

## ELECTRONIC SUPPLEMENTARY INFORMATION

### Electrochemical calcium extraction from 1D-Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub>

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### Experimental section.

#### *Synthesis.*

Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> was prepared by the Pechini method.<sup>1</sup> 30 ml of a 1M solution of Ca(NO<sub>3</sub>)<sub>2</sub> (99% tetrahydrate, Sigma-Aldrich) and 20 ml of a 1M solution of Co(NO<sub>3</sub>)<sub>2</sub> (98%, hexahydrate, Sigma-Aldrich) in water were mixed with 10.5 g citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, 99%, Sigma-Aldrich) and put together in a glass vial to which 6.25 g of ethyleneglycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, 99%, Sigma-Aldrich) was added (note that this corresponds to 3:2:5:10 molar ratios for Ca:Co:C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>:C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>). The solution was subsequently stirred over night at room temperature and further heated to promote water evaporation which induced enhanced viscosity of the mixture and the evolution of nitrous oxide gas. Once the gel formed dried, it was placed in an alumina crucible and heated under air first at 600°C for 6 hours and then at 950°C for 8 hours and subsequently cooled to room temperature.

#### *Structural characterization.*

Synchrotron X-ray diffraction patterns were collected in MSPD beamline (ALBA synchrotron, Cerdanyola del Vallès, Spain) using Mythen detector and  $\lambda=0.6199$  Å. The samples, either pristine Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> or powder recovered from cycled electrodes after dismantling the electrochemical cells inside Ar-filled glove box, were embedded in a 0.5 mm diameter borosilicate glass capillary, and rotated during data collection. Scanning electron microscopy (SEM) studies on Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> powder and composite electrodes were performed using a FEI Quanta 200 FEG microscope equipped with an energy-dispersive X-ray spectrometer (EDS).

#### *Electrochemical cell testing.*

For electrode preparation, Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> was mixed with carbon black (Super P, Timcal, Switzerland) to enhance electronic conductivity and with polyvinylidene fluoride (PVDF, Arkema) used as binder in a weight ratio of 80:10:10. The mixture was further dispersed in N-methyl-2-pyrrolidone (Aldrich, ≥99.9%), grinded in a ball mill and casted on 18 μm thick aluminium foil (Goodfellow, 99%) with a blade gap of 300 μm and vacuum dried at 80°C for 24h. Electrochemical tests were performed in three-electrode Swagelok cells against Ca metal (Alfa Aesar, 99.5%) as counter (CE) and reference (RE) electrodes. The electrolyte was 0.45 M Ca(BF<sub>4</sub>)<sub>2</sub> dissolved in a 1:1 volume mixture of ethylene carbonate (EC) and propylene carbonate (PC) purchased from Solvionic (99.9%), with water content lower than 50 ppm (Karl-Fisher titration). A potential shift of the Ca pseudo RE has been reported when operating in

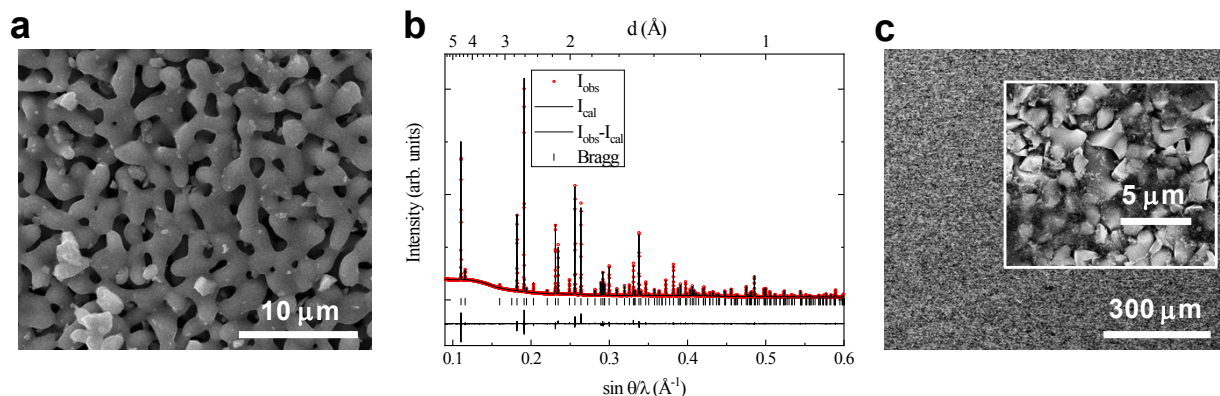
electrolytes using EC:PC as solvent, with absolute value up to 1 V strongly depending on the experimental conditions.<sup>2</sup> Thus, all electrochemical potentials were reported vs. the Ca pseudo RE. Cells were assembled in Ar filled glove box with less than 1 ppm of O<sub>2</sub> and H<sub>2</sub>O and were tested using potentiodynamic cycling with galvanostatic acceleration (PCGA) on a Bio-Logic VMP3 potentiostat either at 100 or 115°C. The potential was scanned with steps of 5 mV for a duration limited by current threshold of C/200. The stability of Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> under the experimental conditions was ascertained by ageing assembled cells at open circuit potential (OCP) for 30 hours at 100 and 115°C and further recovering the electrodes for diffraction.

