## Insights into the reversibility of the aluminum graphite battery

Giuseppe Antonio Elia,<sup>‡\*a</sup> Ivana Hasa, <sup>‡bc</sup> Giorgia Greco,<sup>d</sup> Thomas Diemant, <sup>e</sup> Krystan Marquardt, <sup>a</sup> Katrin Hoeppner, <sup>a</sup> Rolf Jürgen Behm,<sup>be</sup> Armin Hoell,<sup>d</sup> Stefano Passerini<sup>\*bc</sup> and Robert Hahn<sup>\*f</sup>

<sup>a</sup> Technische Universität Berlin, Research Center of Microperipheric Technologies, Gustav-Meyer-

Allee 25, D-13355 Berlin, Germany.

<sup>b</sup> Helmholtz Institute Ulm, Helmholtzstraße 11, D-89081 Ulm, Germany.

<sup>c</sup> Karlsruhe Institute of Technology, P.O. Box 3640, D-76021 Karlsruhe, Germany.

<sup>d</sup> Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Straße 15, D-12489

Berlin, Germany.

<sup>e</sup> Ulm University, Institute of Surface Chemistry and Catalysis, Albert-Einstein-Allee 47, D-89081 Ulm, Germany.

<sup>f</sup> Fraunhofer-Institut für Zuverlässigkeit und Mikrointegration, Gustav-Meyer-Allee 25, D-13355

Berlin, Germany.

<sup>‡</sup> Authors equally contributed to the work.

Corresponding Authors:

elia@tu-berlin.de, stefano.passerini@kit.edu, robert.hahn@izm.fraunhofer.de

**Supporting Info** 

**Figure S1a** shows the current *vs.* potential profile of linear sweep voltammetry performed to evaluate the electrochemical stability window of the investigated EMIMCl:AlCl<sub>3</sub> 1:1.5 electrolyte. The measurement shows a negligible current flow within the -0.05-2.45 V range *vs.* Al/Al<sup>3+</sup>, indicating this interval as the electrolyte electrochemical stability window. **Figure S1b** reports the stripping/deposition measurement of a symmetrical Al/ EMIMCl:AlCl<sub>3</sub> 1:1.5/Al cell, illustrating the ability of the investigated electrolyte to sustain efficient stripping/deposition processes of the aluminum metal, with a polarization limited to less than 20 mV.





**Figure S1 (a)** Anodic (blue curve) and cathodic (red curve) linear sweep voltammograms of Al/EMIMCl:AlCl<sub>3</sub>/glassy carbon cells recorded at a scan rate of 0.1 mV s<sup>-1</sup>. (**b**) Voltage *vs*. time plot recorded upon stripping/deposition measurement performed on a symmetrical Al/EMIMCl:AlCl<sub>3</sub>/Al cell using a current of 0.1 mA cm<sup>-2</sup> and a deposition-stripping time of 5 hours. All measurements are performed at  $25^{\circ}$ C.

**Figure S2a** shows the current *vs.* potential plot of the cyclic voltammetry performed on the Al/ EMIMCl:AlCl<sub>3</sub>/PG cell. The voltammogram clearly resolves the presence of three peaks during the anodic scan at 1.85, 2.15 and 2.35 V *vs.* Al/Al<sup>3+</sup>, and three reversible processes occurring at 1.77, 2.05 and 2.17 V *vs.* Al/Al<sup>3+</sup>, which are associated to the multistage process of the anion intercalation between the graphene layers of the graphite. **Figure S2b** reports the average polarization values of the Al/EMIMCl:AlCl<sub>3</sub> 1:1.5/PG cell during the cycling test measured at 25 mA g<sup>-1</sup>, 50 mA g<sup>-1</sup>, 75 mA g<sup>-1</sup>, 100 mA g<sup>-1</sup>, evidencing an increase of the average cell polarization of about 0.15 V going from 25 mA g<sup>-1</sup> to 50 mA g<sup>-1</sup>, however a limited cell polarization increase is evidenced rising the current to 100 mAg<sup>-1</sup>.





**Figure S2 (a)** Cyclic voltammograms of Al/EMIMCl:AlCl<sub>3</sub>/PG cell recorded at a scan rate of 0.1 mV s<sup>-1</sup>. (b) Average polarization of the Al/EMIMCl:AlCl<sub>3</sub>/PG cell during the cycling test measured at 25 mA g<sup>-1</sup>, 50 mA g<sup>-1</sup>, 75 mA g<sup>-1</sup>, 100 mA g<sup>-1</sup>, 25°C temperature.

Stage (n)	$d_{(n+2)} / d_{(n+1)}$	Strongest 00l peak
1	1.50	002
2	1.33	003
3	1.25	004
4	1.20	005
5	1.17	006
6	1.14	007
7	1.12	008

**Table S1** correlates the calculated  $d_{(n+2)} / d_{(n+1)}$  ratio, with the most dominant stage phase and the most dominant (001) peak <sup>1,2</sup>.

**Table S1** Stage, indices of the strongest (001) reflection and  $d_{(n+2)} / d_{(n+1)}$  ratio observed upon AlCl<sub>4</sub><sup>-</sup> intercalation in graphite <sup>1,2</sup>.

