents of basal plane surface area and “non-basal plane surface” area of graphites and their impact on anode performance in lithium ion batteries

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Abstract

For graphites as anode materials in lithium ion batteries, the chemistry and morphology of the prismatic surfaces of graphite play a major role in chemical and electrochemical reactivity, interaction with the solid electrolyte interphase (SEI), kinetics for lithium intercalation and de-intercalation, etc. whereas the basal plane surfaces have only minor or no influence on these reactions. We show how gas adsorption data, such as those, which is used for determination of the Brunett–Emmet–Teller (BET) surface area of solids, can be used to estimate the absolute and relative extents of basal plane surface area and “non-basal plane surface” area of graphites used as anode materials in lithium ion batteries. The “non-basal plane surfaces” can be further sub-divided into prismatic surfaces and “defect surfaces” (the latter contain surface groups and other surface defects). In particular, the relation of the first cycle irreversible capacity to the different types of surfaces will be highlighted. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium ion battery; Graphite anode; Nitrogen adsorption; Adsorptive potential; Surface energy distribution; Surface area

1. Introduction

Solid electrolyte interphase (SEI) formation on graphite anodes in lithium ion cells inevitably involves the irreversible consumption of both charge capacity and material (lithium and electrolyte). This “irreversible capacity” C_{irr} depends largely on the electrode surface accessible to the electrolyte. Basically, the electrode structure (type of binder, binder content, porosity, mechanical properties, etc.) and the type of graphite (characterised by properties, such as surface area, particle shape and particle size distribution, etc.) determine this surface.

The structure of layered graphite gives rise to basically two kinds of surfaces, prismatic (edge) surfaces and basal plane surfaces. Ideal (=defect and contaminant free) basal plane surfaces are homogeneous and “smooth” and consist only of carbon atoms. In contrast, the prismatic surfaces are heterogeneous and “rough” and apart from carbon may contain various, mostly oxygen-containing surface groups. It is well known that the prismatic and basal plane surface

areas of graphite show a different physical, chemical and electrochemical behaviour in many respects [1,2].

For graphite as anode material in lithium ion batteries, it is widely accepted that the chemistry and morphology of the prismatic surfaces of graphite play a major role in chemical and electrochemical reactivity, interaction with the SEI, etc., e.g. [3–5]. In accordance with the fact that surface group reduction and solvated intercalation take place at the prismatic surfaces, it was concluded in previous work [4], that prismatic surface areas of graphite contribute more to C_{irr} than basal plane surface areas (when surfaces of the same area size are compared) and thus deduced “. . . that the ratio of the basal to the prismatic surfaces is an important factor in determining the dependence of charge losses on the graphite . . . surface area.” [4]. This finding was confirmed in works by Chung et al. [6] and Zaghbi et al. [7], who made calculations on the effect of the ratio of prismatic and basal plane surfaces of flake type graphite on C_{irr} by using idealised graphite structures as models for their calculation. In line with these works, Bar-Tow et al. [8] have reported that the SEI products at basal plane surfaces and prismatic surfaces of highly oriented pyrolytic graphite (HOPG) may differ considerably. Finally, apart from its special effect on the extent of SEI formation and C_{irr} , the extent of prismatic

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surfaces determines also the kinetics of the graphite electrode towards the charge/discharge reaction of the graphite anode in a lithium ion cell, which is lithium intercalation and de-intercalation via the prismatic surfaces. In conclusion, the information about the relative and absolute extents of prismatic and basal plane surface areas in a graphite material are essential for understanding and controlling the irreversible and reversible reactions of the graphite anode in lithium ion cell.

The adsorption of nitrogen at 77 K is a commonly used measurement for the determination of the total specific surface area (in $\text{m}^2 \text{g}^{-1}$) of graphites and other materials through application of the well known BET equation. Basically, C_{irr} increases with the BET surface area and for similar electrode structures and similar types of graphite there seems to be a more or less linear correlation between the BET surface area and C_{irr} [4].

The determination of the BET surface area is based on the premise that the surface of the solid adsorbent is homogeneous, and thus, the whole surface adsorbs the same extent of nitrogen per area, such that the calculation of the nitrogen volume forming a mono-layer on the adsorbent allows to determine the surface area. Any surface heterogeneities leading to different degrees of (multi-layer) nitrogen adsorption at different surface sites are not accounted for in the BET theory. This means that the surface area of a heterogeneous materials measured by nitrogen adsorption and calculated via a theory, such as the BET theory, may be not the “true” surface area of the material. From this point of view, the — at first sight — trivial conclusion, that C_{irr} increases linearly with the BET surface area, is in fact quite surprising for that case where materials with heterogeneous surfaces such as flake type graphites are investigated.¹

