

Emerging Calcium Batteries

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ABSTRACT

This review depicts the present landscape in the field of calcium batteries, presenting a critical analysis of the state-of-the-art and estimating performance indicators to foresee the development of this technology. The practical realization of rechargeable Ca batteries still relies on the identification of suitable electrode and electrolytes. Despite reversible calcium plating-stripping being recently demonstrated, efforts are still needed to improve kinetics and efficiency and to allow a wider range of electrolyte formulations. In the very last years the spectrum of searched electrolytes and cathodes expanded to achieve proof-of-concept full Ca-batteries. Widening the electrochemical stability window of the electrolyte is crucial to push the development of positive electrodes operating at high potential. So far, only few interesting examples of inorganic cathode materials have been demonstrated. Sulfur and organic positive electrodes remain interesting pathways to follow. This work reviews electrode (positive and negative, including alloying and conversion compounds) and electrolyte materials, developed or modelled, and goes beyond, by addressing technical issues for potential Ca-cells upscaling. Based on a techno-economic analysis of different cell configurations, the performance figures-of-merit of this technology are discussed and related for the first time to EU targets and priorities established for the successful deployment of post-lithium batteries.

KEYWORDS: Calcium batteries; Anode materials; Cathode materials; Electrolytes; Key Performance Indicators; Techno-economic analysis.

HIGHLIGHTS:

- Properties of anode, cathode and electrolyte materials for Ca-batteries
- Estimates of key performance indicators for future development
- Techno-economic aspects for technology upscaling

LIST OF ABBREVIATIONS

- 1D: One dimension
- 2D: Two dimensions
- 3D: Three dimensions
- ACN: Acetonitrile
- BatPaC: Battery Performance and Cost
- BL: γ -butyrolactone
- Ca(B(hfip)₄)₂: Calcium tetrakis(hexafluoroisopropoxy)borate
- Ca(Tf)₂: Calcium trifluoromethanesulfonate
- Ca(TFSI)₂: Calcium bis(trifluoromethanesulfonyl)imide
- CIB: Ca-ion battery
- DGM: Diglyme
- DMAc: Dimethylacetamide
- DMC: Dimethyl Carbonate
- DME: Dimethoxy Ethane
- DMF: N,N-dimethylformamide
- DFT: Density Functional Theory
- DMSO: Dimethyl Sulfoxide
- EC: Ethylene Carbonate
- EG: Expanded Graphite
- EMC: Ethyl Methyl Carbonate
- GCB: Graphitized Carbon Black
- KB: Carbon Additive
- LHCE: Localized High Concentration Electrolytes
- LIB: Lithium-Ion Battery

- MCMB: Mesocarbon Microbeads
- PC: Propylene Carbonate
- PBAs: Prussian Blue Analogues
- PITT: Potentiostatic Intermittent Titration Technique
- rGO: reduced Graphene Oxide
- SHE: Standard Hydrogen Electrode
- TBA: Tetrabutylammonium
- THF: Tetrahydrofuran
- TFSI: bis(trifluoromethanesulfonyl)imide
- TEGDME: Tetraethylene Glycol Dimethyl Ether

1. Introduction

The XXI century is venturing into a breaking technology transition in the way energy is produced, stored and consumed [1]. In the next decades energy consumption is expected to monotonically rise following the industrial and societal growth across the world [2,3]. However, the production of energy through combustion of fossil fuels or nuclear fission of uranium minerals is facing the increasing competition of the so-called green-energy sources [3,4]. The latter technologies exploit renewable conversion of sunlight, geothermal power as well as wind and marine tides/waves energy, with minimal CO₂ release [5]. Besides the cost competition, the expected global shift in the energy production, i.e., from combustion to renewable, is further pushed by both environmental and strategic considerations. Overall, it will open extraordinary new challenges for a reliable and large-scale energy storage, doubling the technology demands posed by the electrification of transport [3,4,6,7].

At the beginning of this century, the study of aprotic battery chemistries beyond lithium-ion batteries (LIB) was the exotic divertissement of a limited bunch of visionary scientists across the world [8–11]. This landscape massively changed in the last twenty years and worldwide intense research and development efforts are invested by public and private stakeholders (universities, research centres and private companies) to develop new battery technologies beyond lithium [12–17]. Aprotic sodium-ion batteries (NIB) are, by large, the most widely investigated chemistry alternative to LIB, given the chemical similarity of sodium to lithium, and its relatively small atomic weight (3.3 times that of lithium) [9]. One should in fact have in mind that the shuttle ion (e.g. Li⁺, Na⁺, etc.) is a redox inactive mass in any active material and therefore its increase leads unavoidably to lower gravimetric energy and power density. Other battery chemistry alternatives, much less explored than sodium, comprise potassium, magnesium, calcium and zinc [8,10,11]. Focusing on multivalent elements, i.e. Mg, Ca, Al and Zn, the ability to drive multiple electron exchange for every charge transfer event counterbalances the larger atomic weight compared to both Na and Li [18]. In fact,

multivalent rechargeable batteries have theoretical figures that can compare with the present state of the art in the field [8,10,11,13–15].

Calcium is a divalent alkaline earth metal with an extraordinarily strong oxidative ability in consideration of the -2.87 V vs SHE (standard hydrogen electrode) redox potential for the Ca^{2+}/Ca couple [13,19], to be compared to the -3.04 V vs SHE of the lithium metal electrode. In comparison to other elements under study for battery applications, calcium is the multivalent metal with the most negative redox potential (Figure 1a) and an ionic radius very similar to Na^+ (Figure 1b), a cation easily intercalated/deintercalated in/from a variety of materials [11].

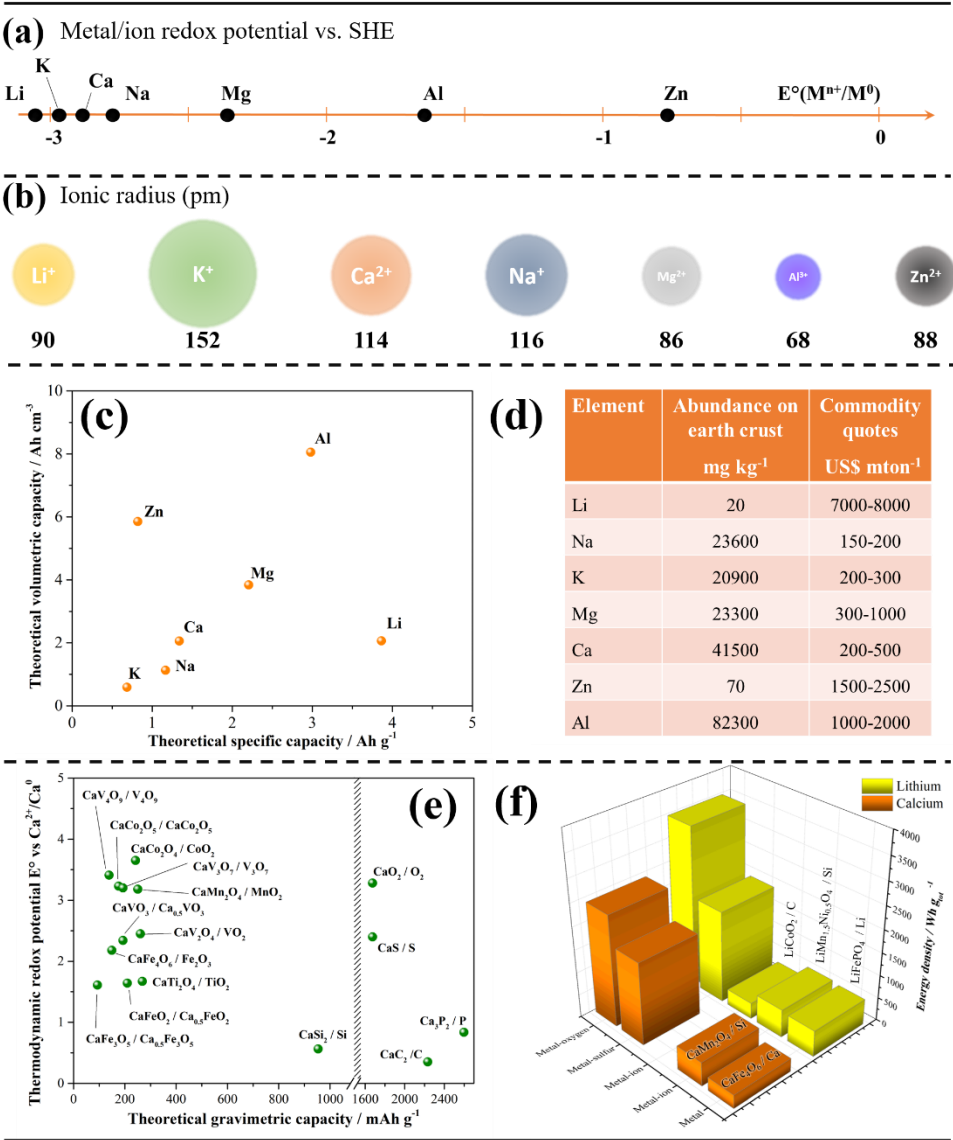


Figure 1. (a) Metal/ion redox potential vs SHE (standard hydrogen electrode), (b) mean size of the ionic species (Shannon ionic radius for 6-fold coordinated cations) [20,21], (c) theoretical

capacities of metal electrodes in electrochemical cells and (d) abundance on earth-crust and mean commodity costs of mono- and multi-valent atomic species used in beyond-lithium batteries. (e) Combines theoretical evaluations of the thermodynamic redox potential and specific capacities for several redox couples involving Ca^{2+} ions; (f) Estimates of the theoretical energy densities for calcium-based batteries compared to lithium-based analogues. The estimates of the standard redox potentials of the various assumed couples have been obtained by the available literature thermodynamic Gibbs energy of formations or semi-empirical evaluations [22–26]; theoretical capacities and estimated energy densities are normalized to the sum of the masses of the active materials (i.e. positive and negative electrodes).

