Influence of the electrode nano/micro structure on the electrochemical properties of graphite in aluminum batteries

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Supporting information

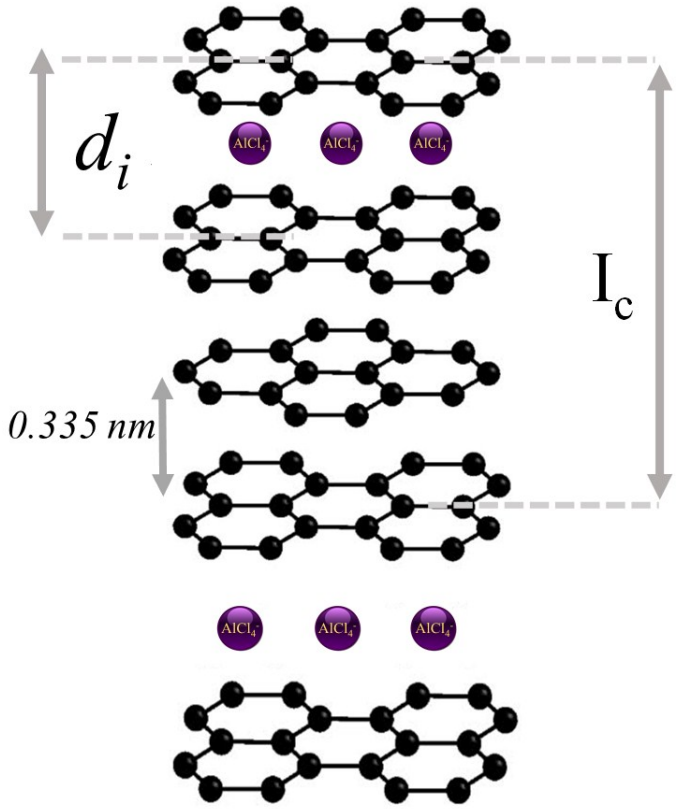

Figure S1 Scheme of a graphite intercalated compound (GIC) indicating the periodic repeat distance I_c and the gallery height d_i.

Table S1 Calculated values from the ex-situ X-ray diffraction measurements of the $AlCl_4^-$ intercalation into pyrolytic graphite: Charged 25 mAh g^{-1} (Ch25-green), fully charged (FullCh-red), discharged 50 mAh g^{-1} (Dis50-orange), and fully discharged (FullDis-yellow)

	Ch25	**FullCh**	**Dis50**	**FullDis**
2θ (00n + 1), degree	27.78	28.28	28.28	27.66
2θ (00n + 2), degree	24.11	23.37	23.87	24.25
$2\theta_{(n+1)}$ / $2\theta_{(n+2)}$ ratio	1.15	1.21	1.18	1.14
Dominant stage (n)	6	4	5	6
I(00n + 1)	7	5	6	7
$d_{obs\ (n+1)}$, nm	0.331	0.325	0.330	0.330
I(00n + 2)	8	6	7	8
$d_{obs\ (n+2)}$, nm	0.377	0.388	0.381	0.381
Periodic repeat distance (I_c),/ nm	2.6±0.7	1.9±0.7	2.3±0.7	2.6±0.7

$$I(q) = Cq^{-\alpha} + C_0 \tag{S1}$$

Equation S1 The power function used to fit the SAXS curve in the range of 0.06 $nm^{-1} \leq q \leq 1\ nm^{-1}$ where C, C_0, and α are fitting parameters.

$$V_{Amplitude} = A\frac{\int_{-\infty}^{\infty} \frac{exp(-u^2)}{\gamma^2/2\sigma^2 + ((q-q_c)/\sqrt{2}\sigma - u)^2} du}{\int_{-\infty}^{\infty} \frac{exp(-u^2)}{\gamma^2/2\sigma^2 + u^2} du} \tag{S2}$$

Equation S2 The amplitude version of the Voigt peak used to fit the SAXS curve in the range of 1 $nm^{-1} \leq q \leq 4\ nm^{-1}$ where A is the amplitude of the Voigt peak, q_c is the location parameter, σ is the width of Gaussian contribution, and γ is the width of the Lorentzian contribution.

Table S2 Fitting parameters of the SAXS curves of the samples investigated. C_0, C, and α are the fitted parameters obtained from equation (S1). A, q_c, σ, and γ are the fitted parameters obtained from equation (S2). I_c is the calculated periodic distance (error calculated by error propagation from the Bragg law).

Parameter		Pristine	Ch25	FullCh	Dis50	FullDis
Power law	C_0, a.u.	0.01±0.01	0.20±0.01	0.34±0.02	0.27±0.02	0.20±0.03
	C, a.u.	1.80±0.01	1.05±0.02	0.59±0.02	0.34±0.01	0.61±0.01
	α	3.70±0.01	3.60±0.01	3.54±0.02	3.70±0.01	3.58±0.02
First peak	A, a.u.	-	0.46±0.05	0.65±0.01	1.02±0.02	1.73±0.03
	q_c, nm^{-1}	-	2.33±0.03	3.28±0.01	3.13±0.01	2.42±0.04
	σ, nm^{-1}	-	0.29±0.04	0.10±0.01	0.08±0.01	0.17±0.03
	γ, nm^{-1}	-	0.05±0.05	0.00±0.05	0.15±0.01	0.16±0.05
	I_c, nm	-	2.6±0.2	1.9±0.1	2.0±0.1	2.6±0.1
Second peak	A, a.u.	-	-	-	0.50±0.02	-
	x_c, nm^{-1}	-	-	-	2.85±0.01	-
	σ, nm^{-1}	-	-	-	0.15±0.01	-
	γ, nm^{-1}	-	-	-	0.08±0.01	-
	I_c, nm	-	-	-	2.2±0.1	-

Table S3 Periodic repeat distance and dominant stage values calculated from the SAXS measurements and by ex-situ X-ray diffraction, and the gallery expansion, Δd, (obtained by SAXS I_c) of the $AlCl_4^-$ intercalated ion into pyrolytic graphite at different charging states.