In this contribution, we show how the same type of gas adsorption measurements employed for the BET method can be used to estimate not only the total surface area, but to individually estimate the absolute and relative extent of prismatic and basal plane surfaces present in a graphitic material, by employing a deconvolution technique. This method is based on a model for describing adsorption on an energetically heterogeneous surface developed by Ross and Olivier [9,10]. The premise of the model is that the surface of a real solid is composed of small patches (i) that adsorb nitrogen with different affinities (or different adsorptive potential²) and (ii) that adsorb independently of one another. It is further assumed that the distribution of adsorptive potentials³ among these patches can be represented by a

continuous distribution function. In the case of physical adsorption, this adsorptive potential is largely determined by the density of the adsorbent constituent atoms at the adsorbing interface. For graphite, this means that the basal plane, having a higher areal density of carbon atoms, will have a greater adsorptive potential, hence, adsorb more strongly than the less dense prismatic surfaces.

At any equilibrium pressure, p , under isothermal conditions, the quantity adsorbed per unit area, q , on a given surface patch will depend only on the adsorptive potential of that patch according to the function $q = q(p, \varepsilon)$. The observed total amount adsorbed, Q , at pressure p is then the sum of the contributions from each surface patch, i.e. given by the convolution integral

$$Q(p) = \int q(p, \varepsilon) f(\varepsilon) d\varepsilon \quad (1)$$

where $Q(p)$ is an experimental adsorption isotherm, $f(\varepsilon)$ the adsorptive potential distribution by area, and $q(p, \varepsilon)$ a function describing the theoretical adsorption isotherm on an energetically uniform surface patch having an adsorptive potential ε . In this work, the function $q(p, \varepsilon)$ is evaluated by using non local density functional theory (DFT) [12], which has been verified to accurately describe experimental data obtained on an energetically uniform surface. The mathematical task of inverting Eq. (1) to extract the adsorptive potential distribution from adsorption data has been described in detail elsewhere [11]. Thus, the use of Eq. (1) provides the possibility to refine the correlation of C_{irr} to the nature, as well as to the extent, of the surface.

2. Experimental

The materials investigated were TIMREX[®] synthetic graphite powders KS6, KS10, KS44, KS75 and KS75KM, (Timcal group), with different surface area and particle size distribution. For example, KS6 means that 90% of the particles are $<6 \mu\text{m}$. The KS75KM has been prepared from the KS75 by a special milling procedure.

The adsorption isotherms were measured over six decades of pressure using a Micromeritics ASAP2010 equipped with 1000, 10 and 1 Torr pressure transducers. The standard instrument software was employed, and the DFTPlus data reduction software was used to produce the adsorptive potential distributions.

Galvanostatic half cell experiments (Li counter and reference electrodes) were performed at a specific current of $\pm 10 \text{ mA g}^{-1}$ and with the cut-off of 2.0/0.005 V versus Li/Li⁺. Composite electrodes have been made from the respective graphite and 4 w/o poly(vinylidene) fluoride binder. The electrolyte was made from 1 M LiN(SO₂CF₃)₂ and ethylene carbonate (EC)/dimethyl carbonate (DMC), 1/2 by volume. More experimental details can be found in [4].

¹ We note that the correlation of C_{irr} with the specific capacitance (e.g. [6]) is also influenced by the surface heterogeneity of graphite as the double layer capacity of basal plane surfaces of highly crystalline graphites such as HOPG is typically more than a magnitude smaller than that at the prismatic surface [1].

² The unit of the adsorptive potential is Kelvin (K) [11].

³ Instead of the term “distribution of adsorptive potentials”, the terms “surface energy distribution” or “adsorptive energy distribution” can be used synonymously.

3. Results and discussion

The adsorptive potential distributions of the TIMREX[®] graphites KS75 and KS 75KM are shown in Fig. 1. For the other graphite samples similar graphs exist, but are not shown here for space reasons. The surface areas calculated by the BET method and by the DFT method are gathered in Table 1 for all graphite samples. The adsorptive potential distributions are quite broad indicating considerable surface

