Electrochemical calcium extraction from 1D- $\text{Ca}_3\text{Co}_2\text{O}_6$

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The electrochemical oxidation of a transition metal oxide through calcium extraction is achieved for the first time. The 1D framework of $\text{Ca}_3\text{Co}_2\text{O}_6$ is maintained upon oxidation and the new phase formed exhibits a modulated structure. The process occurs at high potential and is partially reversible, which opens prospects for a calcium battery proof-of-concept.

The study of intercalation compounds¹ led to the identification of redox reactions in host transition metal compounds involving reversible (usually topotactic) insertion and deinsertion of M^{n+} ions. While intercalation of multivalent cations ($n>1$) remained an academic curiosity, studies involving Li^+ turned out to be a cornerstone in the development of the Li-ion battery technology.² Despite the cost reduction, this technology is now reaching its fundamental limits in terms of energy density, one of the crucial parameters for application (e.g. dictates the autonomy range in transport applications). The “holy grail” to achieve the largest energy densities is the use of light electropositive metals as negative electrodes.³ Intensive research on battery concepts based on Li metal, such as Li-S and Li-air technologies, has proven many intrinsic issues related to the dendritic growth of Li and mechanistic bottlenecks to be show-stoppers.^{4,5,6} Moreover, the risks of limited Li supply and/or significantly increased price cannot be ignored.⁷ Therefore, innovative sustainable battery chemistries based on abundant elements and enabling higher energy densities must be developed.^{8,9} A leap-frogging concept is the use of multivalent metal anodes such as Mg, Ca or Al with theoretical volumetric capacities exceeding values for Li metal and much lower cost.¹⁰ Besides, they are very abundant in the Earth’s crust (8th, 5th and 3rd, respectively) and not plagued by dendrite formation, hence intrinsically safer. A proof-of-concept of Mg metal based battery was already provided in 2000,¹¹ but its

commercialization has remained elusive due to the corrosive nature and low electrochemical stability window of the electrolytes employed and the fundamentally limited diffusion of the highly polarizing Mg^{2+} ions in the solid state. Ca^{2+} ions have a much lower charge to radius ratio than both Mg^{2+} and Al^{3+} and thus inherently offer promise for faster diffusion in solids (electrodes) and weaker cation-anion as well as cation-solvent interactions in liquids (electrolytes) and hence suitable power rates.

Ca metal based batteries have been almost unexplored, as reversible plating and stripping of calcium with conventional organic electrolytes were for long believed impossible.^{12,13} This hindered the investigation in calcium intercalation cathode materials. The achievement of reversible plating/stripping of Ca either at moderate temperature in wide potential window electrolytes¹⁴ or at room temperature with limited electrochemical stability electrolytes¹⁵ opened the way to exploratory screening of potential cathode materials to achieve a proof-of-concept for the full Ca-based rechargeable battery. Nonetheless, the development of multivalent cathodes is challenging.^{16,17} Firstly, the know-how in the Li-ion battery field cannot be directly translated to the multivalent chemistries, as these are plagued with side reactions and hence the use of rigorous protocols is a must.¹⁸ Besides conventional intercalation hosts like layered TiS_2 ,¹⁹ some appealing compounds potentially exhibiting suitable ion migration pathways within their crystal structure such as CaMoO_3 or CaMn_2O_4 were found to display too large energy barriers for Ca^{2+} diffusion.^{20,21} Alternative metastable polymorphs, predicted to possess low migration barriers from DFT calculations,²² do not seem to be achievable even under high pressure and elevated temperatures.