The theoretical properties of calcium metal electrodes, in terms of gravimetric and volumetric specific capacities (Figure 1c), overcome those of potassium, sodium (both gravimetric and volumetric) and zinc (gravimetric), and is similar to that of lithium (volumetric), thanks to the favourable combination of intermediate atomic weight and density. Compared to aluminium and magnesium, calcium has a larger ionic radius and a smaller electronegativity [20,21], thus suggesting on one hand a lower coordination binding in the liquid phase thanks to the smaller charge density, and on the other hand a less covalent bonding in solid lattices. Furthermore, it is highly abundant on Earth's crust, much more than Li, Na, K, Mg and Zn, and industrially inexpensive (Figure 1d) [27–29].

The theoretical battery performance of a variety of calcium-based electrodes can be evaluated using the formula weight and the corresponding thermodynamic properties, or approximate estimates using semi-empirical models [22–26,30]. An unavoidably partial survey carried out considering materials chemistries analogous to the lithium-case is shown in Figure 1e, where the thermodynamic redox potentials and specific capacities of various class of materials are summarized for (a) calcium-transition metal (first row) ternary oxides as well as binary calcium (b) carbide, (c) silicide, (d) peroxide, (e) sulfide and (f) phosphide. Stoichiometries have been adapted from materials

1 experimentally reported in the CD “Crystallographic Open Database” [31]. Even though calcium has
2 an atomic weight 7 times larger than lithium, the specific capacities of the oxides vary in the 100-250
3 mAhg⁻¹ range, matching the figures of lithium intercalation positive electrodes also for what concerns
4 the thermodynamic potentials. Similarly, silicon, phosphorus and carbon negative electrodes can
5 reach large theoretical capacities at relatively low redox potentials. On the other hand, calcium
6 carbide is expected to suffer great kinetic limitation/overpotentials being the crystal structures of all
7 CaC₂ polymorphs remarkably different from graphite[32–35]. Turning to alloy/conversion
8 electrodes, outstanding theoretical performance is achievable for Ca-O₂ as well as for Ca-S leading
9 to the formation of calcium peroxide and calcium sulfide.
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21 Starting from the theoretical specific capacities and redox potentials shown in Figure 1e, a
22 tentative evaluation of the relative merit of various calcium-based battery chemistries can be drawn
23 in comparison with LIB (Figure 1f). We can assume as a baseline the theoretical energy performance
24 of the LiCoO₂/C LIB (360 Wh kg⁻¹, calculated assuming a $\Delta E^\circ=3.6$ V and a specific capacity
25 normalized by the sum of both positive and negative electrode materials) [36]. Ca-ion batteries (CIB)
26 constituted by CaMn₂O₄ and Si can disclose a theoretical energy density of about 520 mWh g⁻¹,
27 overcoming the benchmark LIB (see above) and approaching the theoretical figures of the
28 LiMn_{1.5}Ni_{0.5}O₄/Si and LiFePO₄/Li formulations [36]. Both Sulphur battery chemistry, i.e. Ca-S and
29 Li-S, have a comparable theoretical performance (approximately 1800-2000 Wh kg⁻¹) that is, in both
30 cases, exceeded by the Ca-O₂ and Li-O₂ ones (~2400 and ~3500 Wh kg⁻¹, respectively).
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46 Overall, aprotic calcium-based battery chemistries can theoretically achieve performance of
47 interest, not far to those of lithium-based ones. The research in the field is still in its infancy and, as
48 far as we know, less than one hundred of specific scientific papers can be tracked on the most popular
49 scientific literature databases online.
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56 Here we review the most relevant achievements in the still young field of calcium-based
57 batteries. Our goal is to draw a comprehensive picture of the current landscape in the field and, based
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on this state-of-the-art, estimate possible performance indicators to foresee the future development of this technology.

This review is organized in sections. Besides this introduction (section 1), three separated parts summarize the most remarkable innovations reported so far in the literature: positive electrodes (section 2), calcium metal and electrolytes (section 3) and other negative electrodes (section 4). A following part (section 5) addresses technical and economic aspects for potential upscaling (section 5). The last part (section 6) is an overall forward where we discuss the expected impact of this technology and possible innovation lines.

2. Positive electrode materials

2.1 Intercalation chemistry

Early attempts to study calcium ion intercalation in transition metal disulfides and oxides for Ca-based rechargeable batteries dates back to the 1960s [17,37]. Since then, however, such chemistry did not receive considerable attention, due to the lack of appropriate electrolytes, until Ponrouch et. al reported the successful Ca plating/stripping using conventional Li-ion organic solvents in 2016 [38]. Such result opened the door to the serious exploration of cathode materials [39–41]. However, being the field in its infancy, the number of reports on positive electrode materials in the literature is still limited [42,43].

Different types of materials are being studied with various degrees of success, namely, layered oxides, spinel, perovskites, carbon-based materials, metal chalcogenides, phosphates and nitrides [10]. Besides, conversion-type materials are a promising solution for the development of calcium electrochemical energy storage technologies. Designing cathode materials proved to be challenging, as Ceder and coworkers reported in their study of ion mobility (Li^+ , Mg^{2+} , Zn^{2+} , Ca^{2+} , and Al^{3+}) in spinel Mn_2O_4 , olivine FePO_4 , layered NiO_2 , and orthorhombic $\delta\text{-V}_2\text{O}_5$ [14]. A summary of the eligible electrode materials for Ca batteries with their corresponding electrolytes is reported in Table 1. The

table includes both theoretical and experimental studied materials. The cathodes without the paired electrolyte have been studied only from a theoretical point of view.

