## **Supporting Information**

## Surface Functionalization of Silicon, HOPG, and Graphite Electrodes: Toward an Artificial Solid Electrolyte Interface

Dominique S. Moock,<sup>†</sup> Sven O. Steinmüller,<sup>†</sup> Isabelle D. Wessely,<sup>§</sup> Audrey Llevot,<sup>II</sup> Benjamin Bitterer,<sup>II</sup> Michael A. R. Meier,<sup>II</sup> Stefan Brase,<sup>‡,§</sup> Helmut Ehrenberg,<sup>†</sup> and Frieder Scheiba<sup>†</sup>\*

† Institute for Applied Materials and ‡ Institute of Toxicology and Genetics (ITG), Karlsruhe
Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-

Leopoldshafen, Germany

§ Institute for Organic Chemistry (IOC), Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, D-76131 Karlsruhe, Germany

I Institute for Organic Chemistry (IOC), Karlsruhe Institute of Technology (KIT), Straße am Forum 7, D-76131 Karlsruhe, 10 Germany

\* Corresponding author. E-mail: frieder.scheiba@kit.edu

**Materials**. Solvents, reagents and chemicals were purchased from SIGMA-ALDRICH, ABCR, ALFA AESAR, BASF, FISHER SCIENTIFIC and CARBOLUTION. All solvents and commercially available chemicals were used without further purification unless stated otherwise.

Silicon wafers with [100] orientation were purchased from Si-Mat Silicon Materials. They were dipped into HF solutions for 5 min to remove the native oxide layer. After this, the wafer was rinsed with Millipore water and then stored under argon. Highly oriented pyrolytic graphite (HOPG) were purchased from SPI in SPI-2 grade. Before using, they were cleaned by taking a piece of tape, press it onto the HOPG and pull it off. The so freshly cleaned HOPG was then used in the experiments. Graphite electrodes were produced of 90% natural graphite Mechano-Cap 1P1 (H.C. Carbon GmbH) and 10% polyvinylidene fluoride (PVDF). A slurry from 2.0 g of this mixture and 7.0 mL *N*-methyl-2-pyrrolidone (NMP) was prepared. This slurry was coated onto a copper foil with a layer thickness of 250 µm (wet).

## **Analytic and Equipment**

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was carried out using a ToF-SIMS 5 instrument (IONTOF GmbH, Muenster, Germany). Surface spectroscopy was performed with  $Bi^{3+}$  as primary ion (ion current about 0.5 pA) for secondary ion generation. Scan rates of measurements were adjusted to keep the ion dose density below  $10^{11}$  ions/cm<sup>2</sup> per polarity, securing that the static SIMS limit of about  $10^{12}$  ions/cm<sup>2</sup> was not reached while performing positive and negative polarity measurements at identical sample position. High mass resolution measurements were performed on two different positions of each sample to obtain spectral data and surface images of an area of  $2000 \times 2000 \,\mu\text{m}^2$  using 200 pixels per 1000  $\mu\text{m}$ . The spectral data were analyzed and exported with the SurfaceLab software (version 6.7te) of the instrument.

The images were obtained using the *stageraster* scan option were several smaller image patches, here  $400 \times 400 \ \mu\text{m}^2$  were stacked together for large overview scans. The recorded data were flight time corrected using the "Advanced ToF Correction" feature of the SurfaceLab software (version 6.7) of the instrument. Brighter colors indicate higher intensity values. Color scales of specific fragments have always the same values. The sample was prepared under argon atmosphere in the glovebox of the XPS spectrometer. The transfer of the samples into the interlock of the ToF-SIMS was done in a special transfer box from IONTOF GmbH. This ensured that the samples had no contact with the atmosphere at any time.