These arguments prompted us to explore 1D crystal structures, which may facilitate cation migration along the inter-chain spaces, such as the family of compounds with general formula $\text{A}_{1+x}(\text{A}'_x\text{B}_{1-x})\text{O}_3$, with A being an alkaline earth element. Its crystal structure exhibits columns of BO_6 and $\text{A}'\text{O}_6$ polyhedra (octahedral and trigonal prisms respectively) running along the *c* direction,^{23,24,25} Amongst these, the $\text{Ca}_3\text{Co}_2\text{O}_6$ compound (with $\text{A}=\text{Ca}$, $x=0.5$ and A' and B corresponding to Co)²⁶ is especially interesting. It exhibits a K_4CdCl_6 -type crystal structure consisting of infinite columns of alternating face-shared

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CoO₆ trigonal prisms and octahedra²⁷ (Fig. 1) and, since it contains cobalt as the redox center, holds promise of high potential operation. This compound has been widely studied for its magnetic properties²⁸ but to the best of our knowledge, its potential use in calcium batteries was never suggested, despite the attractive theoretical capacity (160 mAh g⁻¹) related to extraction of one mole of Ca²⁺ per formula unit to yield Ca₂Co₂O₆. In this article we demonstrate that the electrochemical extraction of Ca²⁺ from its crystal structure is feasible with the formation of a modulated structure, formally belonging to the A_{1+x}(A'_xB_{1-x})O₃ series. Hints of reversibility are observed and possible limiting factors for Ca²⁺ reinsertion into the crystal structure are discussed. While in a preliminary stage, our findings open new avenues towards the exploration of 1D structures as electrodes in multivalent batteries which, coupled to suitable electrolytes, could enable the development of the next generation high energy density battery technologies.

Calcium extraction from electrodes containing Ca₃Co₂O₆ as the active material was attempted electrochemically (see Experimental section, ESI). The scanning electron microscopy (SEM) image of the as prepared composite electrode (Fig. 1S, ESI) exhibits the homogeneous distribution of its components (Ca₃Co₂O₆, carbon black and PVDF). The magnification (in the inset) allows one to infer that micrometric particles retain their initial morphology within the composite. The electrolyte used was 0.45 M Ca(BF₄)₂ in a 1:1 volume mixture of ethylene carbonate (EC) and propylene carbonate (PC), as it enables Ca electrodeposition at moderate temperatures (> 50°C) and exhibits a wide operation potential window,¹⁴ being suitable for the investigation of materials with activity in the 3–4 V range. Typical potential vs. capacity profiles of Ca₃Co₂O₆ composite electrodes are shown in Fig. 2a. Upon oxidation, a first sloping region is observed followed by a pseudo-plateau at about 3.6 V vs. the Ca pseudo-RE with a total electrochemical capacity of 180 mAhg⁻¹. This capacity can be associated with the extraction of Ca²⁺ from the crystal structure and hence the *y* value in Ca_{3-y}Co₂O₆ can be deduced (top abscissa axis in Fig. 2a), assuming no additional redox phenomena take place. The curves depicted in Fig. 2a correspond to progressive Ca²⁺ extraction from Ca₃Co₂O₆ of *y* = 0.15, 0.6 and 1.2 moles per formula unit (at points labeled A, B and C in red, purple and blue, respectively). Since the decomposition of the electrolyte at 100°C cannot be fully ruled out, the amount of extracted Ca²⁺ might be overestimated, particularly for the most oxidized electrodes. Indeed, it is unrealistic to believe that *y* > 1 values can be achieved, as this would correspond to Co formal oxidation states higher than 4.

Fig. 1. Crystal structure of 1D-Ca₃Co₂O₆: infinite columns of face-shared CoO₆ octahedra and CoO₆ trigonal prisms form a hexagonal lattice, while Ca²⁺ ions form chains between the columns. The space group is $R\bar{3}c$ and cell parameters $a = 9.061$ Å and $c = 10.367$ Å.²⁷

The electrochemical reduction of fully oxidized Ca₃Co₂O₆ electrodes to 1.2 V vs. the Ca pseudo-RE at 100°C resulted in a capacity of 76 mAhg⁻¹ (point D in green). Remarkably, the reduction proceeds with a very large overpotential, indicating that the process is limited either thermodynamically or kinetically. Analogous experiments performed at slightly higher temperature (115°C, not shown) gave similar results.