Class	Phase/compound	Electrolyte	References
Oxide	V ₂ O ₅ /PC	0.4 M Ca(ClO ₄) ₂ , PC	[44]
	α -V ₂ O ₅	0.45M Ca(BF ₄) ₂ 0.3M Ca(ClO ₄) ₂ Ca(TFSI) ₂ , EC:PC (1:1 v) 0.3M Ca(ClO ₄) ₂ , ACN	[45]
	V ₂ O ₅ ·0.63 H ₂ O	1 M Ca(NO ₃) ₂ , H ₂ O	[46]
	CaV ₆ O ₁₆ ·7H ₂ O	4.5 M Ca(NO ₃) ₂ ·4H ₂ O + Ca(OH) ₂ , pH=10	[47]
	α -MoO ₃	0.5 M Ca(TFSI) ₂ , AN	[48]
	α -MoO ₃	0.5 M Ca(TFSI) ₂ , DME	[49]
Perovskite	CaMO ₃ (M = Mo, Cr, Mn, Fe, Co, and Ni)	0.4 M Ca(BF ₄) ₂ in EC: PC	[50]
	Oxygen-deficient CaMnO ₃		[51]
Spinel	Mn ₂ O ₄		[16]
Post-spinel	CaMn ₂ O ₄ (Marokite)	0.4M solution of Ca(BF ₄) ₂ , EC:PC (1:1 v)	[52]
	Ca ₂ Mn ₂ O ₅ / CaMn ₄ O ₈		[51]
Oxide	1D - Ca ₃ Co ₂ O ₆ (Ca _{1.16} CoO ₃)	0.45 M Ca(BF ₄) ₂ , EC/PC (1:1 v)	[53]
	1D - Ca ₃ Co ₂ O ₆		[54]
	2D – Ca ₃ Co ₄ O ₉ (Misfit compound)		[54]
	3D – Ca ₂ Co ₂ O ₅ (Brownmillerite)		[54]
	CaCo ₂ O ₄ (CaFe ₂ O ₄ -type)	1M CaCl ₂ , H ₂ O 1M Ca(ClO ₄) ₂ ·4H ₂ O, AN	[55]
	Ca ₃ Co ₂ O ₆ , CaCo ₂ O ₄ , [Ca ₂ CoO ₃][CoO ₂] _{1.62}	Ca(TFSI) ₂ EC:PC (1:1 v)	[56]
	Ca ₂ Fe ₂ O ₅		[51]
	Ca ₄ Fe ₉ O ₁₇	0.45 M Ca(BF ₄) ₂ , EC/PC (1:1 v)	[57]
Mineral	K _{0.31} MnO ₂ 0.25H ₂ O (Birnessite)	1M Ca(NO ₃) ₂ , H ₂ O	[58]
	CaMn(CO ₃) ₂ (Kutnahorite)		[59]
	CaMnSi ₂ O ₆ (Johannsenite)		[59]
Carbon-based	Expanded Graphite (EG)	0.7 M Ca(PF ₆) ₂ , EC:DMC:/EMC (4:3:2 vol)	[60]
Prussian Blue	K ₂ BaFe(CN) ₆	1M Ca(ClO ₄) ₂ , AN 1M Ca(ClO ₄) ₂ , AN +17%DI	[61]
	K ₂ Fe-PBA	0.5 mol/L Ca(TFSI) ₂ , AN + KB (carbon additives)	[62]
Chevrel Phase	Ca _x Mo ₆ S ₈		[63]
Metal Chalcogenide	TiS ₂	0.45 M Ca(BF ₄) ₂ , EC:PC	[64]
	TiS ₂	0.3 M Ca(BF ₄) ₂ /Ca(TFSI) ₂ , PC	[65]
	VS ₄ /rGO	0.25 M Ca[B(hfip) ₄] ₂ , DME	[15]
Nitride	CaTaN ₂	0.45 M Ca(BF ₄) ₂ , EC:PC (1:1 vol)	[66]
Phosphate	Na ₂ FePO ₄ F	0.2 M Ca(PF ₆) ₂ , EC:PC (3:7 vol)	[67]
	VOPO ₄ 2H ₂ O	0.8 M Ca(TFSI) ₂ , EC:DMC:PC:EMC (2:3:2:3 vol)	[68]
Sulfur	CNTs/S	0.25M Ca(CF ₃ SO ₃) ₂ , TEGDME ≈ 0.2/0.35 M Ca(CF ₃ SO ₃) ₂ + 0.5M LiCF ₃ SO ₃ , TEGDME	[69]
Oxygen	O ₂	ZrO ₂ stabilised (Molten Salt)	[70]
	O ₂	1 M LiTFA (CF ₃ SO ₃ Li), TEGDME 1M Ca(TFA) ₂ , TEGDME	[71]
	O ₂	DMSO with 0.4 M Ca(ClO ₄) ₂ saturated with a mixture of 80% Ar and 20% O ₂	[30]

Table 1. Summary of Ca-based battery positive electrode materials reviewed in this work.

One of the earliest reports on using metal oxides in 2005 was provided by Bervas et al., who synthesised a nanocomposite 2D aerogel of nanostructured V_2O_5 and PC (propylene carbonate) as intercalation material for Ca^{2+} ions [44]. The water in hydrated V_2O_5 is replaced by propylene carbonate (PC) molecules to maintain interlayer spacing for facile intercalation of Ca^{2+} ions ensuring a very high electrolyte–cathode contact area. The nanocomposite aerogel displayed a specific capacity of 270 mAh g⁻¹ at 7.58 mA g⁻¹ and an average voltage of ca. 3.2 V vs. Ca^{2+}/Ca and 350 mAh g⁻¹. Several years later, Verrelli et al. reported α - V_2O_5 as intercalation material for Ca batteries as an especially intriguing case. They proved that intercalation of Ca^{2+} in orthorhombic α - V_2O_5 occurs only very partially [45]. However, Chae et al. [46] demonstrated the practical use of double-sheet vanadium oxide $V_2O_5 \cdot 0.63 H_2O$ synthesized via the electrochemical oxidation process on a graphite foil substrate. The material exhibited a reversible capacity of 204 mAh g⁻¹ at 0.1 C rate in an aqueous electrolyte, with an average discharge voltage of 2.76 V vs. Ca^{2+}/Ca , and capacity retention of 86% after 350 cycles. A different approach to explore the use of V_2O_5 in aqueous electrolyte was reported by Simon et al. [47]. They successfully synthesised 1D $CaV_6O_{16} \cdot 7H_2O$ nanomaterial obtained via an ultra-fast (few minutes) molten-salt method (Figure 2a). The low-cost and easy method reflects what Ca batteries are aimed for. The 1D $CaV_6O_{16.7}H_2O$ nanomaterials resulted in a high capacity of 205 mAh g⁻¹ at 0.3 C discharge rate, with 97% capacity retention after 200 cycles. Surprisingly, that material performed exceptionally at high rates (12 C) with a discharge capacity of 117 mAh g⁻¹. Such performance is a consequence of the favourable 1D structure and nanoscale morphology, which assist the Ca^{2+} ion mobility.

A layered orthorhombic MoO_3 (α - MoO_3) has been recently demonstrated as a cathode material for calcium-ion batteries in a Ca-based organic electrolyte (0.5 mol/L $Ca(TFSI)_2$ in acetonitrile (AN) [48]. α - MoO_3 with graphitized carbon black (GCB) showed a relatively high reversible capacity of approximately 120 mAh g⁻¹ per one-electron reaction in comparison with the theoretical value of 186 mAh g⁻¹. The intercalation mechanism was studied by Cabello et al. in

1 Ca(TFSI)₂-dimethoxyethane (DME) electrolyte [49]. They demonstrated the preservation of the α -
2 MoO₃ structure and the absence of CaMoO₃ perovskite-type structure upon electrochemical
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4 intercalation of non-solvated calcium. The composition Ca_xMoO₃ should be limited to $x \sim 0.3$ to
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6 achieve reversible electrochemical cycling. Furthermore, Arroyo-De Dompablo et al. [50] identified
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8 CaMoO₃, via DFT calculations, as the most promising perovskite compound, considering the cubic
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10 and orthorhombic perovskite structures for Ca_xMO₃ ($x = 0, 0.25, 0.5, 0.75$ and 1 , $M = \text{Mo, Cr, Mn,}$
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12 Fe, Co, and Ni). Although they successfully synthesised CaMoO₃, many electrochemical cycling
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14 attempts using different conditions (i.e. C rate and temperatures) failed to detect any Ca²⁺ de-insertion.
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19 Another example of metal oxide, the spinel Mn₂O₄, was investigated as electrode material for
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21 several multivalent battery systems. Persson et al. [16] estimated the intercalation ion mobility of
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23 Mg²⁺ and Ca²⁺ in the Mn₂O₄ spinel phase, confirming it as a promising host lattice for Mg and Ca-
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25 based rechargeable batteries. Arroyo-De Dompablo et al. [52] reported a joint DFT computation and
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27 experimental study on three polymorphs of CaMn₂O₄ as a potential cathode material for Ca-ion
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29 batteries. They observed higher Ca²⁺ ions mobility in the spinel-like phase compared to the other two
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31 post-spinel polymorphs. This is due to the large polyhedral faces of the spinel-like phase, which
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33 results in a migration barrier of 0.5 eV, hence easier Ca²⁺ mobility. On the other hand, the post-spinel
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35 polymorphs exhibit small polyhedral faces with strong coordination sites resulting in migration
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37 barrier above 1 eV and a remarkable hindrance in the Ca²⁺ extraction. Besides the theoretical study,
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39 the same group synthesised one of the post-spinel phases, a microcrystalline CaMn₂O₄ marokite
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41 phase. MnO₂ and CaCO₃ were mixed, grounded, and reduced in pellet and the synthesis was carried
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43 out through a solid-state route at 1200°C for 72h. However, as reported above, the synthesised post-
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45 spinel CaMn₂O₄ phase did not show any electrochemical activity due to high migration barrier
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47 towards Ca²⁺ ions.
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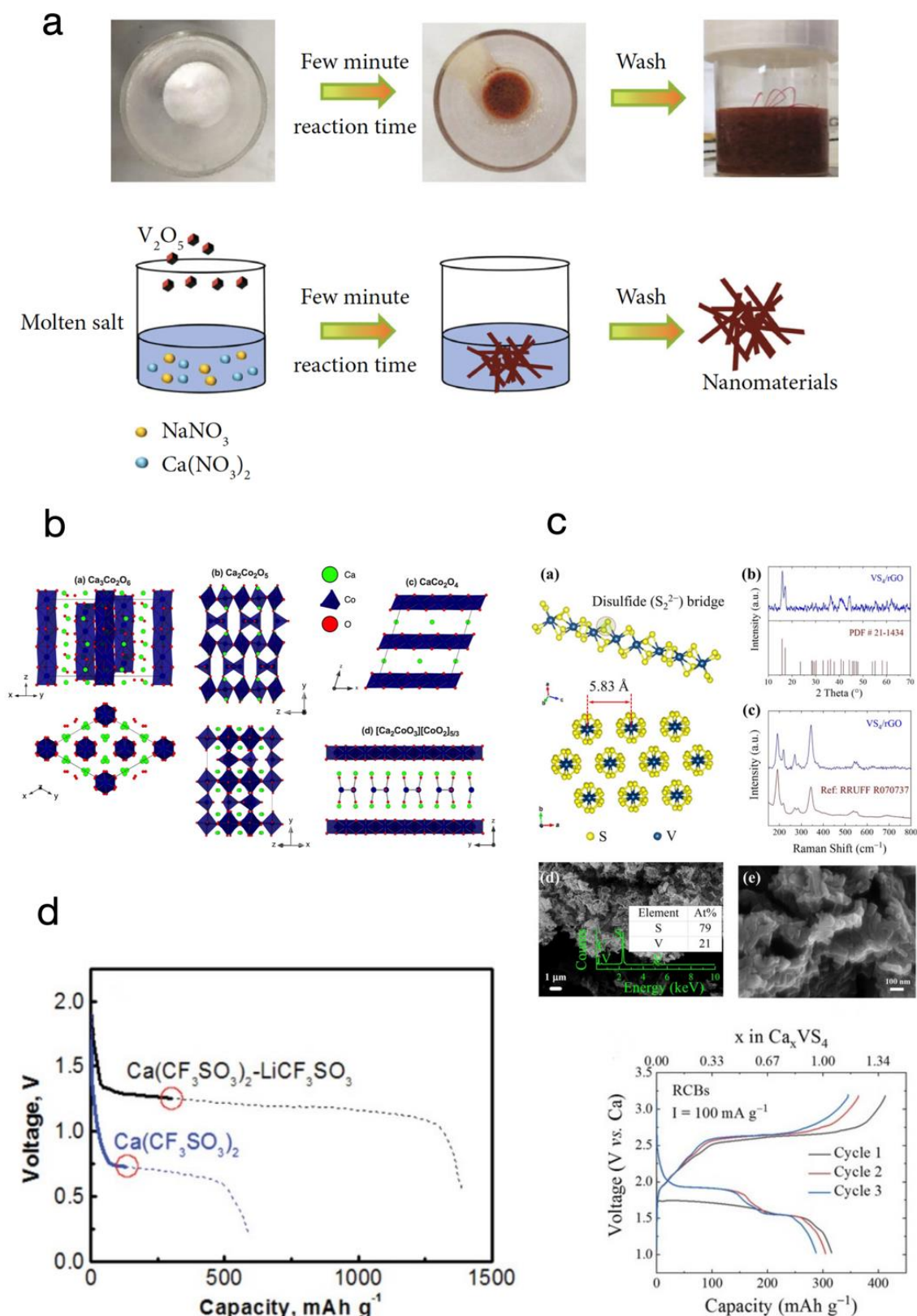