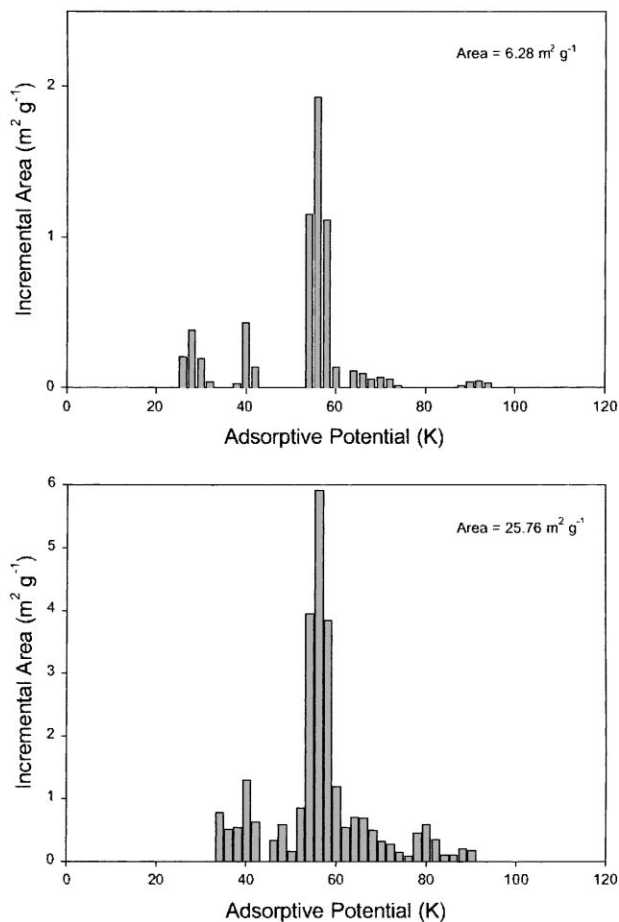


Fig. 1. Incremental area vs. adsorptive potential plots of TIMREX[®] graphites KS75 (top) and KS75KM (below).

heterogeneity. From previous work with a graphite exposing almost only basal planes to the surface [11], it is known that the adsorptive potential distributions centred at 57 ± 2 K represents the basal plane surface. From physical considerations (see above), the lower adsorptive potential portions may represent the prismatic surface. Dislocations and defects, such as surface steps or surface groups (=defect surface), which result in a higher affinity to the adsorbed nitrogen than pure carbon atom basal plane surfaces, can account for the higher adsorptive potential portions of the distribution. By integrating under the increments, we determined the relative extents of basal plane surface area, prismatic surface area, and “defect surface” area (Table 1). Table 1 displays also the ratio of basal plane surface area to “non-basal plane surface” area, the latter accumulates both the prismatic surface area and “defect surface” area. For the KS6, KS10, KS44 and KS75 samples, we have measured very similar ratios of the prismatic surface area to the basal plane surface area to the “defect surface” area as well as for the ratio of the basal plane surface area to the “non-basal plane surface” area. This means that the relative extents of the respective surfaces in a certain graphite material are very similar — considering that these graphites are technical products the similarity is astonishing. However, the absolute values are of course different as graphite powders with different total surface areas are compared.

At contrast, the milled sample KS75KM displays a quite different ratio of the respective surface areas, mainly due to a much higher relative extent of “defect surface”, which indicates the introduction of “new” surfaces, e.g. new defects and surface groups, by the milling procedure. This is confirmed by Fig. 1, showing a much wider distribution of adsorptive potentials in case of the KS75KM.

In addition, we noted, because of the excellent description of the data provided by Eq. (1), that there is no evidence of porosity in these materials for pores <50 nm.

Fig. 2 displays the correlation of the irreversible capacity, C_{irr} , of graphite electrodes with the surface area of graphite powders measured by gas adsorption and calculated by the DFT method. There seems to be linear correlation between C_{irr} and the DFT surface area, except for sample KS75KM.

Table 1

BET surface areas, DFT surface areas, prismatic, basal plane and “defect” surface areas, ratio of prismatic surface area to basal plane surface area to “defect surface” area and ratio of basal plane surface area to “non-basal plane surface” area of various TIMREX[®] graphites, derived from gas adsorption data

TIMREX graphite	BET surface area (m ² g ⁻¹)	DFT surface area (m ² g ⁻¹)	Prismatic surface area (m ² g ⁻¹)	Basal plane surface area (m ² g ⁻¹)	“Defect surface” area (m ² g ⁻¹)	Ratio of prismatic surface area (%):basal plane surface area (%):“defect surface” area (%)	Ratio of basal plane surface area (%):“non-basal plane surface” area (%)
KS6	17.12	18.02	3.67	12.31	2.05	20.4:68.3:11.3	68.3:31.7
KS10	12.54	13.43	2.94	9.36	1.13	21.9:69.7:8.4	69.7:30.3
KS44	7.30	7.84	1.65	5.37	0.82	21.0:68.5:10.5	68.5:31.5
KS75	5.67	6.28	1.41	4.35	0.53	22.4:69.3:8.3	69.3:30.7
KS75KM	25.34	25.76	4.83	16.26	4.68	18.8:63.1:18.1	63.1:36.9

