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# **Supporting Information for:**

# **Egyptian Blue: from Pigment to Battery Electrodes**

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## **Electrodes Preparation**

The materials used for this study are: calcium copper silicate or Egyptian Blue (<120 μm, Kremer Pigmente, Aichstetten, Germany), TIMCAL Super P (99.9%, Bironico, Switzerland), Poly(vinylidiene fluoride) (PVDF) (53000 MW, Sigma-Aldrich, St. Louis, MO, USA), 1-Methyl-2-pyrrolidinone (NMP) (99.5%, Sigma-Aldrich, St. Louis, MO, USA), Yttria Stabilized Zirconia (YSZ) grinding media (Spherical 5.0 mm, Inframat Advanced Materials, Manchester, CT, USA), 1.2 M LiPF<sub>6</sub> in DMC:EC (70:30 vol%, BASF, Florham Park, NJ, USA).

Milling was performed on the EB using an 8000M Mixer/ Miller (SPEX SamplePrep, Metuchen, Germany). Powders and grinding media with a ratio of 1:10 were added to 60 mL high density polyethylene vessel. Ethanol (200 Proof, Decon Labs, Inc., King of Prussia, PA, USA) was added until the powder and grinding media was completely submerged. The vessel is then sealed and wrapped with Parafilm and milled for 30 minutes at 5-minute intervals with time to cool in between.

The electrode slurry contained EB (70 % weight, wt.), polyvinylidene fluoride, PVDF, (10% wt.) and Super P Li carbon (20% wt.) and was mixed in N-Methyl-2-Pyrrolidone (NMP) using mortar and pestle. The slurry was then cast onto copper foil (13 µm, BF-PLSP, Circuit Foil,

Luxembourg) using a 0.2 mm doctor blade. The cast was then allowed to air dry at room temperature and then placed in a vacuum oven at 120 °C for 16 h. After drying, electrodes were cut into 11 mm in diameter discs. The thickness of the electrodes was  $\approx$  45 µm and the average loadings for the as received EB was ~3.3 mg/cm<sup>2</sup> and for the milled EB was ~2.6 mg/cm<sup>2</sup>. For comparison, a carbon black electrode was made from Super P Li carbon (85% wt.) and PVDF (15% wt.) in NMP with same procedure described above for the EB.

#### **Materials Characterization**

X-ray diffraction (XRD) patterns were recorded using a Scintag PDS 2000 diffractometer equipped with a Cu-K<sub> $\alpha$ </sub> radiation and Ni filter. Diffraction patterns with the 2 theta range from 10 to 60° were collected in 0.02° steps with a count time of one second per step. Scanning electron microscopy (SEM) images were captured using a TM3030Plus Tabletop Microscope (HITACHI, Tokyo, Japan). All Fourier transform infrared spectra (FTIR) were collected using an ALPHA FTIR spectrometer (Bruker, Coventry, England) in attenuated total reflectance (ATR) mode from a germanium crystal. The X-ray absorption spectroscopy (XAS) data was recorded at the Cu Kedge (8979 eV) at the Stanford Synchrotron Radiation Laboratory, SLAC National Accelerator Laboratory (beamline 2-2). A Si (111) double crystal monochromator was used and detuned by 30% to reject higher harmonics. The Cu XAS was measured in transmission mode. Ion chambers for measuring the incident beam  $(I_0)$ , transmission  $(I_t)$  and a Cu foil for energy reference (I<sub>ref</sub>) were measured simultaneously. I<sub>0</sub> was filled with N<sub>2</sub> and I<sub>t</sub> and I<sub>ref</sub> were filled with mixture of 60% N<sub>2</sub> and 40% Ar. The ATHENA program (available through the DEMETER software package, version 0.9.25)<sup>1</sup> was used to reduce the data. Ex-situ X-ray absorption measurement were done on electrochemically cycled EB. The electrochemically cycled electrodes were removed from the coin cells using a de-crimping setup in an Ar-filled glovebox and rinsed using DMC. Then, the electrodes were detached from the current collectors and sandwiched between Kapton tapes and put in the beamline for the XAS measurement.

#### **Electrochemical Measurements**

In an Ar-filled glovebox, CR2032 stainless steel coin cells were assembled into half cells with lithium ribbons (99.9%, Sigma-Aldrich) as the counter electrode. The separators used were Celgard 2325 and glass microfiber (GF/A, Whatman, GE Healthcare, Little Chalfont, United Kingdom). Electrolyte of 1.2 M LiPF<sub>6</sub> in a mixture of ethylene carbonate, EC, and dimethyl

carbonate, DMC in a 1:2 respectively by weight ratio was used. Cyclic voltammetry at a scan rate of 0.2 mV/s was conducted between 5 mV and 3.5 V vs Li/Li<sup>+</sup> using Biologic VSP2 at room temperature. The room temperature galvanostatic cycling was performed on either the Biologic VSP2 or MACCOR Battery Testing System (MACCOR, Inc, Tulsa, OK, USA) battery testing system. All the electrochemical tests were carried out between 5.0 mV and 3.0V vs Li/Li<sup>+</sup> at 20, 100, and 500 mA/g. Electrochemical impedance spectroscopy (EIS) with frequency from 100kHz to 10 mHz were performed at 5 mV using a BioLogic VMP3 electrochemical workstation.