Figure 2. a) Representation scheme of the molten salt method synthesis process. The 1D $\text{CaV}_6\text{O}_{16.7}\text{H}_2\text{O}$ nanomaterial is obtained via ultra-fast molten salt method for aqueous Ca-ion

batteries. Adapted and reprinted with permission Taberna [47]; b) Ball-and-stick images of considered calcium cobalt oxides materials. Adapted and reprinted with permission [56]; c) Morphology and structural characterizations of VS₄/rGO (sub-panels a-e) and Charge–discharge profiles of VS₄/rGO in the first three cycles at 100 mA g⁻¹ in the Ca cells. Adapted and reprinted with permission [15]; d) Illustration of discharging a Ca | Ca(CF₃SO₃)₂ | S/C cell and a Ca | Ca(CF₃SO₃)₂-LiCF₃SO₃ | S/C cell to specific cathode capacities of, respectively, 125 and 290 mAh g⁻¹. Adapted and reprint with permission [69].

Calcium cobaltite represents a class of oxide materials that were investigated in several studies. In particular, Ca₃Co₂O₆ has attracted the attention as possible Ca-ion electrode due to its 1D crystal structure, which may facilitate cation migration along with the inter-chain spaces. It belongs to the family of compounds with general formula A_{1+x}(A'_xB_{1-x})O₃, with A being an alkaline earth element, A' and B the transition metals (herein, A=Ca, x=0.5 and A' and B corresponding to Co). Its crystal structure exhibits columns of BO₆ polyhedra (octahedral and trigonal prisms) running along the c direction [72,73]. Palacin et al [53] theoretically and experimentally investigated the compound for the electrochemical insertion of Ca²⁺ ions. The microcrystals, prepared by Pechini method, successfully allowed for the extraction of Ca²⁺ ions through a two-phase mechanism with the formation of the modulated structure Ca_{1.16}CoO₃, using as electrolyte a solution of 0.45 M Ca(BF₄)₂ dissolved in a 1:1 volume mixture of ethylene carbonate (EC) and propylene carbonate (PC). However, the reversibility of the electrochemical process was apparently.

Calcium cobaltites have been also studied by Torres et al [54] that tackled the DFT analysis of three phases with distinct Co-O dimensionality. 3D-Ca₂Co₂O₅ (brownmillerite type structure), 2D-Ca₃Co₄O₉ (a misfit compound) and 1D-Ca₃Co₂O₆ (K₄CdC₁₆ structural type). For all the materials, the Co⁴⁺/Co³⁺ redox couple works in the 3–4 V, which is compatible with the known electrolytes. They found out a low volume variation associate with the Ca-ions insertion (less than 8%) and an energy barrier for Ca²⁺ migration of 1.3 eV for the 3D, and 0.9 eV for both the 2D and 1D oxides. Different

1 cobalt oxides were also explored by Cabello et al. [55] that tested CaCo_2O_4 in a full cell configuration
2 using V_2O_5 as counter electrode, instead than Ca metal, and an acetonitrile (AN) based electrolyte.
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4 The performance of the material was poor with a discharge capacity below 100 mAh g^{-1} and limited
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6 reversibility. Another interesting combined work, theoretical and experimental, concerning the same
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8 cobaltite family, was reported by Zapol et al. [56]: their screening of different Ca cobaltite materials
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10 (Figure 2b) using density functional theory calculations, was validated by synthesis and
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12 electrochemical measurements.
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17 A less explored class of cathode compounds for Ca batteries is that of Fe-based oxides. Only
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19 computational data of the perovskite CaFeO_3 and the related brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$ compounds
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21 have been reported [50,51]. Unfortunately, Ca-perovskites are not competitive materials due to
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23 hindered Ca mobility (energy barrier of 2 eV). In the brownmillerite structure, instead, the presence
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25 of oxygen vacancies with respect to perovskite creates a new pathway with much lower energy barrier
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27 (1 eV). Black et al. [57] reported DFT calculations of several Fe-based oxides with general
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29 stoichiometry $\text{CaFe}_{2+n}\text{O}_{4+n}$ and the relative synthesis, characterization and electrochemistry of two of
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31 those compounds, $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_4\text{Fe}_9\text{O}_{17}$. $\text{Ca}_4\text{Fe}_9\text{O}_{17}$ showed the lowest cation migration energy
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33 barrier for an oxide (0.72 eV) but with a calcium deintercalation voltage of 4.16 V (for full Ca de-
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35 insertion), which is beyond the stability range of current Ca electrolytes.
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41 Prussian blue analogues (PBA) have been also explored as potential cathode for Ca^{2+}
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43 intercalation batteries. The general formula of PBA shows $\text{A}_x\text{MM}'(\text{CN})_6 \cdot n\text{H}_2\text{O}$, where the A_x in the
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45 A sites is a guest ion or molecule such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} or H_2O , M and M' are transition metals
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47 and the ambidentate CN- ligand is bridging the two metals M and M' in a corner-shared octahedral
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49 configuration [74]. Hexacyanoferrates have a cubic lattice with relatively large interstitial spacing
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51 that, when enlarged by the replacement of one of the two transition metals with the large redox-
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53 inactive Ba^{2+} , can easily accommodate Ca^{2+} . Padigi et al. [61] synthesized potassium barium
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55 hexacyanoferrate ($\text{K}_2\text{BaFe}(\text{CN})_6$) by employing a room temperature wet chemical precipitation
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57 technique. At that time, the study of the water content in the electrolyte was really interesting but the
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cathode was able to deliver only 30 cycles with a reversible specific capacity of 55.8 mAh g⁻¹, which is about 80% of the estimated theoretical capacity of 70 mAh g⁻¹ for K₂BaFe(CN)₆.