	I_c (XRD) / nm	***I_c (SAXS) / nm***	***n (XRD)***	***n (SAXS)***	***Δd / nm***
Ch25	2.6±0.7	2.6±0.1	6	6	0.59
FullCh	1.9±0.7	1.9±0.1	4	4	0.56
Dis50	-	2.0±0.1	-	4	0.66
Dis50	2.3±0.7	2.2±0.1	5	5	0.53
FullDis	2.6±0.7	2.6±0.1	6	6	0.59

Table S4 Electrode parameters as determined by CT. *n (tomo)* is the dominant stage evaluated by equation 3. The segmentation threshold level is also indicated.

Sample	***Degree of anisotropy***	***Fractal dimension***	***Otsu threshold***	***Electrode thickness µm***	***Thickness Calculated µm***	***n (tomo)***
Pristine	2.24	2.64	104	106±6	100	∞
Ch25	2.75	2.66	106	129±12	131	6
FullCh	2.99	2.69	105	144±18	147	4
Dis50	3.28	2.71	106	147±9	147	4
FullDis	3.08	2.67	105	134±5	131	6

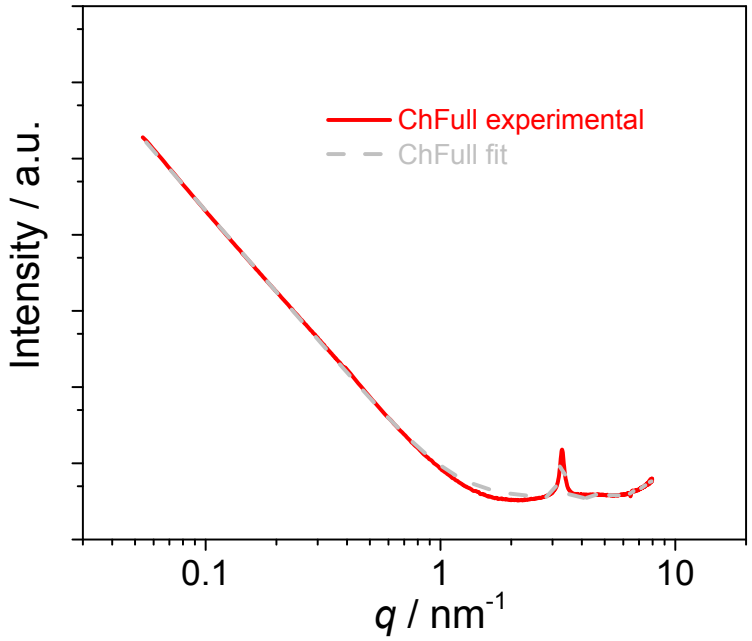

Figure S2 Small-Angle scattering curves at 10 keV of the fully charged PG electrode (red line) and fitted curve (grey dashed line).

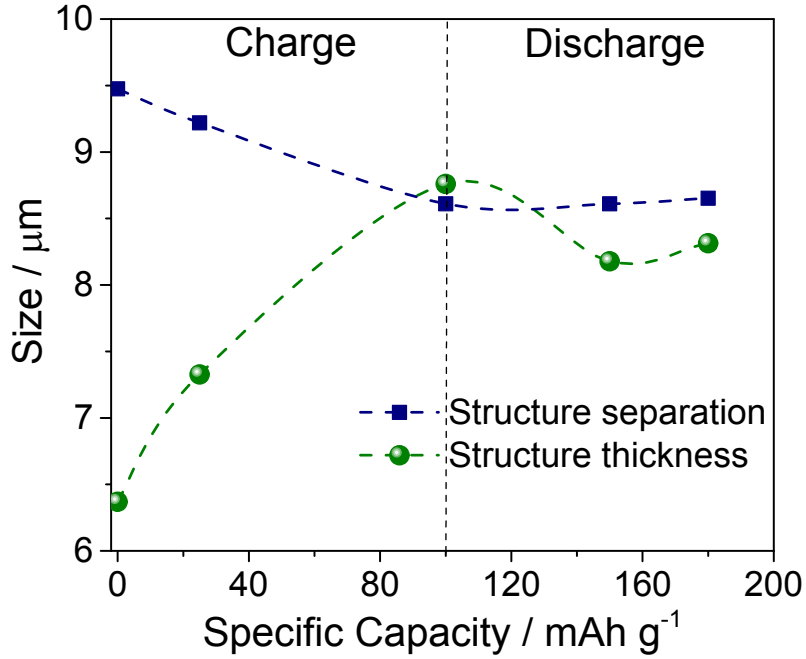

Figure S3 Structure thickness and structure separation of PG electrodes. The lines are a guide for the eye only.