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Supplementary information

Anion secondary batteries utilizing reversible BF_4 insertion/extraction two-dimensional Si material

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Experimental Section

Materials

In an inert atmosphere, tetrafluoroboric acid diethyl ether complex (2ml) was added to 2-(dimethylamino) ethanol (4.2ml) at 0ºC, and the solution was stirred for 2 hours at room temperature. After the reaction was complete, the mixture was dried under reduced pressure to obtain ionic liquid as colourless oil.

A solution of as-prepared ionic liquid (546.8mg) in acetone (3ml) was added to layered polysilane ($[Si_6H_6]$, 104.8mg) in dimethylformamide (2ml), and the mixture was refluxed for 3 days at 110 ºC. After the reaction, the mixture was filtered and the residue was washed with dimethylformamide and acetone several times. The obtained pale yellow solid was dried under reduced pressure to afford **1** $[Si_{10}H_8(OCH_2CH_2NH(CH_3)_2)_2](BF_4)_2$, (78.9mg)].

Electrochemical tests

Electrochemical tests were done in Swagelok-type cells. The cells were assembled in an argon-filled glove box, using Li metal as the counter electrode and 1M tetraethyl ammonium tetrafluoroborate ($TEABF_4$) in propylene carbonate (PC) as the electrolyte. The working electrodes were prepared with the active material **1**, carbon black (ECP), and polytetrafluoroethylene (50:45:5 by weight).

The anion batteries were assembled using **1** as the anode and graphite as the cathode. The anode electrodes were prepared by the same method mentioned above. The material (10mg) was placed on a stainless steel mesh. For fabrication of the cathode, mesocarbon micro bead graphite (Osaka Gas) powders were mixed with Polyvinylidene difluoride (95:5 by weight) in *N*-methylpyrrolidone. The obtained slurry was coated onto Al foil and roll-pressed to obtain the cathode (15mg). The electrochemical cells were assembled in the Ar-filled glove box by using both electrodes. 1M $LiBF_4$ in PC as an electrolyte and a porous glass filter as a separator were used. The cells were cycled in the voltage range of 0 and 3V at a rate of $100mAg^{-1}$.

Thermal properties

For differential scanning calorimetry experiments, the anion cells were charged to 3V and then disassembled in an Ar-filled dry box. An aluminium hermetic pan was used to collect 3-5mg samples of the anode and cathode. The measurements were carried out in a T-zero Q-1000 differential scanning calorimeter (TA Instruments) using a temperature scan rate of $5°Cmin^{-1}$.

Computational approach

The modified Si layer was built based on a graphene layer having increased cell dimensions to yield Si-Si bond lengths of ~2.34Å (as determined from the experimental results). We attached 2-(dimethylamino) ethanol anions (deanol) to the Si layer via the O atom, at a coverage indicated by the experiments. This equates to two molecules per unit cell; one located above and one located below the Si layer. Under-coordinated Si atoms were capped with H atoms. A second structure was built which also contained two BF_4 anions per unit cell. To balance the negative charge on the structure, the amine group on each deanol group was protonated. Application of periodic boundary conditions in the x- and y- directions creates the extended surfaces of the modified nanosheets along the (111) surface plane. A vacuum spacer of ~9Å in the z-direction was inserted to prevent interactions between adjacent Si layers.

Density functional theory calculations were performed using the Vienna *ab initio* Simulation Package (VASP) using the projector augmented wave method[11] and Generalised Gradient Approximation (GGA) with the exchange and correlation functional of Perdew, Burke, and Ernzerhof (PBE). A plane wave basis set with an energy cut off of 400eV was employed.

The modified Si layer (with and without the BF_4 anions) was optimized by allowing each atom to relax until the total energy was converged to $<10^{-4}$eV and the Hellmann-Feynman force was < 0.01eV/Å. A k-point mesh of 8×8×1, including the Γ point, was used for the Si layer, which was shown previously to give convergence of the total energy to 0.1meV/atom. *Ab initio* molecular dynamics simulations of the relaxed Si layers were performed using VASP with Γ point sampling in the Brillouin zone. These simulations confirmed that the deanol-modified Si layer, modelled according to the experimental data is stable at finite temperature.