## Results and Discussion.

### Characterization of Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub>.

Scanning electron microscopy (SEM) indicates that as prepared Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> consists of uniform particles with average size of a few μm (Figure S1a). This has been confirmed by synchrotron X-ray diffraction, as no extra peaks can be detected in the pattern, which reveals absence of crystalline impurities. Results of Rietveld refinement (Figure S1b) are in very good agreement with the crystal structure reported in<sup>3</sup> (ICSD-246281).

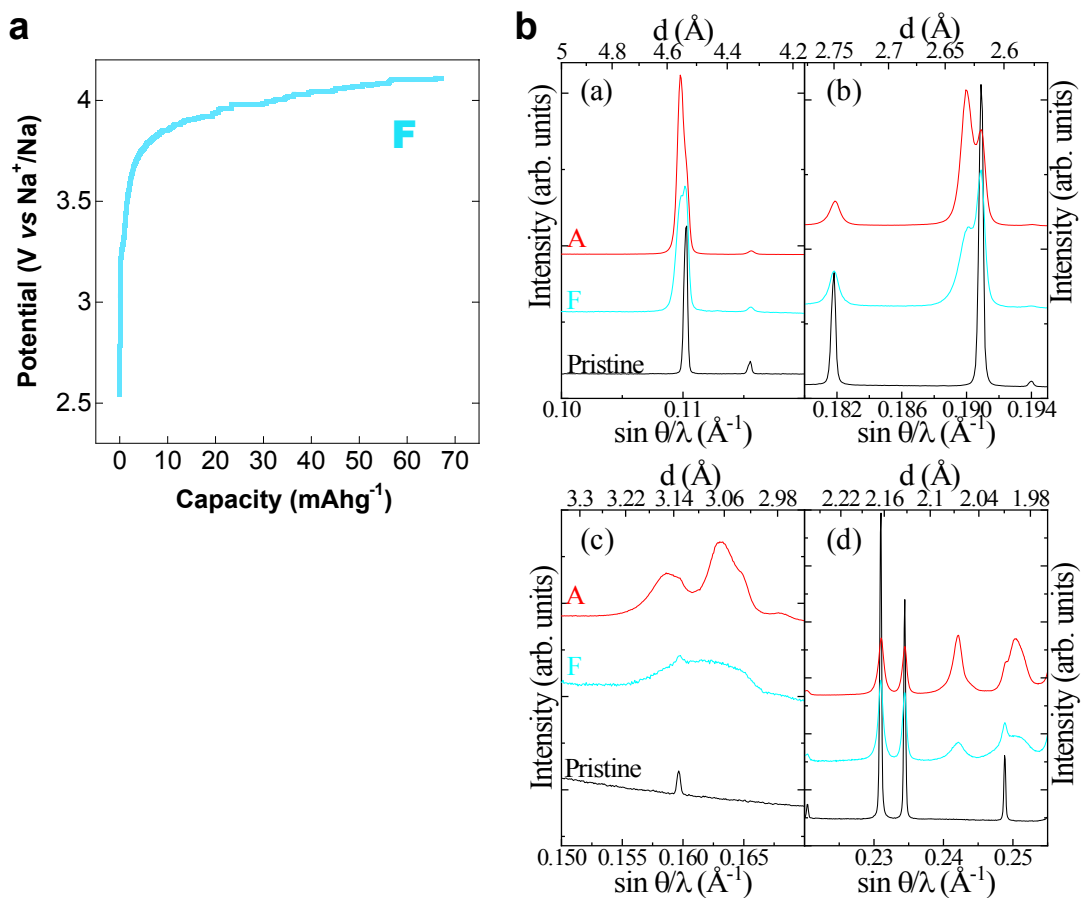
Figure S1c depicts a SEM micrograph of the as prepared composite electrode, exhibiting the homogeneous distribution of the mixed Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> active material, carbon black additive and PVDF binder. The magnification (in inset) allows to infer that micrometric particles retain their initial morphology within the composite (Figure S1a).



**Fig. S1:** a) Typical SEM image of the as synthesized powder, exhibiting interconnected micrometric Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> particles. b) Synchrotron X-ray diffraction pattern of the Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> powder. Rietveld fit is shown with the observed dots as red points, the calculated profile as full black line and difference and reflection markers offset below. The refinement has been done starting from the crystal structure in ICSD database (ICSD-246281, space group *R*-3*c*, no. 167). Agreement factors are  $R_{wp}=2.42\%$  and  $R_B=2.46\%$  and cell parameters  $a=9.0772(6)$  Å,  $c=10.3803(6)$  Å. c) SEM micrograph of the pristine composite electrode with homogeneously distributed components (active material, additive and binder). Inset shows a magnification on Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> particles.