Fig. 2b depicts the synchrotron X-Ray diffraction patterns of as-prepared Ca₃Co₂O₆ and samples recovered from electrodes at different redox states. Upon the progressive oxidation of Ca₃Co₂O₆, the peaks at $d = 4.330$ and 2.751 Å gradually decrease in intensity to finally disappear for the most oxidized electrode (C in blue), while those at $d = 4.536$ and 2.619 Å, (100) and (300), respectively, decrease at the expense of new reflections at $d = 4.553$ and 2.631 Å (zoom-in panels (i) and (ii)). In addition, new peaks also appear upon oxidation and gradually grow. Some of them (at $d = 3.15$ and $d = 1.65$ Å) are related to the formation of minor amounts of CaF₂ due to electrolyte salt decomposition, but others (shown in panels (iii) and (iv)) do not correspond to any known possible impurity and cannot be indexed with a rhombohedral unit cell. The fact that these are indeed related to a phase formed by the oxidation of Ca₃Co₂O₆ was further confirmed by results of an analogous experiment at room temperature using a Na counter electrode (Fig. S2, ESI).

Fig. 2. a) Potential vs. capacity profiles from potentiodynamic cycling with galvanostatic acceleration (PCGA) experiments at 100°C and C/200 rate in $\text{Ca}_3\text{Co}_2\text{O}_6$ //Ca cells, progressively oxidized (labeled A in red, B in purple, C in blue), or oxidized and reduced (D in green). b) SXR diffraction patterns of pristine $\text{Ca}_3\text{Co}_2\text{O}_6$ electrode (in black), samples shown in (a) and sample E in grey). For details on labels see text. Patterns have been vertically shifted for clarity. c) Expanded views on specific zones.

After oxidation to *ca.* 3.7 V vs. the Ca pseudo RE, the estimated composition based on the electrochemical capacity is $\text{Ca}_2\text{Co}_2\text{O}_6$ and diffraction patterns indicate that there is no $\text{Ca}_3\text{Co}_2\text{O}_6$ remaining in the electrode. The elucidation of the crystal structure for the oxidized phase was possible considering the homologous series of phases of general formula $(\text{Ca}_{n+2}\text{Co}_{n+1}\text{O}_{3n+3})^{24}$ having $\text{Ca}_3\text{Co}_2\text{O}_6$ (alternation of octahedral and prismatic Co in the columns, $n=1$) and hypothetical CaCoO_3 (2H perovskite with only octahedral Co and isostructural to BaCoO_3 , $n=\infty$) as end members. For intermediate n values (n is an integer), the columns consist on a sequence of n -octahedra and one prism. As an alternative to this structurally related notation, the formula of these phases

can also be expressed as $\text{Ca}_{1+x}\text{CoO}_3$, as typically done for isostructural $\text{Sr}_{1+x}\text{TiS}_3$,²⁹ and $\text{Sr}_{1+x}\text{NiO}_3$.³⁰ These complex structures are best described as an incommensurate composite in which two c parameters are needed to account for the different parts of the structure: c_1 for the Co columns and c_2 for the Ca chains. The propagation vector describing the incommensuration is of the type $\mathbf{k} = (0,0,\gamma)$ and is directly related to the stoichiometry of the system by the expression $1+x = 2\gamma$, and to the cell parameters as $\gamma = c_1/c_2$, thus rendering $x = 2c_1/(c_2-1)$.^{26, Error! Bookmark not defined.} Fig. 3 shows the refinement done based on the diffraction pattern for sample C, done using Jana2006 program³¹ taking the structure reported for $\text{Sr}_{1.261}\text{CoO}_3$ as initial model with superspace

group $R\bar{3}m(00\gamma)0s$.³² The agreement is quite satisfactory ($R_{wp} = 5.35\%$, $R_B = 5.16\%$), yielding lattice parameters $a = 9.127(1)$ Å, $c_1 = 2.4226(3)$ Å and $c_2 = 4.1857(3)$ Å, giving $\gamma = 0.5789(2)$. The peak at $d \approx 3.06$ Å corresponds to $(2\bar{1}01)$ in the 4D description and its position is directly related to the c_2 cell parameter (Ca chains). As the c_1 cell parameter (CoO₃ chains) hardly depends on the Ca content, the position of the $(2\bar{1}01)$ peak, directly related to the propagation vector γ , enables a very accurate estimation of the Ca content. The results render $x = 0.158$ for the fully oxidized phase (i.e. Ca_{2.32}Co₂O₆, $y = 0.68$), in agreement with the conclusions derived from electrochemical experiments and the existence of some electrolyte decomposition.