X-ray photoelectron spectroscopy (XPS) was performed with a K-Alpha XPS instrument (Thermo Fisher Scientific, East Grinstead, England) with an attached glovebox. Four random points on each sample were analyzed using a microfocussed, monochromated Al K $\alpha$  X-ray source (400 µm spot size). The spectra were fitted with several Voigt profiles (binding energy uncertainty of +/- 0.2 eV). Plasmon loss features of the silicon substrate were additionally fitted to gain the real signal background and therefore correct signals of elements (e.g. Cl 2p spectra). The analyzer transmission function, Scofield sensitivity factors,<sup>34</sup> and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2M formalism.<sup>35</sup> All spectra were referenced to the C 1s peak (C-C, C-H) at 285.0 eV binding energy controlled by the means of the well-known photoelectron peaks of metallic Cu, Ag, and Au. All the samples were prepared under argon atmosphere in the glovebox attached to the XPS.

NMR spectra were recorded on a Bruker *Avance* 500 (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 125 MHz) on solutions in Acetonitril- $d_3$ . Chemical shifts (*d*) are expressed in parts per million (ppm) and are referenced to CH<sub>3</sub>CN (<sup>1</sup>H: 1.94 ppm, <sup>13</sup>C: 118.3 ppm) as internal standard. All coupling

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constants (J) are absolute values and J values are expressed in Hertz (Hz). The description of signals includes: s = singlet, bs = broad singlet, d = doublet, m = multiplett. The spectra were analysed according to first order. The signal structure in <sup>13</sup>C-NMR was analysed by DEPT (Distortionless Enhancement by Polarization Transfer) and is described as follows: + = primary or tertiary C-atom (positive signal), -= secondary C-atom (negative signal) and C<sub>quart.</sub> = quarternary C-atom (no signal). IR spectra were recorded with a FT-IR Bruker IFS 88 spectrometer with OPUS software using the attenuated total reflection technique (ATR). The absorption band is given in wave numbers  $\tilde{\nu}$  in cm<sup>-1</sup>. The forms and intensities of the bands were characterized as follows: vs = very strong 0 - 9% T, s = strong 10 - 39% T, m = medium 40 - 9%69% T, w = weak 70 - 89% T, vw = very weak, 90 - 100% T. EI (Electron Ionization) and FAB (Fast Atom Bombardment) mass spectra were obtained using a Finnigan MAT 95 mass spectrometer. The indication of the molecular fragments was carried out as the ratio of mass to charge m/z; the intensity of the signals was expressed in percent relative to the intensity of the base signal (100%). The following abbreviations were used for the **HRMS** (High Resolution Mass Spectrometry): calc. = calculated data, found = measured data.

**4-(2-(Trimethylsilyl)ethinyl)aniline.** 1.61 g  $[Pd(PPh_3)_2Cl_2]$  (2.28 mmol, 0.1 eq), 1.20 g PPh<sub>3</sub> (4.56 mmol, 0.2 eq), 0.44 g CuI (2.28 mmol, 0.1 eq) and 5.00 g 4-Iodoaniline (22.8 mmol, 1.0 eq) were dissolved in 200mL of degassed THF:Diisopropylamine (4:1). Then 4.87 mL trimethyl acetylene (34.2 mmol, 1.5 eq) was added and the mixture was stirred at room temperature overnight. Afterwards the mixture was filtered, washed with hexane and the combined organic phases were washed with NH<sub>4</sub>Cl and water and dried over MgSO<sub>4</sub>.

