Solid-electrolyte interphases (SEI) in nonaqueous aluminum-ion batteries

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Supporting Information
Figure S1: SEM micrograph (top) and relative EDXS spectrum (bottom) of pyrolytic graphite paper, after a typical galvanostatic charge-discharge test (20 cycles at a current rate of 50 mA g$^{-1}$).
Figure S2: Cyclic voltammogram (third cycle, 10 mV s$^{-1}$) of a Swagelok-type cell built using pyrolytic graphite paper as cathode.
Figure S3: Nyquist plots of a Swagelok-type cell built using pyrolytic graphite paper as cathode before and after the first charge discharge cycle at 50 mA g\(^{-1}\). It can be seen from the graph that the high-frequency region of the plots changes significantly after the first charge-discharge cycle. This is consistent with our interpretation of the formation of an SEI. A simple Randles circuit (bottom schematic) was used for fitting the plot relative to the pristine cathode. On the other hand, for the cycled cathode, a resistor-constant phase element parallel pair is added in series to the rest of the circuit (top schematic), which is indicative of a poorly-conducting film coating the electrode.\[[1]\]
Figure S4: SEM micrograph of the PAN-derived carbon film.

Figure S5: (a) Cyclic voltammetry (third cycle, 10 mV s$^{-1}$) and (b) Galvanostatic charge-discharge profiles (tenth cycle) of a Swagelok-type cell built using the PAN-derived carbon film.
Figure S6: X-ray diffractogram (a) and Raman spectrum (b) of pyrolytic graphite paper.

Figure S7: Specific capacities and coulombic efficiencies relative to typical galvanostatic charge-discharge cycles performed on Swagelok-type cells using PVDF-coated CNF as cathodes, at various current rates. A specific charging capacity cutoff of 44 mAh g\(^{-1}\) was used in combination with the upper voltage cutoff of 2.45 V in the experiments.
Figure S8: Top: cyclic voltammograms at multiple scan speed of Swagelok-type cells using uncoated (a) and PVDF-coated CNF (b) as cathodes. Bottom: Capacitive current contribution to the voltammetric current for uncoated (c) and PVDF-coated CNF (d), obtained from the above cyclic voltammetry data at different scan speeds, using the technique proposed by Wang et al. [2]
Figure S9: SEM micrograph of PVDF-coated CNF (non-catalyzed).

Figure S10: Galvanostatic profiles (tenth cycle) of Swagelok-type cells built using electrosprayed PVDF as cathode.
Figure S11: Schematic representation of the custom-built Swagelok-type cell used in this work.

Figure S12: SEM images of cycled cathodes that have been washed by submerging samples in a vial of solvent and agitating: (a) control - no washing, (b) Washed with cyclohexane, (c) washed with N,N'-dimethylformamide, (d) washed with ethanol (e) washed with water. Visually the water had the most effect, removing a lot of the webbing in the sample but some remained after washing. Other solvents had no effect. Both webbing and fibers had near identical elemental compositions and were not affected by washing.
Figure S13: Galvanostatic profiles (tenth cycle, 100 mA g$^{-1}$) of a Swagelok-type cell built using CNF carbonized at the lower temperature of 900 °C.

Figure S14: TEM micrographs of cobalt acetate-catalyzed CNFs: single nanofiber (a) and surface detail (b). The presence of localized graphitic regions in the bulk of the material can be observed, while the surface remains relatively unaltered.
References

(1) Impedance spectroscopy: theory, experiment, and applications, Third edition; Barsoukov, E., Macdonald, J. R., Eds.; Wiley: Hoboken, NJ, 2018.

(2) Wang, J.; Polleux, J.; Lim, J.; Dunn, B. The Journal of Physical Chemistry C 2007, 111, 14925–14931.