## **Li-ion Diffusion Coefficient Calculations:**

The Li-ion diffusion coefficient was calculated based on the following equation:<sup>2</sup>

$$D_{Li}^{+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}$$
(S1)

Where  ${}^{D}_{Li}$  + is the diffusion coefficient, *R* is gas constant (8.314 J mol<sup>-1</sup>K<sup>-1</sup>), *T* is temperature in K, *A* is the electrode area, *n* is the number of electrons transferred, *F* is the Faradic constant, *C* is lithium concentration, and  $\sigma$  is Warburg factor, which can be obtained using the linear Randles equation:<sup>3</sup>

$$Z' = \sigma \omega^{-1/2} + R_D + R_L \tag{S2}$$

Therefore, the Warburg factor can be obtained by fitting the real part (Z') of EIS and square root of angular frequency ( $\omega$ ) in the low frequency range, as shown in Figure S2.



## Figure S1. Randles plots of the electrodes before and after milling.

#### Cyclic voltammogram



Figure S2. Cyclic voltammogram of milled EB at 0.2 mV/s.

## **Theoretical calculation**

In this work we carry out density functional theory calculations using the Vienna Ab-initio Simulation Package (VASP) with the projector-augmented wave (PAW) method.<sup>4-7</sup> The recently developed SCAN meta-GGA is used for its superior performance in description of different chemical bonds and transition metal compounds.<sup>8-10</sup> The PAW method is employed to treat the core ion-electron interaction and the valence configurations are taken as  $1s^22s^1$ ,  $3s^23p^64s^2$ ,  $3d^{10}4s^1$ ,  $3s^23p^2$ , and  $2s^22p^4$  for Li, Ca, Cu, Si, and O, respectively.<sup>9-13</sup> An energy cutoff of 520 eV is used to truncate the plane wave basis. We use  $\Gamma$ -centered meshes with a spacing threshold of 0.15 Å<sup>-1</sup> for K-space sampling. Geometries of the reaction models, as shown in Figure S3, were allowed to relax until the maximum ionic forces were below a threshold of 0.01 eV Å<sup>-1</sup>.



Figure S3. Relaxed geometry of the imaginary lithiated  $CaCu(Si_2O_5)_2$  phase,  $Li_4CaCu(Si_2O_5)_2$ . Spectator atoms are labeled as green Li, red O, blue Si, grey blue Ca, and golden Cu. Black lines indicate the unit cell boundary.

This tetragonal structure has a space group of *P*-4*c*2, number 116. Wyckoff positions are [Li: 4i (0, 0.5, 0.055), 4i (0.5, 0, 0.102), and 8j (0.556, 0.322, 0.182)], [Ca: 2d (0.5, 0.5, 0.5), and 2c (0, 0, 0)], [Cu: 4i (0, 0.5, 0.250)], [Si: 8j (0.233, 0.343, 0.158), and 8j (0.152, 0.758, 0.146)], and [O: 8j (0.051, 0.260, 0.109), 4e (0.227, 0.227, 0.25), 4f (0.213, 0.787, 0.25), 8j (0.396, 0.277, 0.099), 8j (0.237, 0.562, 0.116), and 8j (0.244, 0.904, 0.089)].

Table S1. Reaction energies ( $\Delta E_1$  and  $\Delta E_2$ ) of the two assumed reactions and calculated total energies (*E*) of unit cells of phases involved in the reactions. The number of unit formula contained in the employed unit cell of corresponding phases (*N*u.f.) and the unit cell volume (*V*) are also in list.

Phases	N <sub>u.f.</sub>	$V(Å^3)$	E(eV)
Cu	4	45.050	-60.560
Li	2	40.390	-4.758
Si	2	39.980	-20.016
$CaCu(Si_2O_5)_2$	4	806.070	-689.880
$Li_2Si_2O_5$	4	402.740	-327.131
Li <sub>2</sub> SiO <sub>3</sub>	2	115.650	-100.311
CaSiO <sub>3</sub>	6	397.350	-328.905
$Li_4CaCu(Si_2O_5)_2$	4	896.570	-722.726
$\Delta E_1 (eV)$	-18.202		
$\Delta E_2 (eV)$	-20.809		

# POSCAR file for imaginary Li<sub>4</sub>CaCu(Si<sub>2</sub>O<sub>5</sub>)<sub>2</sub>

Li<sub>4</sub>CaCuSi<sub>4</sub>O<sub>10</sub>

7.6299096418519259	0.00000000000000000	0.0000000000000000
0.00000000000000000	7.6299096418519259	0.00000000000000000
0.00000000000000000	0.00000000000000000	15.4009539957552501
Ca Cu Si O Li		
4 4 16 40 16		

