Supporting Information for

Limitations of chloroaluminate ionic liquid anolytes for aluminum-graphite dual-ion batteries

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Chemicals and Battery Components. 1-ethyl-3-methylimidazolium chloride (EMIMCl, 99%, IoLiTec), $AlCl_3$ (99%, granules, Acros), Al foil (MTI Corporation), pristine graphite flakes (99.9%, 10 mesh, Alfa Aesar), cellulose/polyester separator (30μm, FPC3018, Mitsubishi Paper Mills, Ltd) were used as received.

Chloroaluminate Ionic Liquid Preparation. The EMIMCl-based ionic liquids were prepared by slowly mixing the solid EMIMCl powder and $AlCl_3$ granules in an argon-filled glove box. During mixing, an isothermal reaction occurs to give a light-yellow liquid, which was subsequently treated with Al foil at 150 °C for 6 h until it was nearly colorless.

Assembly and Testing of the Al-Graphite Dual-Ion Batteries. Pristine graphite flakes were dried at 200 °C under vacuum overnight. No binders or solvents were used to prepare graphite electrodes. The graphitic material (*ca*. 5 mg over ≈ 1 cm^2) was homogeneously distributed and pressed on the surface of separator soaked with *ca*. 7 mg of $AlCl_3$:EMIMCl ionic liquid. Then, flakes were covered with a glassy carbon electrode. All electrochemical measurements were performed on a VMP3 multichannel workstation (BioLogic) in an argon-filled glovebox (<1 ppm O_2, <1 ppm H_2O) using the homemade cell as illustrated on Figure 2a.

