Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2020

ELECTRONIC SUPPLIMENTARY INFORMATION

Lithium-Enriched Graphite Anode Surfaces Investigated using Nuclear Reaction Analysis

Matthew Chebuske,[a] Seiichiro Higashiya,[a] Spencer Flottman[a], Hassaram Bakhru,[a] Byron Antonopoulos,[c] and Odysseas Paschos,[c] Forrest S. Gittleson,[b] and Harry Efstathiadis[a*]

[a] *State University of New York Polytechnic Institute, 257 Fuller Road, Albany, NY 12203, USA;*

[b] *BMW Group Technology Office USA, 2606 Bayshore Parkway, Mountain View, CA 94043;*

[c] *BMW AG, Petuelring 130, 80788 Munich, Germany;*

* Corresponding author: hefstathiadis@sunypoly.edu

Experimental Methods

Materials

Full graphite-NMC111 Li-ion cells were assembled using anodes that consisted of 95.8 %wt MAG-D20 graphite (Hitachi Chemical), 3.2 %wt CMC/SBR binder (Dow Chemical/JSR, respectively) and 1 %wt HS100 acetylene black (Denka) on copper foil. The cathode consisted of 91.5 %wt NMC 111 (BASF), 4.4 %wt Super C65 (Imerys), and 4.1 %wt PVDF binder (Kureha) on Al foil. 18 mm diameter disc electrodes were punched and dried at 80°C for 12 h in a vacuum oven before use. The electrolyte was 3:7 ethylene carbonate:ethyl methyl carbonate with 2 %wt VC and 1 M $LiPF_6$ (LP 572, Gotion, Fremont, CA). Cells were assembled in an argon-filled glove box using a PAT-Cell design (EL-Cell GmbH, Hamburg, Germany) and a sleeve with Al_2O_3-containing PET fiber separator and Li reference (ECC1-00-0210-A/X).

SEI formation methods and rate tests

Cell formation protocols were modified from Antonopoulos *et al*. to fit the full cell format.[1] Discharge rate cycling followed the formation procedure and involved varying the discharge rate after every 3 cycles with the charge rate held constant. Charge-discharge cycling and the electrode potentials were controlled and measured by a WaveNow potentiostat (Pine Research Instrumentation, Durham, NC). Details of the formation and cycling procedures follow:

- Standard formation: The cell was charged at C/10 to 3.6 V, then the potential was maintained at 3.6 V until the current was equal to or less than C/20.

- Fast formation: The cell was charged at 1C to 3.5 V, then the potential was maintained at 3.5 V until the current was equal to or less than C/10. Subsequently, the cell was charged at C/10 to 3.6 V and the potential was maintained at 3.6 V until the current was equal to or less than C/20.
- EIS formation: The cell was charged at C/10 to 3.0 V, then rested for 30 min at the open circuit potential (OCP). Subsequently, the cell was subjected to 20 cycles of potentiostatic EIS modulation (10 mV amplitude, OCP, 100 kHz to 0.1 Hz, 10 frequencies per decade) using a PARSTAT 2273 (Princeton Applied Research, Oak Ridge, TN). The cell was then charged at C/10 to 3.6 V and the potential was maintained at 3.6 V until the current was equal to or less than C/20.
- Discharge rate cycling: The cell was charged to 4.1 V at C/10 with a constant voltage hold at 4.1 V until the current was equal to or less than C/20 then discharged to 2.8 V at C/10. The cell was charged to 4.1 V at 1C with a constant voltage hold at 4.1 V until the current was equal to or less than 1/20C. Discharges were conducted to 2.8 V at rates ascending from C/3 to 3C (3 cycles each) with a 1C balancing charge rate. 20 min rest periods were placed every after charge and discharge stage.

After cycling, cells were disassembled in an argon glove box and anodes were rinsed three times with 10 mL of dimethyl carbonate (DMC) for 10 min.

References

1 B. K. Antonopoulos, C. Stock, F. Maglia and H. E. Hoster, *Electrochim. Acta*, 2018, **269**, 331–339.