<sup>1</sup>H-NMR (500 MHz, Acetonitril-*d*<sub>3</sub>):  $\delta$  (ppm) = 0.20 (s, 9 H, C*H*<sub>3</sub>), 4.44 (bs, 2 H, N*H*), 6.57 (d, <sup>3</sup>*J* = 8.5 Hz, 2 H, 2-C*H*, 6-C*H*), 7.15 (d, <sup>3</sup>*J* = 8.5 Hz, 2 H, 3-C*H*, 5-C*H*). – <sup>13</sup>C-NMR (125 MHz, Acetonitril-*d*<sub>3</sub>):  $\delta$  (ppm) = 0.12 (+, CH<sub>3</sub>), 91.4 (C<sub>quart</sub>, C<sub>Alkin</sub>), 107.5 (C<sub>quart</sub>, C<sub>Alkin</sub>), 111.3 (C<sub>quart</sub>, 4-C), 114.9 (+, 2-CH, 6-CH), 133.9 (+, 3-CH, 5-CH), 149.8 (C<sub>quart</sub>, 1-C). – MS (ESI, +), m/z (%): 190.1 (M<sup>+</sup> + H). – HR-MS (C<sub>11</sub>H<sub>16</sub>NSi): calc. 190.1047, found 190.1044.

**4-(2-(Trimethylsilyl)ethinyl)benzene diazonium tetrafluoroborate**. 2.6 mL BF<sub>3</sub>·OEt<sub>2</sub> were added to a flask at -20 °C. Then 1.0 g 4-(trimethylsilyl) aniline (1 eq, 5.3 mmol) dissolved in 15mL THF were added dropwise. After the addition was complete, 2.8 mL tert-butyl nitrite (4 eq, 21.1 mmol) in 7 mL THF was added slowly to the mixture. Afterwards the reaction was mixed further for 10 min at -20 °C and then allowed to warm to 0 °C in an ice-water bath over 20 min. By addition of diethyl ether, the product was precipitated, filtered, and washed with diethyl ether. To purify the product, it was dissolved in cold acetonitrile and reprecipitated with cold diethyl ether.

<sup>1</sup>H-NMR (500 MHz, Acetonitril- $d_3$ ):  $\delta$  (ppm) = 0.29 (s, 9 H, C $H_3$ ), 7.87 (d, <sup>3</sup>J = 9.0 Hz, 2 H, 3-CH, 5-CH), 8.44 (d, <sup>3</sup>J = 9.0 Hz, 2 H, 2-CH, 6-CH). – <sup>13</sup>C-NMR (125 MHz, Acetonitril- $d_3$ ):  $\delta$  (ppm) = -0.74 (+, CH<sub>3</sub>), 102.4 (C<sub>quart</sub>, C<sub>Alkin</sub>), 109.6 (C<sub>quart</sub>, C<sub>Alkin</sub>), 113.8 (C<sub>quart</sub>, 1-C), 133.5 (+,

3-CH, 5-CH), 135.3 (+, 2-CH, 6-CH), 137.3 (C<sub>quart</sub>, 4-C). – IR (ATR):  $\tilde{v}$  (cm<sup>-1</sup>) = 3113 (vw), 2960 (vw), 2285 (w), 1576 (m), 1473 (vw), 1413 (w), 1311 (vw), 1288 (w), 1252 (w), 1228 (w), 1182 (w), 1123 (w), 1100 (w), 1039 (s), 839 (s), 762 (m), 705 (w), 627 (w), 537 (m), 523 (w), 489 (w), 340 (vw). – MS (FAB, 3-NBA), *m/z* (%): 201 [M<sup>+</sup>], 173 [M<sup>+</sup> – N<sub>2</sub>]. – MS (EI, 70 eV, 90 °C), *m/z* (%): 192.1 [M<sup>+</sup> – N<sub>2</sub> + F]. – HR-MS (C<sub>11</sub>H<sub>13</sub>N<sub>2</sub><sup>128</sup>Si): calc. 201.0848, found 201.0850.



Figure S1: ToF-SIMS images of Fragment  $SiC_3H_9^+$  of surface silicon (first row), HOPG (second row) and graphite electrode (third row).



Figure S2: ToF-SIMS images of Fragment  $C_2S^-$  of surface silicon (first row), HOPG (second row) and graphite electrode (third row).



Figure S3: C 1s spectra of untreated (top left), electrografted (top right), deprotected (bottom left) and the thioether containing (bottom right) silicon, HOPG and graphite electrode.