#### Direct

 0.1521494521293776 0.2424876110865502 0.6458291674141788 0.2326062867198018 0.6572335155466645 0.6579688975051240 0.8478505628706271 0.7575123889134496 0.6458291674141788 0.7673936982802007 0.3427664844533356 0.6579688975051240 0.6572335155466645 0.2326062867198018 0.8420311024948760 0.7575123889134496 0.8478505628706271 0.8541708325858212 0 3427664844533356 0 7673936982802007 0 8420311024948760 0.2424876110865502 0.1521494521293776 0.8541708325858212 0.3427664844533356 0.2326062867198018 0.3420311324948784 0.2424876110865502 0.8478505628706271 0.3541708625858165 0.6572335155466645 0.7673936982802007 0.3420311324948784 0.7575123889134496 0.1521494521293776 0.3541708625858165 0.8478505628706271 0.2424876110865502 0.1458291524141883 0.7673936982802007 0.6572335155466645 0.1579688825051264 0.1521494521293776 0.7575123889134496 0.1458291524141883 0.2326062867198018 0.3427664844533356 0.1579688825051264 0.0508291177332969 0.2600984571151071 0.1092048791364317 0.2368429314731163 0.5615546989515151 0.1161998078003029 0.9491708632667052 0.7399015278848953 0.1092048791364317 0.7631570685268837 0.4384453310484876 0.1161998078003029 0.5615546989515151 0.2368429314731163 0.3838001771996924 0.7399015278848953 0.9491708632667052 0.3907951058635635 0.4384453310484876 0.7631570685268837 0.3838001771996924 0.2600984571151071 0.0508291177332969 0.3907951058635635 0.4384453310484876 0.2368429314731163 0.8838002071996948 0.2600984571151071 0.9491708632667052 0.8907951358635661 0.5615546989515151 0.7631570685268837 0.8838002071996948 0.7399015278848953 0.0508291177332969 0.8907951358635661 0.9491708632667052 0.2600984571151071 0.6092048641364339 0.7631570685268837 0.5615546989515151 0.6161997928003052 0.0508291177332969 0.7399015278848953 0.6092048641364339 0.2368429314731163 0.4384453310484876 0.6161997928003052 0.0963368393363059 0.2438051542859478 0.9110215561917079

0.2768118899883701 0.6036453088353746 0.9006454866739482 0.9036631906636966 0.7561948457140520 0.9110215561917079 0.7231880950116319 0.3963546611646157 0.9006454866739482 0.6036453088353746 0.2768118899883701 0.5993545133260518 0.7561948457140520 0.9036631906636966 0.5889784438082921 0.3963546611646157 0.7231880950116319 0.5993545133260518 0.2438051542859478 0.0963368393363059 0.5889784438082921 0 3963546611646157 0 2768118899883701 0 0993544913260498 0.2438051542859478 0.9036631906636966 0.0889784218082901 0.6036453088353746 0.7231880950116319 0.0993544913260498 0.7561948457140520 0.0963368393363059 0.0889784218082901 0.9036631906636966 0.2438051542859478 0.4110215851917070 0.7231880950116319 0.6036453088353746 0.4006455156739472 0.0963368393363059 0.7561948457140520 0.4110215851917070 0.2768118899883701 0.3963546611646157 0.4006455156739472 0.2133904135619551 0.2133904135619551 0.7500000000000000 0.2271855982360332 0.7728143717639642 0.7500000000000000 0.7866096164380547 0.7866096164380547 0.7500000000000000 0 7728143717639642 0 2271855982360332 0 750000000000000 0.2271855982360332 0.2271855982360332 0.2500000000000000 0.2133904135619551 0.7866096164380547 0.2500000000000000 0.7728143717639642 0.7728143717639642 0.25000000000000000 0.7866096164380547 0.2133904135619551 0.2500000000000000 0.500000000000000 -0.00000000000000 0.6021297559838376 -0.00000000000000 0.50000000000000 0.3978702440161552 -0.00000000000000 0.50000000000000 0.8978702440161553 0.50000000000000 -0.0000000000000 0.1021297559838449 0.5559287500880664 0.3215272159892645 0.1821315158984086 0.3215272159892645 0.5559287500880664 0.3178684841015915 0.6784727840107354 0.4440712499119335 0.3178684841015915 0.4440712499119335 0.6784727840107354 0.1821315158984086 0.5559287500880664 0.6784727840107354 0.6821315158984086 0.6784727840107354 0.5559287500880664 0.8178684841015914 0.3215272159892645 0.4440712499119335 0.8178684841015914 0.4440712499119335 0.3215272159892645 0.6821315158984086 0.50000000000000 -0.0000000000000 0.9453999654004723 -0.00000000000000 0.5000000000000 0.5546000345995277 -0.00000000000000 0.5000000000000 0.0546000345995275 0.50000000000000 -0.0000000000000 0.4453999654004726

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