Fig. 3. a) Crystal structure of Ca_{2.3}Co₂O₆ (labelled C in Figs. 2 and 3) showing an incommensurate modulation. b) Rietveld refinement of the crystal structure based on the diffraction pattern, using the $R\bar{3}m(00\gamma)0s$ superspace group.

Attempts to further oxidize the compound result in the appearance of additional low intensity peaks whose origin could not be identified and a plateau close to 4 V with observation of enhanced amount of CaF₂ in the patterns, resulting from electrolyte decomposition. These results unambiguously prove that electrochemical extraction of Ca²⁺ from Ca₃Co₂O₆ is feasible at 100°C in Ca cells and also at room temperature using Na counterelectrodes (Fig. S2, ESI). Nonetheless, in order to suggest the use of 1D-Ca₃Co₂O₆ as potential positive electrode material in Ca batteries, reversibility of the extraction process has to be assessed.

The refinement of the crystal structure based on diffraction patterns corresponding to samples fully oxidized and further reduced in calcium cells seem to indicate some Ca²⁺ reintercalation. The $(2\bar{1}01)$ peak in samples D and E (oxidized and reduced at 100°C and 115°C, respectively) is shifted to smaller d -spacing (panel (iii) in Fig. 2c) with respect to sample C, only oxidized, which corresponds to a smaller c_2 value and hence a somewhat larger x in Ca_{1+x}CoO₃. Along the same line, sample E seems to consist of a mixture of phases with different values of x (all larger than 0.16). Besides that, a broad signal appears close to $(2\bar{1}00)$ and (3000) peaks (placed at $d = 4.558$ and 2.633 Å, respectively; see arrows in Fig. 2c, panels (i) and (ii)) at the positions of (100) and (300) diffraction peaks of the pristine Ca₃Co₂O₆ ($x = 0.5$) phase.

In summary, electrochemical experiments coupled to diffraction experiments clearly indicate that the extraction of Ca²⁺ from this 1D-inorganic transition-metal oxide is feasible and proceeds through a two phase mechanism with the formation of a modulated structure with composition Ca_{1.16}CoO₃. The reversibility of the redox process seems to be rather limited. This may be indicative of some kinetic or thermodynamic issues: while slow solid state diffusion seems unlikely (Ca²⁺ extraction was possible even at room temperature), the charge transfer process and/or the formation of a passivation layer around the Ca₃Co₂O₆ particles at the end of the electrode oxidation might be associated with high impedance. Yet, this hypothesis is dismissed by the similar and rather small impedance values recorded at open circuit potential (OCP) and at the end of oxidation (Fig. S3, ESI), indicating no significant differences in the electronic conductivity. Thus, any sur-

face passivation layer formed at the end of oxidation, would not enhance the overall resistivity of the system. Another reason for the limited reversibility would be the difference in solvation and desolvation energies for Ca^{2+} in the electrolyte solvents. This is in agreement with strong interactions between Ca^{2+} and the solvent molecules, assessed by Raman spectroscopy,¹⁸ which would penalize Ca^{2+} desolvation and thus reinsertion into the oxidized phase. This is also consistent with a recent modelling study³³ on

the Mg-anion (anion = Cl^- , TFSI $^-$) adsorption and dissociation on MoO_3 surfaces concluding that the main barrier for cation intercalation is Mg^{2+} desolvation at the cathode-electrolyte interface. Despite such issues, our results open new research directions for the exploration of 1D structures enabling multivalent ion migration and proof-of-concept of full calcium cells while at the same time challenge scientists for the development of new electrolytes.

Conflicts of interest

There are no conflicts to declare.

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