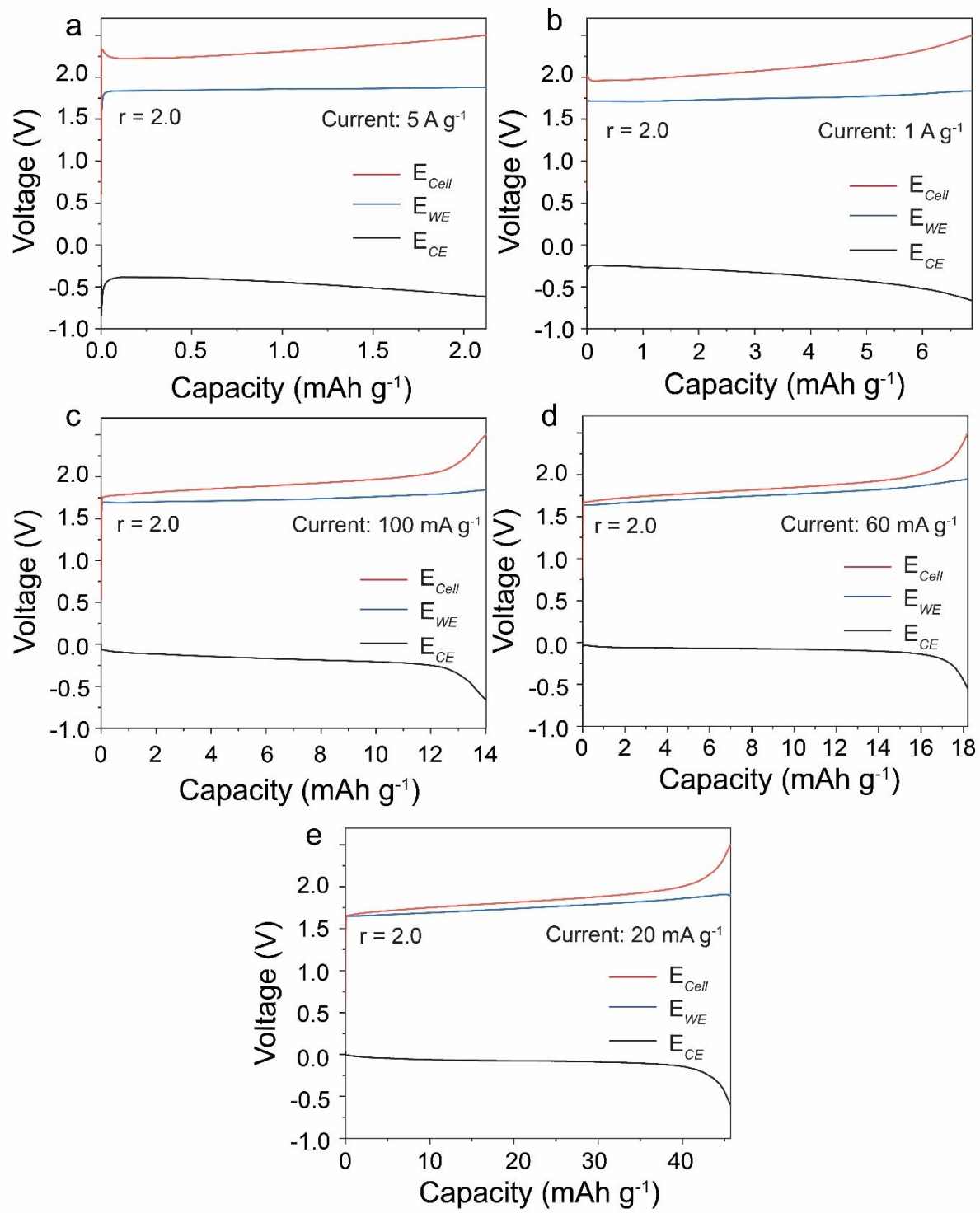

Figure S1. Galvanostatic curves of chloroaluminate ionic liquid (r = 2) anolyte (E_{CE}), graphite (E_{WE}) and full cell (E_{Cell}) measured during charge versus Al foil reference electrode. Cells were charged at room temperature at different current densities of 5 A g-

[1] (a), 1 A g^{-1} (b), 100 mA g^{-1} (c), 60 mA g^{-1} (d) and 20 mA g^{-1} (e) with upper cell voltage limit of 2.5 V *vs.* Al^{3+}/Al.

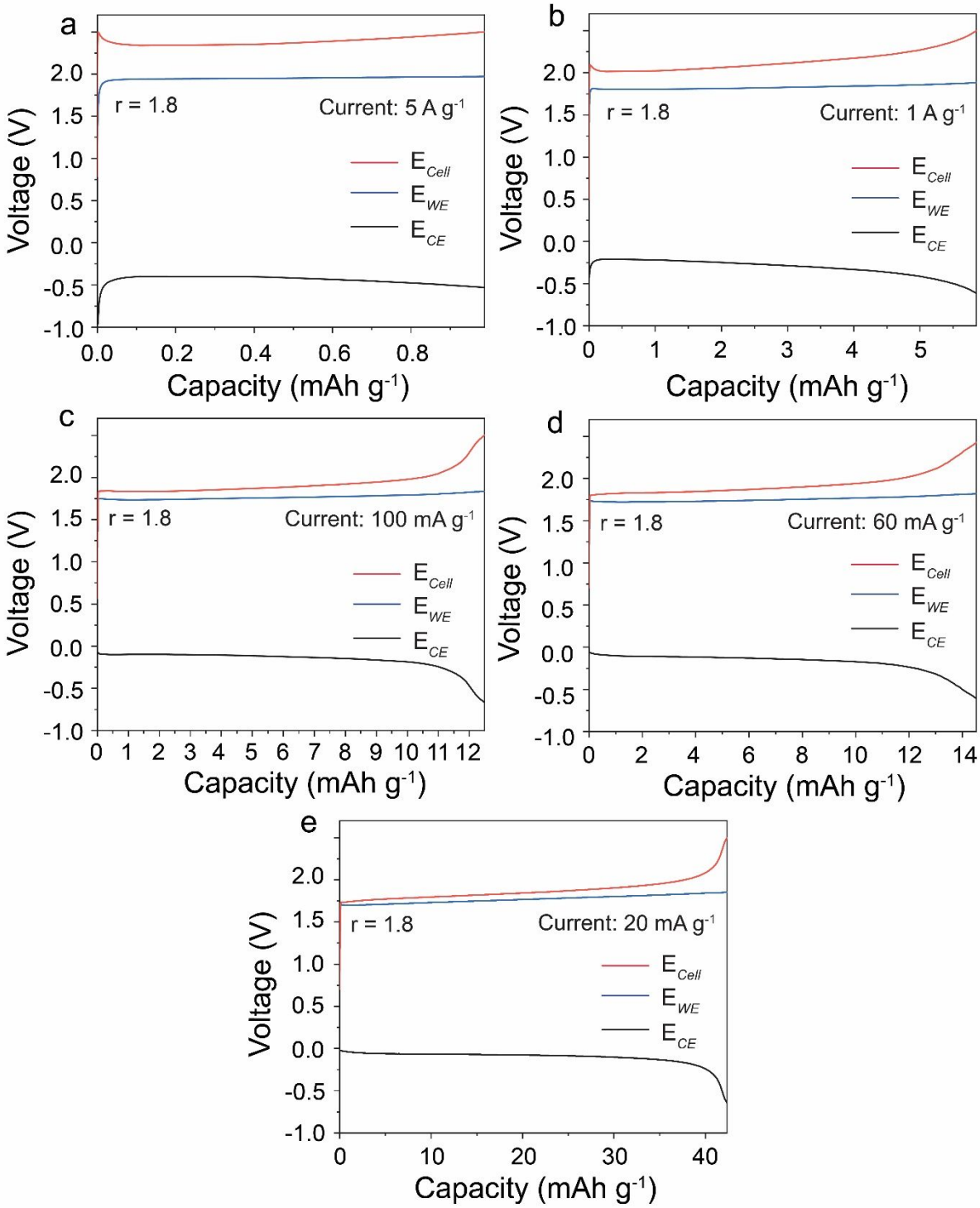

Figure S2. Galvanostatic curves of chloroaluminate ionic liquid (r = 1.8) anolyte (E_{CE}), graphite (E_{WE}) and full cell (E_{Cell}) measured during charge versus Al foil reference electrode. Cells were charged at room temperature at different current densities of 5 A g^{-1} (a), 1 A g^{-1} (b), 100 mA g^{-1} (c), 60 mA g^{-1} (d) and 20 mA g^{-1} (e) with upper cell voltage limit of 2.5 V *vs*. Al^{3+}/Al.