Supporting figures

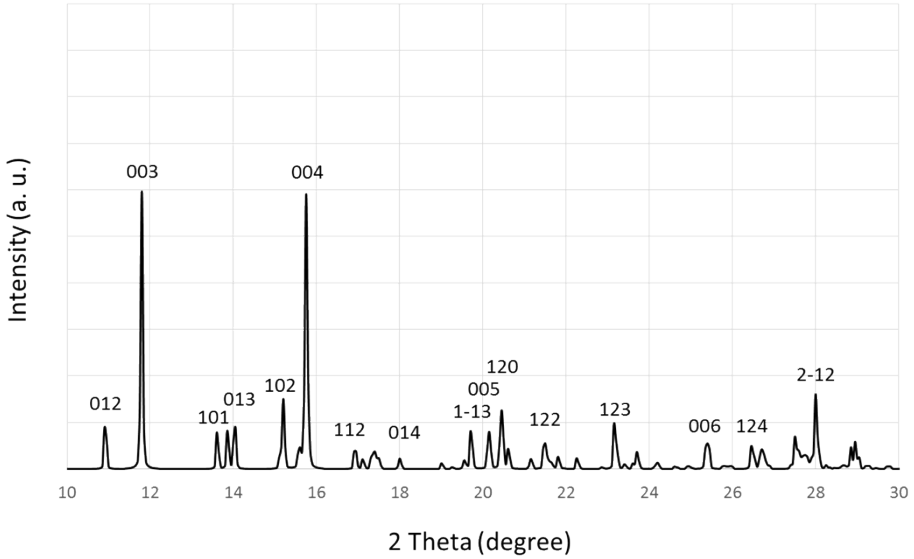

Figure S1. Calculated XRD pattern of **1**. This optimization was calculated at 0 K.

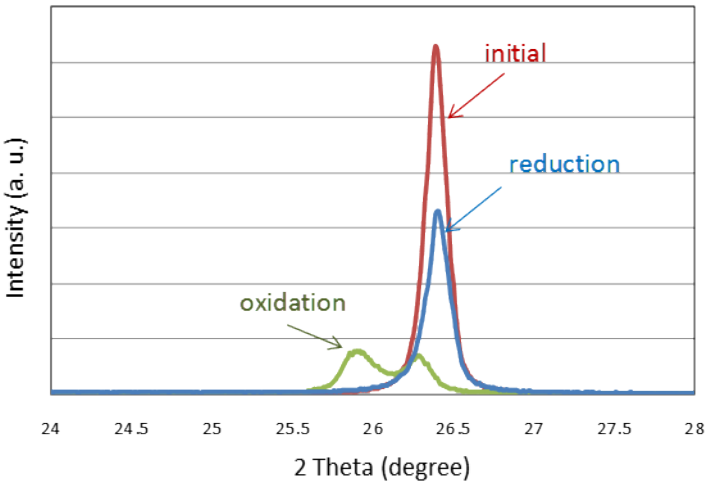

Figure S2. XRD patterns of graphite. Red, blue, and green lines represent the initial graphite, oxidized (BF_4^- intercalated) graphite, and reduced (BF_4^- deintercalated) graphite, respectively.

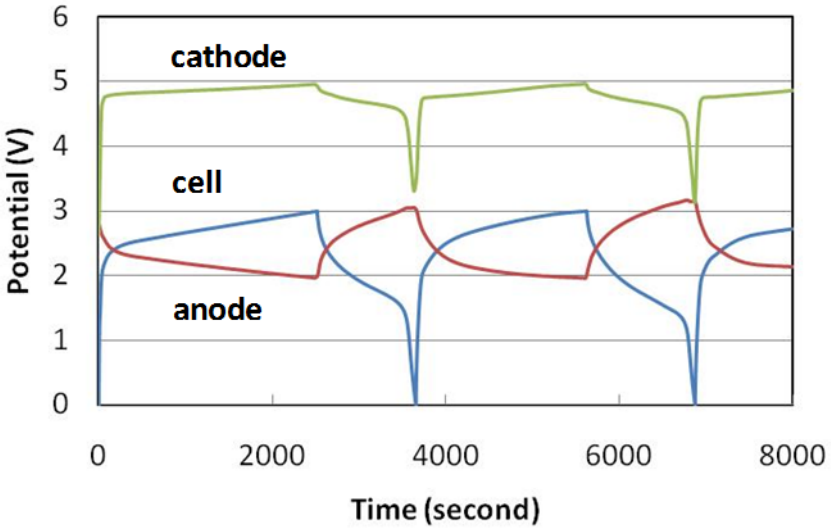

Figure S3. Potential profiles of graphite cathode and the BF_4-modified siloxene anode vs. Li metal reference electrode in the anion battery during galvanostatic charge/discharge processes.