Even though barium, in the form of stable compounds such as potassium barium hexacyanoferrate, is less toxic than barium dust, alternative approaches replacing barium with more benign, larger radii and lighter elements, were explored. The PBA K_xMFe(CN)₆ · nH₂O (M = Ni, Mn and Co) were synthesized by Tojo et al. [62] and presented as potential new cathode materials to reversibly insert/extract Ca²⁺ using a Ca-based organic electrolyte. KNiFe-PBA with carbon additives (KB) in 0.5 mol L⁻¹ Ca(TFSI)₂ in AN showed reversible capacities of 40 mAh g⁻¹ even after 12 cycles without destruction of the open framework structure of KNiFe-PBA.

Molybdenum chalcogenides Mo₆X₈ (X = S, Se, Te), known as Chevrel phases, constitute an outstanding family of materials presenting numerous and spectacular properties. Smeu et al. [63] reported interesting computational analyses about Chevrel phases for Ca batteries. However, nothing has been yet demonstrated in their practical use for those batteries [75]. Another “classical” dichalcogenide was explored by Tchitchekova et al. [64] that compared the electrochemical intercalation of Ca²⁺ and Mg²⁺ in layered TiS₂ using alkyl carbonate-based electrolytes. And for the first time, reversible electrochemical Ca²⁺ insertion was proved in this compound using both X-ray diffraction and differential absorption X-ray tomography at the Ca L₂-edge. The study opens some positive expectations for the application of TiS₂ in calcium batteries. Verrelli et al. [65] moved a step forward in this direction by experimentally studying the reversible electrochemical insertion of calcium in TiS₂ in Ca(BF₄)₂ and Ca(TFSI)₂ in PC at different temperatures. They proved that reversible electrochemical insertion of calcium in TiS₂ occurs in Ca(TFSI)₂ in PC electrolyte at 100 °C, 60 °C and even room temperature via the formation of solvent co-intercalated phases.

Furthermore, Li et al. [15] reported VS₄/rGO composite as an insertion cathode based on anion based redox reactions for Ca batteries and a new borate electrolyte based on calcium tetrakis(hexafluoroisopropoxy) borate (Ca[B(hfip)₄]₂). VS₄, synthesized hydrothermally in the presence of graphene oxide (GO), could promote the conversion of VS₂ to VS₄ efficiently and the

1 reduction of GO to rGO (final rGO content 8%wt). VS₄/rGO cathode provided a capacity of around
2 300 mAh g⁻¹ in the initial cycles (accommodation of around 1 Ca²⁺ ion per VS₄ formula unit). The
3
4 combination of VS₄/rGO with the borate-based electrolyte results in a promising system for new
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6 rechargeable Ca-batteries (Figure 2c). Further exploring non-oxidic compounds, Verrelli et al. [66]
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8 turned their attention to ternary A_xTa_yN_z (A= Mg and Ca) tantalum nitrides prepared via direct solid-
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10 state reaction from the binary nitrides Ta₃N₅ and A₃N₂. However, de-intercalation in this compound
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12 was only achieved electrochemically at 100 °C. Results of DFT calculations seem to indicate that
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14 those reaction mechanisms for CaTa₃N₅ oxidation, additional and/or alternative to deintercalation, are
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16 taking place, which they related to the loss of crystallinity observed upon oxidation and the
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18 irreversibility of the process.
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24 Lately, phosphate compounds [67] have been proposed as cathode materials for Ca batteries.
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26 Wang et al. [68] proposed VOPO₄·2H₂O due to its higher working potential (2.8 V vs. Ca²⁺/Ca)
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28 respect V₂O₅. VOPO₄·2H₂O exhibits a reversible capacity of 100.6 mAh g⁻¹ with the average working
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30 potential of, excellent cycling stability (200 cycles) and good rate performance (42.7 mAh g⁻¹ at 200
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32 mA g⁻¹).
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36 Composite electrodes and active materials based on carbon are becoming popular in
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38 multivalent systems. A Ca-ion cell composed by MCMB (Mesocarbon Microbeads) anode combined
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40 with expanded graphite (EG) cathode employing 0.7 M Ca(PF₆)₂ in ethylene carbonate/dimethyl
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42 carbonate/ethyl methyl carbonate (EC/DMC/EMC, 4:3:2 v/v/v) electrolyte has been chosen by Wu
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44 et al [60] for their Ca-DCB (Calcium-based Double Carbon Battery). As the main aim, the paper
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46 focused on the anode process of the Ca²⁺ intercalation in the graphite electrode. However, the anion
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48 intercalation process at the cathode is the heart of the discussion and fewer details are presented for
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50 the anodic process.
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57 2.2 Conversion chemistry 58 59 60 61 62 63 64 65

Employing a nanostructured CNTs-sulfur cathode, and a Li⁺-ion-mediated calcium-based electrolyte, Yu et al. reported the first reversible Ca-S battery and high utilization of the sulfur cathode [69]. The cell can initially deliver $\approx 800 \text{ mA h g}^{-1}$ and, twenty cycles later, $\approx 300 \text{ mA h g}^{-1}$ demonstrating that the employment of Li⁺-ion mediated Ca electrolyte enables the reversibility of Ca-S chemistry.

Poor attention is still being given to Ca-O₂ batteries. Few reports have shown the use of oxygen as cathode material with calcium alloys as anode (Ca-Si [70], Ca-Li [71]). Reinsberg et al. [30] studied the oxygen reduction and evolution reaction in Ca²⁺-containing dimethyl sulfoxide at different electrode materials paving the way to a possible use of calcium metal for Ca-O₂ batteries (Figure 2d).

3. Calcium metal negative electrodes and electrolytes

The low redox potential of Ca metal (-2.87 V vs. SHE), as well as its promising gravimetric and especially volumetric specific capacities (1337 mAh g⁻¹ and 2073 mAh ml⁻¹, respectively) [8] compared to the other alkali and alkaline-earth metals, provide a strong incentive for the development of rechargeable batteries employing Ca metal anode [76]. However, having one of the lowest redox potentials is a gift and a curse at the same time, since it implies a strong tendency towards the reduction of the electrolyte components. This means that either salt, solvent or even both will be reduced at the surface of the metal anode, forming different passive films of variable nature. While this is also the case with Li metal anodes, the small size of Li⁺ (90 pm) and its monovalent charge enable a relatively facile diffusion of the Li⁺ ions through the passive film. On the other hand, Ca²⁺ has twice the charge and is significantly larger (114 pm) [21]. Low redox potential differentiates Ca from Mg metal, which is similarly bivalent but has higher redox potential (-2.37 V vs. SHE), which enables passive film-free surfaces in ether-type solvents [77]. This has contributed to the fact that Mg metal deposition had been demonstrated almost a century ago [78], whereas reversible plating/stripping of Ca metal could be demonstrated only recently [38-40,79]. Ca plating/stripping was already attempted in 1980 by Staniewicz in Ca(AlCl₄)₂-SOCl₂ electrolyte [80]. Although Ca

stripping was confirmed, there was no clear evidence for plating of Ca metal. Corrosion of Ca metal anodes was an evident problem in $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$ solution and could have led to immediate corrosion of Ca deposits. Work on $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$ electrolyte was further elaborated by Meitav and Peled, who were able to indirectly confirm Ca plating on stainless steel electrode with extremely low efficiency, less than 10%, and high overpotentials [81]. The main issue of this electrolyte was CaCl_2 passive layer, which is mainly anion conductor, but poor conductor of Ca^{2+} cations [82,83].

The electrochemical behaviour of Ca electrodes was later thoroughly studied in wide range of solvents by Aurbach et al. Namely, acetonitrile (ACN), tetrahydrofuran (THF), γ -butyrolactone (GBL) and propylene carbonate (PC) were tested together with different calcium ($\text{Ca}(\text{ClO}_4)_2$, $\text{Ca}(\text{BF}_4)_2$) and calcium-free salts (LiAsF_6 , TBAClO_4 , TBABF_4) (TBA is tetrabutylammonium) [82]. The behaviour of the Ca electrodes in all electrolytes was found to be controlled by the formation of relatively thick passivating surface films. Contrary to Li plating, Ca plating on both Ca and noble electrodes was impossible even at overpotentials of 2 V due to the extremely poor Ca^{2+} mobility through the surface films. Presence of impurities such as O_2 and water influenced the formation of such films, which consisted mostly of decomposed electrolyte components, CaCO_3 and $\text{Ca}(\text{OH})_2$. The influence of solvents on the conductivity of the different electrolytes was also demonstrated, the solutions prepared in ACN having by far the highest conductivity, followed by GBL and PC. THF was found to produce the lowest conductivity, where the low solubility of the $\text{Ca}(\text{ClO}_4)_2$ salt was also an evident problem. This fundamental work has strongly impacted the research interest in Ca metal electrodes, which remained relatively weak for a long period of time.