**Table S2** reports the results obtained from the qualitative analysis of the SAXS patterns, revealing a regular distance  $D \approx 1.92$  nm and 3.09 nm for the charged and discharged electrodes, respectively. The latter value is in good agreement with that obtained from the ex-situ X-ray diffraction (see values reported in table S2).

Sample	Mesoporosity	Periodic size
Pristine	Yes	Not revealed
Full charge	Yes	$D\approx 1.92 \ nm$
Full discharge	Yes	$D\approx 3.09 \ nm$

**Table S2** Mesoporosity and periodic size of graphite electrodes as resulting from the qualitative analysis of the SAXS patterns. D is the diameter calculated in first approximation by the formula described in the text.

**Table S3** evidence how in this work has been demonstrated for the first time the long- time scale stability of the cell. This was not the case in previous studies, where the long-term cycling stability was tested at extremely high current values, resulting in thousands of cycles in a few days.

Cathode	Capacity (mAh g <sup>-1</sup> )	Charge/discharge current (mA g <sup>-1</sup> )	Cycle life	Cycle time (day)	Ref
3D Graphite Foam	60	12000	4000	1.7	3
3D graphite	60	5000	7500	5	4
3D graphene mesh	56	3000	200	0.15	5
This work	70	75	2000	160	

**Table S3** Comparison between this work and the data reported in the recent literature on the aluminum battery.

**Figure S3** compares the rate capability of a Al/EMIMCI:AlCl<sub>3</sub>/PG cell at the initial stage of cycling (black triangles) and after 500 (dis-)charge cycles (blue circles). The test shows after prolonged cycling the cell delivers more than 80 mAh g<sup>-1</sup> at the lowest current (25 mA g<sup>-1</sup>) and about 65 mAh g<sup>-1</sup> at the highest current (75 mA g<sup>-1</sup>). This latter value is more than 35% higher than that obtained in the initial rate test.



**Figure S3** Cycling behavior Al/EMIMCl:AlCl<sub>3</sub>/PG cell at increasing currents, i.e., 25, 50, 75, 100 mA  $g^{-1}$ , as recorded in the early stage of the test and after 500 cycles (25 mA  $g^{-1}$ ). Temperature 25°C.

**Figure S4** reports the calculated d-spacing associated to the main reflection observed in the XRD patterns of PG electrodes subjected to charge-discharge cycles, revealing that the value rapidly increases during the first 50 cycles. Subsequently, it stabilizes at about 3.264 Å.



**Figure S4** Evolution of the d-spacing associated to the most intense reflection as detected on PG electrodes subjected to galvanostatic cycling (75 mA  $g^{-1}$  and 25°C).

**Figure S5** presents the fitted XPS spectra in the C 1s region of the pristine PG electrode and of fully discharged PG electrodes recovered after 5 and 500 cycles. The measurements reveal a successive growth of the peak at 286.5 eV associated with the oxidized graphite species, indicating an increasing amount of anionic species trapped in the structure.



**Figure S5** Fitted XPS spectra of the C 1s region recorded on different PG electrodes in the pristine state, after 5 and after 500 cycles, in the fully discharged state.

Figure S6 presents Al 2p and Cl 2p XPS spectra of the aluminum electrodes recorded to reveal modifications of the chemical surface composition after different amounts of cycles. The Al 2p spectrum of the pristine sample show two peaks, one at about 72 eV attributed to metallic aluminum  $^{6}$  and a second one at about 74.5 eV, indicating the surface oxidation of aluminum and the formation of an Al<sub>2</sub>O<sub>3</sub> passivation layer  $^{6}$ . In the spectra of the cycled samples the peak attributed to the metallic aluminum disappears and the peak related to surface oxidized aluminum slightly shift to higher binding energy  $^{6}$ . The Cl 2p spectrum indicates the formation of chlorine species on the aluminum surface  $^{6}$ .



**Figure S6** XP spectra in the Al 2p and Cl 2p regions recorded on different aluminum electrodes in the pristine state and after 5 and 500 cycles. The Al/EMIMCl:AlCl<sub>3</sub>/PG cells were cycled at 75 mA  $g^{-1}$  and 25°C.

## **Bibliographic References**

- 1. B. Özmen-Monkul and M. M. Lerner, *Carbon*, 2010, **48**, 3205–3210.
- 2. G. Schmuelling, T. Placke, R. Kloepsch, O. Fromm, H.-W. Meyer, S. Passerini and M. Winter, *J. Power Sources*, 2013, **239**, 563–571.
- Y. Wu, M. Gong, M.-C. Lin, C. Yuan, M. Angell, L. Huang, D.-Y. Wang, X. Zhang, J. Yang, B.-J. Hwang and H. Dai, *Adv. Mater.*, 2016, 28, 9218–9222.
- M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang and H. Dai, *Nature*, 2015, **520**, 324–328.
- 5. G. Y. Yang, L. Chen, P. Jiang, Z. Y. Guo, W. Wang and Z. P. Liu, *RSC Adv.*, 2016, **6**, 47655–47660.
- 6. D. Briggs, *Handbook of X-ray Photoelectron Spectroscopy Minnesota, USA, 1979.*, Perkin-Elmer Corporation, 1981, vol. 3.