Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Al-C Hybrid Nanoclustered Anodes for Lithium Ion Batteries with High Electrical Capacity and Cyclic Stability

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1. Materials Processing and Characterizations

Synthesis of Al-C hybrid nanoclustered thin films A PECVD system coupled with a pre-evaporator was designed for the experiments. The system consisted of two active zones: a vaporous zone and a radio frequency zone. The base pressure was brought to 1×10^{-6} Torr using a turbomolecular pump, backed by a rotary mechanical pump. Thermal evaporation-assisted PECVD deposition was applied to create the Al-C hybrid nanoclustered films on a Cu foil substrate. The carbon source of C_{60} (Aldrich, CAS No: 99685-96-8) and Al precursor of tetramethyl aluminum (TMA, Aldrich, 99.9 %) as the organometallic source were used as received. TMA was introduced into the deposition chamber using Ar as a carrier gas. The samples were prepared under following conditions: a working pressure of 25 mTorr, H_2/Ar ratio of 0.1, deposition time of 20 min, current of 25 A for thermal evaporation, and RF power (plasma power) at 200 W.

Material Characterizations The compositional distribution of the resulting Al-C hybrid films was analyzed with the backscattered electron images obtained from electron probe microanalyzer (EPMA, JEOL JXA-8900R). The Al-C hybrid nanoclustered electrodes were studied with TEM imaging and selected area electron diffraction (SAED) pattern analysis using a Tecnai F30TEM at an accelerating voltage of 200 kV. For a nuclear magnetic resonance (NMR, Varian VNMRS 400) characterization, thin-sliced bilayered specimens comprising 1.5-μm-thick Al-C hybrid film and 10 μm-thick substrate were carefully prepared and introduced to the sample holder of NMR. XPS analysis for chemical bond and atomic composition analysis was carried out using Ulvac-PHI (PHI

5000 VersaProbe) with a source of monochromatic $Al_{K\alpha}$ (1486.6 eV) at an accelerating voltage of 15 kV under Ar atmosphere.

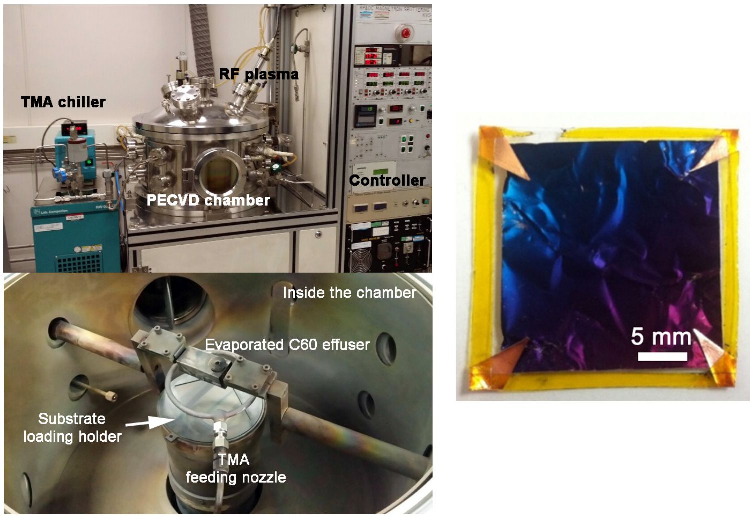

Figure S1. Digital camera images for experimental setup of thermal-evaporation assisted PECVD system (left) and Al-C hybrid clustered anode (right).

2. Electrochemical Measurements

The Al-C hybrid nanoclustered films (thickness = 1.5 μm) were investigated as anode material using pouch-type half cells (size = 2.2 × 2.2 cm^2) assembled in an argon-filled glove box. The half cells comprised lithium metal as counter and reference electrodes, separator, and Al-C hybrid nanoclustered film as the anode electrode. The electrolyte contained 1M $LiPF_6$ in EC:EMC:DMC (1:1:1, v/v/v). Cycling characteristics were tested at current densities of 6, 10, 15, and 20 A/g. To measure the loading mass of Al-C hybridized nanoclusters, the mass of CVD-deposited films was carefully weighed using high-precision microbalance (CPA26P, Sartorius Mechatronics, readability ~ 0.002 mg) on anti-vibration table. Since neither binder nor conductive agents were added in the Al-C hybridized anodes, net weight of the deposited films could readily be obtained from the mass difference before and after the film deposition.

Table S1. Loading mass and applied current for cells with varying Al composition

Al composition (wt %)	Measured loading mass (mg)	Applied current for 6 A/g condition (mA)
10	1.45 ± 0.03	8.7
20	1.55 ± 0.03	9.3
40	1.68 ± 0.03	10.0

3. Electrochemical Impedance Spectroscopic (EIS) Analysis

Electrochemical impedance spectroscopy (EIS) was carried out by applying a 0.1 mV amplitude signal from 1 MHz to 0.1 Hz during the first charge/discharge cycle, using a SOLATRON 1260 workstation with an Auto Lab Electrochemical system. The resulting EIS data for the Al-C hybrid nanoclustered electrode are shown in Fig. S2. The Nyquist plots for the initial 5 cycles imply that the cycles stabilize with minimal charge-transfer resistance from 138 to 15 Ω, which was confirmed by a size decrease in semicircles. This result matches the discussion from cyclic voltammetry tests described in the main text.

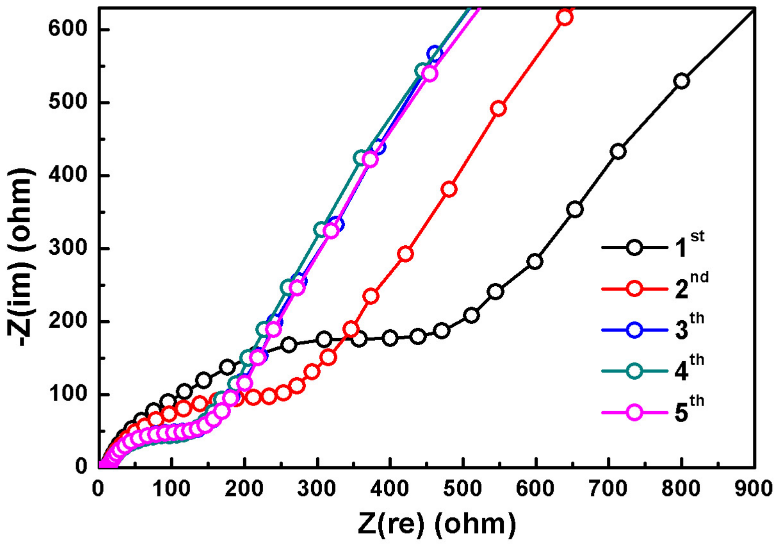

Figure S2. Nyquist plots from 1st to 5th for the Al-C hybrid nanoclustered anodes (40 wt% Al composition)