More than two decades later, in 2015 the seminal work of Ponrouch et al. demonstrated that Ca could be plated from solutions of $\text{Ca}(\text{BF}_4)_2$ in a mixture of ethylene carbonate (EC):PC at 75 and 100 °C [38]. Interestingly, the authors observed Ca deposition also in $\text{Ca}(\text{ClO}_4)_2$ electrolyte although with significantly lower Coulombic efficiency. The researchers hypothesized that the difference might be related to the surface layer composition and its influence on Ca^{2+} migration. The surface film on Ca metal using in $\text{Ca}(\text{BF}_4)_2$ in EC:PC was found to consist mainly of CaF_2 , but also to contain $\text{Ca}(\text{OH})_2$,

1 C=O, C–O and carbonate functionalities. The infrared (IR) spectrum of the surface film did not
2 change after Ca stripping, demonstrating a good stability of the film. The optimum conductivity and
3 efficiency of Ca plating/stripping was found with a concentration of 0.45 M $\text{Ca}(\text{BF}_4)_2$ with a
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Coulombic efficiency around 80% and an oxidative stability up to 4.0 V.

Successful Ca plating/stripping at room temperature was achieved in 1.5 M $\text{Ca}(\text{BH}_4)_2$ in tetrahydrofuran (THF) [39]. The corresponding passivation layer consisted of CaH_2 , which protected the Ca metal from further reaction. It is interesting to note that such Ca deposition from $\text{Ca}(\text{BH}_4)_2$ was obtained only on precious metal surfaces (Au or Pt), which may be necessary for the activation of CaH_2 formation. The average Coulombic efficiency was between 94-96 % and such electrolyte enabled oxidative stability up to 3 V. Another possible limitation of this electrolyte is the nucleophilic nature of BH_4^- anion, which could prevent practical application with electrophilic cathodes (e.g., sulfur, organic compounds, etc.) Further improvement of $\text{Ca}(\text{BH}_4)_2$ electrolyte was achieved by adding LiBH_4 to the electrolyte, which increased the Coulombic efficiency of plating/stripping up to 99.1 % [41,84]. Such improvement was achieved thanks to a reduced coordination number of Ca^{2+} cations in the first solvation shell and represents the highest Coulombic efficiency of Ca plating/stripping up to date.

In 2019 two independent studies reported the synthesis of Ca tetrakis(hexafluoroisopropoxy) borate salt ($\text{Ca}[\text{B}(\text{hfip})_4]_2$) [40,79]. Electrolyte solution of $\text{Ca}[\text{B}(\text{hfip})_4]_2$ in dimethoxyethane (DME) displayed efficiencies between 80 and 90% with an oxidative stability up to 4.5 V vs. Ca^{2+}/Ca (Figure 3). However, considering that this stability limit was evaluated using voltammetry, and that ether based electrolytes are typically cycled in Li batteries below 4 V vs. Li^+/Li , the effective thermodynamic stability limit for this electrolyte is expected to be below 4.5 V and close to the limit observed in lithium systems. High oxidative stability and non-nucleophilic character were a significant improvement over the previously published results and enabled testing of electrophilic cathodes (sulfur, organics) in 2-electrode setups with Ca metal. Nevertheless, both reports mentioned formation of CaF_2 on the metal anode, showing the relative instability of the salt anion and the need

of further improvements in order to get a stable electrochemical performance. One of the two studies mentioned a pre-cycling procedure to decrease the overpotential and improve the reversibility [79], while the other showed further improvement of the electrochemical performance upon addition of Bu_4NCl [40]. The latter study also pointed out the formation of dendrite-like Ca deposits upon cycling, which might be a critical point and needs more attention in future research.

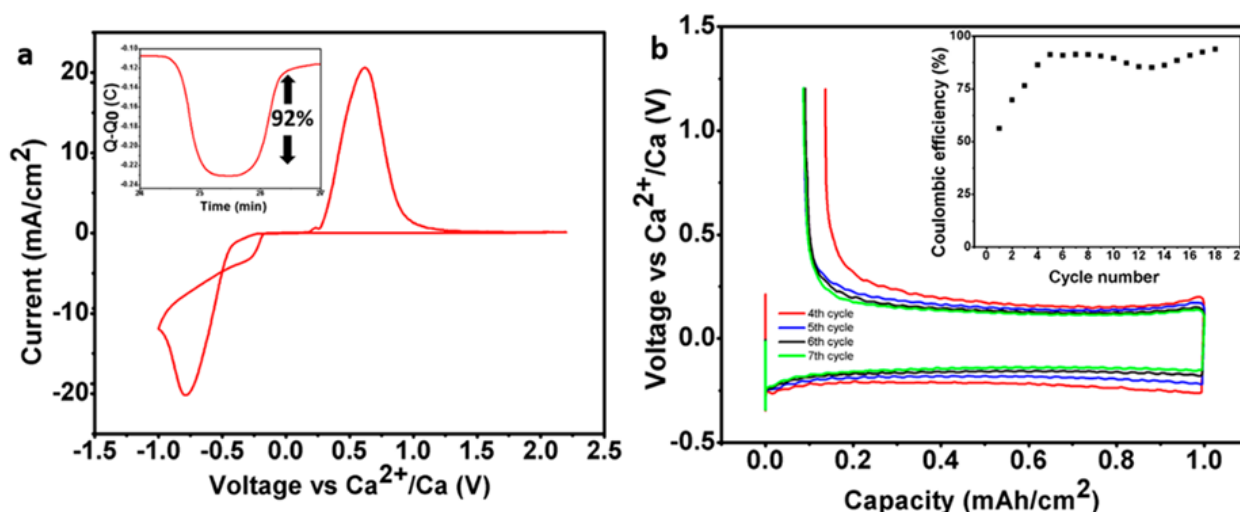


Figure 3. a) Cyclic voltammetry with 0.5 M $\text{Ca}(\text{b}(\text{hfip})_4)_2$ in DME on Au working electrode with Ca reference and counter electrode. Inset is showing the charge passed during plating and stripping process. (4th cycle is shown). b) Galvanostatic cycling with a current density of 0.2 mA cm^{-2} till 1 mAh cm^{-2} , with the inset displaying Coulombic efficiency of cycling. Reprinted with permission from reference [40] from American Chemical Society. Copyright 2019 American Chemical Society.

The influence of different ethereal solvents (THF, DME, diglyme (DGM)) on the performance of $\text{Ca}[\text{B}(\text{hfip})_4]_2$ -based electrolyte was also recently tested [41,85]. The best performance was found using DGM as the solvent, which also seemed to produce Ca deposit with a smoother morphology. In spite of still evident difficulties, recent advances have brought a tremendous progress in the development of Ca electrolytes: in fact, it is now possible to plate and strip Ca at room temperature with efficiencies above 90 % (Table 2), an achievement that seemed almost impossible only a few

years ago. However, the use of Ca metal anode in practical batteries will require Ca plating/stripping with efficiencies well above 99%, possibly close to 99.99%. The realization of such an ambitious goal will require a thorough understanding of the passive film formation, maybe via the realization of tailored surface films, and/or an improvement of the electrolyte salt with higher stability at low potentials.

Electrolyte	Coulombic efficiency	Working electrode	Year
Ca(AlCl ₄) ₂ -SOCl ₂	Only stripping	Ni	1980 [86]
Ca(AlCl ₄) ₂ -SOCl ₂	<10%, indirect evidence	Stainless steel	1982 [87]
Ca(BF ₄) ₂ EC:PC	85%, above 75 °C	Stainless steel	2016 [38]
Ca(BH ₄) ₂ THF	95%	Au	2018 [39]
Ca(B(hfip) ₄) ₂ DME	80%	Pt	2019 [79]
Ca(B(hfip) ₄) ₂ Bu ₄ NCl DME	90%	Au	2019 [40]
Ca(BH ₄) ₂ LiBH ₄ THF	99%	Au	2020 [84]

Table 2. Different electrolytes used for Ca stripping/plating.