*Electrochemical oxidation of  $\text{Ca}_3\text{Co}_2\text{O}_6$  electrodes in Na cell.*

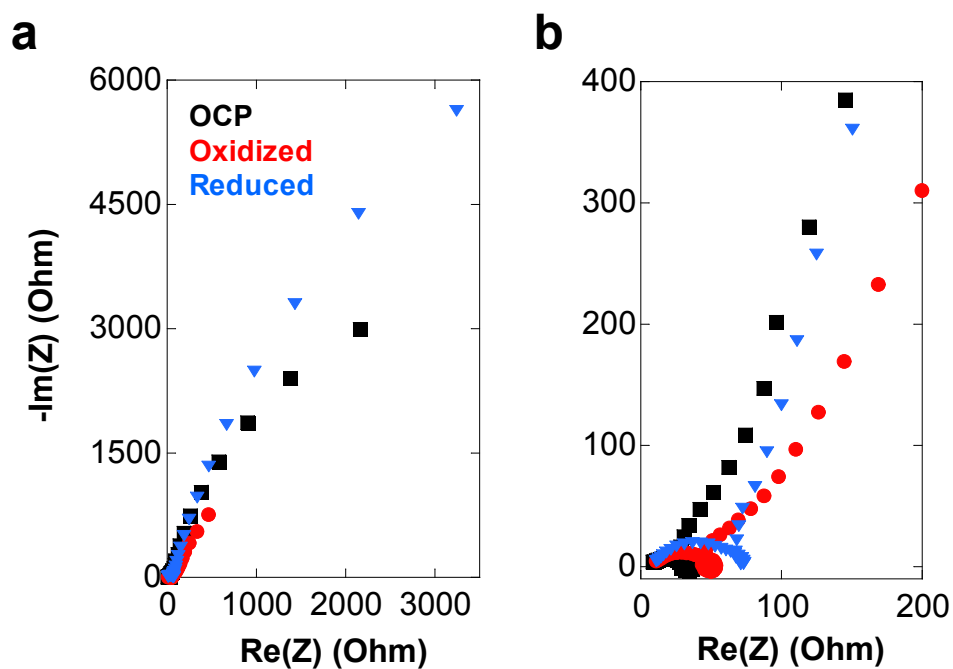
PCGA test (current threshold of C/200) against Na metal (Sigma Aldrich, 99.95%) as counter (CE) and reference (RE) electrode was performed with 1.0 M  $\text{NaPF}_6$  dissolved in a 1:1 volume mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The  $\text{Ca}_3\text{Co}_2\text{O}_6/\text{Na}$  cell was operated at room temperature and the corresponding oxidation curve up to 4.1 V vs.  $\text{Na}^+/\text{Na}$  is shown in figure S2a. Similar evolution of the voltage vs. capacity profile is observed as compared to those in Ca cells, however, with larger electrode polarization. The corresponding Synchrotron x-ray diffraction pattern (labeled F) is presented in figure S2b compared against pristine and sample A, and showing the formation of the same phase as when  $\text{Ca}_3\text{Co}_2\text{O}_6$  electrodes are oxidized in Ca cells.



**Fig. S2:** a) Electrochemical oxidation of  $\text{Ca}_3\text{Co}_2\text{O}_6$  electrodes at room temperature by PCGA (C/200) technique in  $\text{Ca}_3\text{Co}_2\text{O}_6/\text{Na}$  cell. The electrode has been recovered for X-Ray diffraction (XRD) capillary measurement and labeled F. b) Synchrotron x-ray diffraction patterns corresponding to pristine  $\text{Ca}_3\text{Co}_2\text{O}_6$  electrode (in black) and samples A in red, and F in cyan. Panels (a) and (b) show a zoom of the zones where the most intense peaks of pristine  $\text{Ca}_3\text{Co}_2\text{O}_6$ , (100) and (300), decrease while new peaks nearby start to appear. Panels (c) and (d) evidence the progressive appearance of new diffraction peaks.

*Electrochemical Impedance Spectroscopy (EIS) measurements on  $\text{Ca}_3\text{Co}_2\text{O}_6$  electrodes.*

EIS measurements were done under potentiostatic control, by applying perturbation amplitudes of 10 mV with frequencies ranging from 200 kHz to 10 mHz. Impedances were recorded on  $\text{Ca}_3\text{Co}_2\text{O}_6//\text{Ca}$  cell with 0.45 M  $\text{Ca}(\text{BF}_4)_2$  in EC:PC (1:1) volume mixture, operating at 100°C, according to the following scheme: 1) collecting PEIS spectra at open circuit potential (OCP), 2) collecting PEIS spectra at the end of the electrode oxidation, 3) collecting PEIS spectra at the end of the electrode reduction.



**Fig. S3:** Impedance measurements on  $\text{Ca}_3\text{Co}_2\text{O}_6$  electrodes: a) PEIS in the full 200 kHz-10 mHz range for the cell at OCP (black squares), after electrode oxidation (red circles), and at the end of reduction (blue triangles). b) Zoom on the high frequency range.

**References.**

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- <sup>3</sup> C. H. Hervoches, H. Okamoto, A. Kjekshus, H. Fjellvag and B. Hauback, *J. Solid State Chem.*, 2009, **182**, 331.