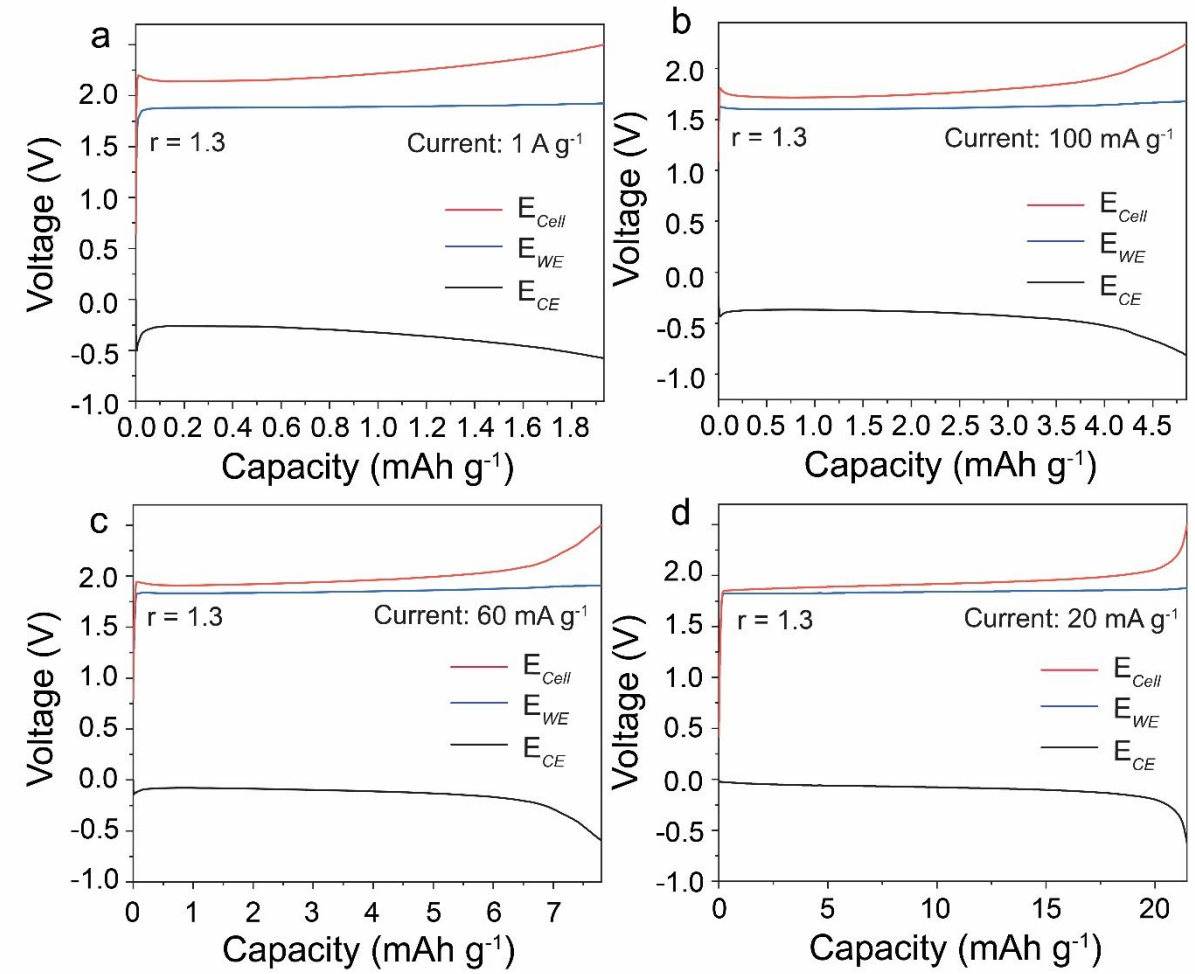

Figure S3. Galvanostatic curves of chloroaluminate ionic liquid (r = 1.3) anolyte (E_{CE}), graphite (E_{WE}) and full cell (E_{Cell}) measured during charge versus Al foil reference electrode. Cells were charged at room temperature at different current densities of 1 A g^{-1} (a), 100 mA g^{-1} (b), 60 mA g^{-1} (c) and 20 mA g^{-1} (d) with upper cell voltage limit of 2.5 V *vs*. Al^{3+}/Al.