In the general “rocking-chair” battery system, the electrolyte should enable a fast and efficient Ca²⁺ transport through both the bulk electrolyte and the interfaces/interphases it creates with the electrodes. The acid character of Ca²⁺ is not as hard as that of the two similar multivalent cations Mg²⁺ and Al³⁺, which means that its de-solvation is simpler and does not require special electrolyte formulations as the other two. This makes in principle the preparation of Ca electrolytes simpler and more similar to Li and Na electrolytes. However, given that Ca batteries have not been in the spotlight until very recently, only a very small number of Ca salts are available commercially. Most of the published work on electrolytes was carried out using one of the following salts: Ca(ClO₄)₂, Ca(BF₄)₂, Ca(NO₃)₂, Ca(BH₄)₂ or calcium bis (trifluoromethanesulfonyl)imide (Ca(TFSI)₂). The synthesis of

1 Ca(PF₆)₂ salt, which is the Ca analogue of LiPF₆, commonly used in standard Li-ion electrolytes, was
2 reported through metathesis reaction from AgPF₆ [85]. More recently, the direct synthesis through
3
4 nitrosonium oxidation of Ca metal was also reported [88]. Interestingly, although certain similarities
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6 between behaviour of Ca(BF₄)₂ and Ca(PF)₆ based electrolytes could be expected, to the best of our
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8 knowledge no study has so far reported on the electrochemical behaviour of Ca metal electrodes in
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10 Ca(PF₆)₂-based electrolytes. The latter salt was however used in studies of Ca-ion batteries with alloy
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12 anodes (vide infra).
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17 Some of the recent research has also concerned the development of aqueous Ca cells, and
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19 aqueous electrolytes based on Ca(NO₃)₂ seem to be the dominant system [89]. There is no systematic
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21 survey in the literature that reveals a clear reason for the choice of this salt, leading one to believe
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23 that its use is simply connected with its historical practice, its wide availability and relatively low cost
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26 [19].
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30 In summary, only recently some interesting results could be obtained in this field, reviving the
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32 interest in Ca-based batteries. This very recent renew has, therefore, for both aqueous and non-
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34 aqueous electrolytes, a lack of systematic studies dealing with the physico-chemical properties of the
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36 Ca salts. This is especially problematic, because electrolytes which demonstrate reversible Ca
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38 plating/stripping have utilized quite a wide range of salt concentrations, and very limited attention
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40 has been devoted until now to the effect of concentration on conductivity and electrochemical
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42 reversibility [38,40]. Some information in this sense, however, can be inferred from studies that
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44 reported only the stripping of calcium. For instance, in the early work by Aurbach et al different salts
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46 were compared in relative wide range of solvents belonging to different classes [90]. The effect of
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48 solvents on the stripping of Ca was also studied using an electrolyte based on Ca(ClO₄)₂, and the best
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50 performance, measured as the overpotential for the insertion of Ca²⁺ in a V₂O₅ host, was found using
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52 ACN as the solvent [90]. Interesting work was performed also by comparison of different monovalent
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54 (Li, Na) and bivalent (Mg, Ca) salts in the mixture of EC:PC [42]. At low concentration (0.1 M),
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56 perchlorate salts displayed conductivities that were directly connected with number of charge carriers
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and their respective charges. At higher concentration (1.0 M), the conductivities did not increase proportionally to the concentration, pointing to the lower amount of available charge carriers. This decrease, however, was less pronounced for the Ca salt than for the Mg one. A comparative study of salts based on the TFSI anion showed less ion pair formation, which is probably connected with a less localised charge on the TFSI anion. A recent comprehensive study evaluated numerous Ca electrolytes with different salt and solvents at different concentrations [91]. The study confirmed that the calcium salt solubility is a major issue, stating the need for development of new highly dissociative salts. Adequate solubility was found with combination of $\text{Ca}(\text{TFSI})_2$, $\text{Ca}(\text{BF}_4)_2$, calcium trifluoromethanesulfonate ($\text{Ca}(\text{Tf})_2$) and high-permittivity solvents (EC, PC, GBL and N,N-dimethylformamide (DMF)). The degree of contact ion-pair and type of coordination was found to be influenced by both the salt concentration and solvent donor number. The concentration upon which electrolytes entered the domain of highly concentrated solutions was found already at 1.2 M. It is important to note that the choice of the solvent is expected to have an effect also on the electrochemical stability window. While the use of carbonate solvents might enable operation with 4 V cathodes, this will not be realistic in ether solvents, where the maximum voltage stability will be probably lower by about 1 V. To summarize, recent advances in Ca electrolytes have enabled reversible Ca plating/stripping at room temperature. Further work is needed to increase reversibility of Ca metal anode and extend operation voltage window towards high-voltage cathodes, a necessary requirement for high-energy density Ca batteries.

4. Other negative electrode materials

Even though the possible use of calcium metal negative electrodes remains promising, especially in the view of the very recent developments exposed above, they are still far from meeting the performance required for commercial cells, particularly concerning their low coulombic efficiency. A viable alternative to calcium metal anodes could be alternative anode materials able to electrochemically react with calcium, which would lead to the new family of Ca-ion batteries (CIB).

In spite of the certain loss in the specific capacity compared to calcium metal anodes, such an approach has a few practical advantages: i) first, the calcium compound at the negative electrode is expected to be much less sensitive to passivation than calcium metal, possibly enabling the use of more classic electrolyte formulations; ii) second, instead of dealing with thin and brittle Ca metal foils or powder, usually complicated to shape, the negative electrodes can be easily formulated through slurry casting.

Similar to the lithium and sodium counterparts, attention was first directed towards carbonaceous compounds. Besides the expected inactivity of calcium dicarbide in batteries due to the unfavourable crystal structure (see introduction above), also graphite-based anodes in CIB have been shown to be practically unmanageable at room temperature due to the very difficult intercalation of calcium to obtain CaC_6 [92]. Surprisingly, very recently it was shown that graphite can effectively work as a reversible intercalation host for Ca^{2+} , but only when the latter is co-intercalated with the dimethylacetamide (DMAc) electrolyte solvent, forming a $[\text{Ca}-(\text{DMAc})_4]\text{C}_{50}$ intercalated compound [93]. Under these conditions, the graphite electrode delivers a stable reversible capacity of 85 mAh g^{-1} over 200 cycles with negligible degradation. The intercalation mechanism, followed in situ by X-ray diffraction, occurs via a classical staging process as it can be appreciated in Figure 4, similarly to lithium or potassium intercalation in graphite.

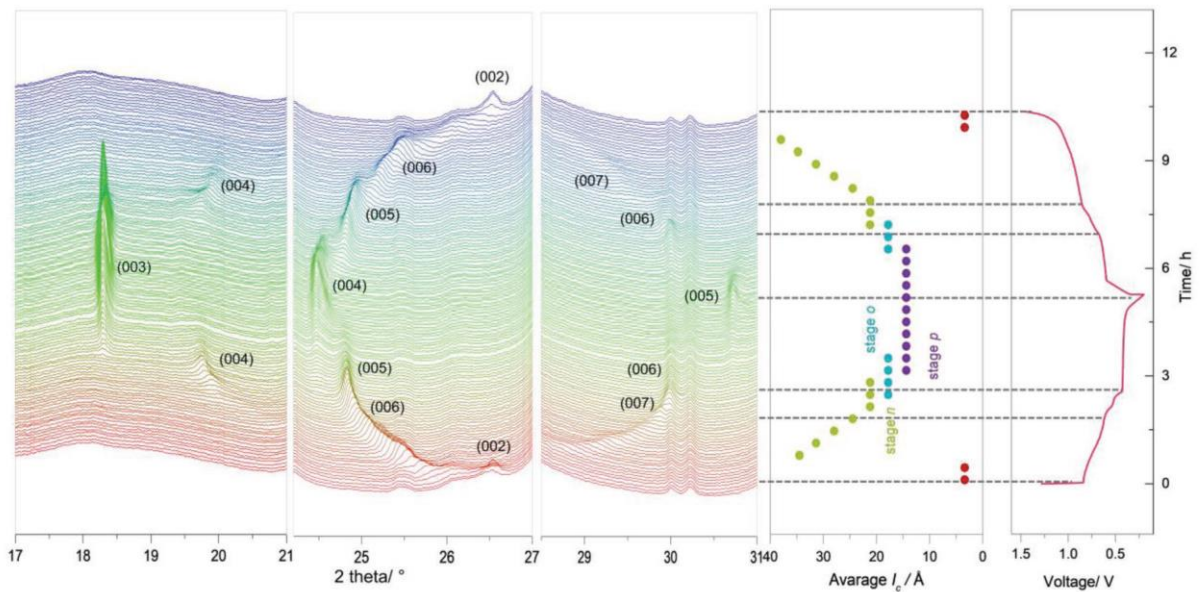


Figure 4. In situ synchrotron XRD analysis of the structural evolution of graphite during calciation and decalciation. Reprinted with permission from Ref [93].

A promising alternative to graphite is represented by alloy anodes, which in addition show very attractive theoretical specific capacities. Using a combined theoretical/experimental approach, for instance, Ponrouch et al. showed that it is in principle possible to employ silicon-based anodes [94]. The full calciation of Si would lead to the CaSi_2 intermetallic compound, with a very interesting theoretical capacity of 991 mAh g^{-1} and a volume expansion of 306%. The average electrochemical potential corresponding to the formation of CaSi_2 is 0.37 V vs Ca^{2+}/Ca as calculated by DFT, with several plateaus between 0.6 and 0.13 V corresponding to the formation of intermediate compositions. In order to show the feasibility of such a system, they proved experimentally by Potentiostatic Intermittent Titration Technique (PITT) the partial decalciation of a commercial CaSi_2 . The decalciated material could be partially re-calciated in spite of large overpotential of about 2 V, which was likely attributed to the collapse of the structure after decalciation. Such problems related to volume expansion and to the instability of the interfaces are not so different from those widely studied in the case of lithium, with an addition of the intrinsic difficulty of working with calcium.