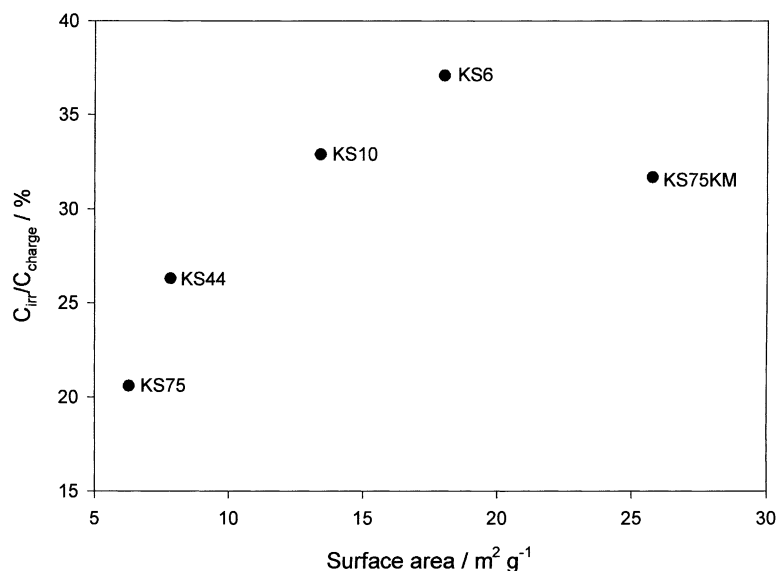


Fig. 2. Irreversible charge loss C_{irr} (relative to the charge capacity) of TIMREX[®] graphites as a function of the surface area measured by gas adsorption and calculated by DFT. The discharge (reversible) capacities in the first cycle range between 327 and 346 Ah kg⁻¹ (with respect to the graphite mass).

This is in line with previous data on these samples, where the electrochemical data has been correlated with the BET surface area [4].

Considering the above-mentioned remarks to the influence of non-basal and basal plane surfaces on C_{irr} , the roughly linear correlation between surface area and C_{irr} for the unmilled samples is again remarkable, because one might expect that the high surface area graphites, with large prismatic surface areas cause C_{irr} values, which are higher than those suggested by the observed linear correlation between DFT surface area and C_{irr} . It might be (i) that the influence of the electrode structure (different particle sizes result in different electrode densities and in different coverage of the graphite particles with the binder, which eventually results in different contact zones with the electrolyte and thus different C_{irr}) levels the differences in surface heterogeneities of the graphite powders, or (ii) that the extent of the non-basal plane surface area (these, however, reach typically >30% here!) is too small to have a more pronounced effect on C_{irr} as has been also proposed in [6], (iii) that the different affinities towards nitrogen adsorption of the basal plane and non-basal plane surfaces are somehow represented by the C_{irr} values, i.e. that the graphite surfaces which adsorb more nitrogen per area also consume more C_{irr} and vice versa or (iv) that other particle or material parameters e.g. particle thickness [4] or crystallinity, which both change after milling, have also an influence.

4. Conclusion

Total surface areas can be determined by gas adsorption measurements and subsequent calculation via a theory based on simplifying assumptions. This measured/calculated sur-

face area may be different to the “true” surface area of the sample, in particular when non-uniform heterogeneous surfaces are investigated. Here, we have demonstrated a method (theory) for the determination of surface heterogeneities of solids by adsorptive potential distribution. Up to our knowledge for the first time, we have quantified the absolute and relative extent of “non-basal plane surfaces” (=accumulated prismatic surfaces and “defect surfaces”) and basal plane surfaces for *practical* graphite powders feasible as anode materials in lithium ion batteries.

The results are quite complex, as the investigated graphites show quite broad distributions of adsorptive potential. The situation is even more complicated after milling of graphite as the distribution becomes broader, indicating an even more heterogeneous surface. This makes a correlation with electrochemical parameters, such as the irreversible capacity C_{irr} difficult, in particular a quantitative correlation.

In addition, the electrode structure has to be considered, meaning that the surface of a *composite graphite electrode*, which is accessible to the electrolyte, can be expected to differ considerably from the surface of *graphite powder*, which is accessible to N₂ at 77 K. In general, in comparison to materials parameters, the preparation technique of the electrode might have a superior influence on C_{irr} , i.e. our electrochemical findings may differ from results obtained in other laboratories, even when the same graphites, binders and electrolytes are used. However, we wish to point out, that it is clear from our results that a linear correlation between the surface area measured by gas adsorption (and then calculated by a certain theory) and C_{irr} can not be expected in all cases, and in particular not in cases, when carbons, such as flake-type graphites with considerably different surface heterogeneities are compared. In a forthcoming report, we will give additional electrochemical, gas

adsorption, SEM and particle size data, which might help to further elucidate the influence of the different graphite surface sites on C_{irr} .

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