Differently from silicon, tin showed to be a much more promising anode material for CIB. A Ca-Sn alloy anode was successfully tested recently in a full cell with a $\text{Ca}(\text{PF}_6)_2$ -based electrolyte [85]. In this case, no characterisation was made on the electrochemical reaction mechanism of Sn with Ca, the paper being mainly concentrated on the mechanism at the cathode side. Nevertheless, the capacity fade of the cell, which lost half of its initial capacity after 50 cycles, was mainly attributed to the parasite reaction at the anode side (i.e., delamination of the tin anode due to volume expansion, lack of passivation on the tin causing it to dissolve into the electrolyte, increase in the cell resistance due to surface film formation).

More recently, a high voltage ($>4.45 \text{ V}$) CIB cell also using Sn as the anode was proposed [95]. In this system, graphite was used as the positive electrode, forming reversible intercalation

1 compounds with the electrolyte anions. This led to quite low capacities slightly below 100 mAh g⁻¹,
2 but also to a remarkable cyclability (more than 300 cycles before capacity starts to fade). The Sn at
3 the negative electrode was shown to undergo calcination up to the formation of Ca₇Sn₆, without
4 reaching the expected most calcinated Ca₂Sn composition. A theoretical study by DFT of the calcination
5 of Sn confirmed that it is practically impossible to go beyond the composition Ca₇Sn₆, thus decreasing
6 the practical theoretical capacity of tin from 903 mAh g⁻¹ for Ca₂Sn to 527 mAh g⁻¹ for Ca₇Sn₆ [96].
7 In the same paper, it was possible to identify threshold voltages which govern the limits of the
8 calcination process of metals. On the other hand, it was also shown that other metalloids (Si, Sb, Ge),
9 (post-)transition metals (Al, Pb, Cu, Cd, CdCu₂, Ga, Bi, In, Tl, Hg), and noble metals (Ag, Au, Pt,
10 Pd) are potential anode candidates, opening the way to a large-scale research of the properties of these
11 elements as possible alloy anodes for CIB.
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27 A more recent approach has concerned the use of organic negative electrode materials at the
28 anode in aqueous batteries. For instance, polyaniline was used at the anode vs. a Prussian blue
29 analogue using a 2.5 M Ca(NO₃)₂ aqueous electrolyte [97]. The battery delivered a stable capacity of
30 more than 100 mAh g⁻¹ for more than 200 cycles at 150 mA g⁻¹. In this case, the negative electrode,
31 which works through the reversible insertion/deinsertion of NO₃⁻, delivered an average reversible
32 specific capacity of 114 mAh g⁻¹. Such a solution remains interesting and viable due to the low cost
33 and toxicity of the used materials.
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44 In summary, most works on CIB were performed using Sn as the negative electrode, showing
45 the practical attraction of alloy anodes. Further studies of Ca-alloy anodes are nevertheless required
46 to better evaluate their potential. Although the use of alloy anodes will reduce the cell voltage and
47 hence the cell energy density, the potential increase in cycling efficiency may yet make this an
48 attractive strategy. However, the number of studies and thus of tested anode materials remains very
49 low, and a lot of alternative systems, such as for instance MXenes or graphene, have been proposed
50 as potentially interesting anodes and will be surely the object of research work in the next years
51 [98,99].
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5. Ca battery cell upscaling feasibility, sustainability and technical aspects

With the still very recent first demonstration of reversible calcium electrodeposition in 2016 [38], research on rechargeable Ca-based batteries is in its infancy and focused on electroactive materials discovery and characterization, as summarized in the previous sections. Full cell development, component upscaling and cell prototyping is still farther ahead on the road. Additionally, the study of such novel battery chemistries requires reliable electrochemical setups and protocols to be able to translate results to full cells, since the typical Li-ion two-electrode cell setup (half-cell configuration with lithium metal as both counter and reference electrode) cannot be directly applied to calcium metal, for which plating/stripping is only viable under very specific conditions. The use of a three-electrode cell setup has thus been proposed as compulsory for these systems [19] and, although the choice of reference electrode is not trivial either, silver wires have often been used as pseudo-reference electrodes [42]. As counter electrode, activated carbon has been more extensively used [44] but electrode balancing (rarely mentioned) is difficult with this capacitive counter electrode (low capacity) in a practical cell. Overall, paralleling progress with other multivalent ion systems, particularly divalent Mg-based batteries, as well as with Na-ion batteries since the ionic sizes of Na^+ and Ca^{2+} are very similar, may lead to a faster rate of development in calcium full cells [100].

5.1 Technical challenges in Ca battery cell prototyping

The possibility of using calcium metal anodes should lead to significant gains in cell energy density, similarly to Li metal-based batteries, while being cheaper and potentially safer due to lower susceptibility to dendrite growth at practical cycling rates [10]. A reduction in safety requirements would also potentially lower the battery pack hardware needs, increasing energy density at system level, as well as reducing whole battery management system complexity. Coulombic efficiencies, reportedly only at 94-96% [39] have recently reached 99% with a $\text{Ca}(\text{BH}_4)_2$ LiBH_4 THF based electrolyte [84] but still need to be improved to a level as high as 99.99% to meet application requirements.

On manufacturing processes, Ca metal requires stringent atmosphere control during metal anode preparation and cell assembly, since traces of oxygen, water or any other contaminant reacting at the electrode surface could lower the kinetics or completely block the plating/stripping process [11]. Both calcium metal anode production and cell assembly lines would have to be encapsulated into high-purity inert atmosphere chambers, leading to significant increase in installation and operational costs for cell manufacturing. As more cost-efficient solution, developing a pre-passivated or surface protected calcium anode would allow process handling in existing dry rooms and cell assembly lines used for Li-based batteries. Another issue to tackle would be the thin anode production ($<100\text{ }\mu\text{m}$) for efficient electrode balancing: the higher material stiffness of Ca vs. “soft” Li (Young’s modulus of $\text{Li} < \text{Na} < \text{Ca} < \text{Mg} < \text{Al}$ are 4.9, 10, 20, 45 and 70 GPa, respectively [101]) would preclude applying a lamination process from ingots as for Li or Na. Other production routes need to be studied, adapted or newly developed, such as ideally cost-efficient roll-to-roll evaporation or deposition methods for high-purity thin foils or Ca powder-based slurry or ink casting onto a current collector, where lightweight and cheaper Al can be used instead of Cu, since no alloying of Ca with Al is expected.

The $\text{Ca}(\text{BF}_4)_2$ salt and mixed carbonate solvent based nonaqueous electrolytes show a large electrochemical window allowing high voltage cathode materials’ operation but require $100\text{ }^\circ\text{C}$ to attain reversibility [38]. This need of high temperature for Ca metal cycling would limit commercial application since it would increase thermal management requirements, energy consumption and operational cost, while at the same time reducing the overall energy density of the system, as well as accelerating the cell degradation leading to shorter service life. In contrast, using other electrolytes based on THF [39] calcium can be plated/stripped at room temperature but the comparatively low anodic stability ($\approx 3\text{ V}$ vs Ca^{2+}/Ca) would still limit the selection of high voltage cathode materials, resulting in lower cell energy density.

1 In terms of safety and sustainability, commercially available calcium salts are few and most
2 electrolytes have relied frequently on $\text{Ca}(\text{ClO}_4)_2$ which is difficult to obtain in anhydrous form and is
3 also explosive. While the $\text{Ca}(\text{TFSI})_2$ and $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ salts also are commercial but much less used,
4 the synthesis of $\text{Ca}(\text{PF}_6)_2$ was reported only recently [85] nevertheless with purity issues due to a very
5 high tendency of anion hydrolysis and leading to HF generation. Besides side-reactions occurring due
6 to insufficient (electro-)chemical stability, there are other intrinsic issues related to the electrolyte
7 composition, e.g., viscosity affecting both ion transport and wetting of the electrodes, ion–ion and
8 ion–solvent interactions, (de)solvation dynamics, and so on, that may also affect electrode and full
9 cell behavior [19]. Developing (near) room temperature electrolytes with anodic stability $> 4 \text{ V}$ vs
10 Ca^{2+}/Ca and easily up-scalable new salts should be pursued, including options such as Localized High
11 Concentration Electrolytes (LHCE) recently developed for Li-based batteries [102-104] that may
12 have promising applicability in multivalent systems for cation solvation [84,105].

13 In a Ca-ion cell configuration, as reported in section 4, more sustainable and safe systems could
14 be developed with aqueous electrolytes, such as 2.5M $\text{Ca}(\text{NO}_3)_2$ for a polyimide (PNDIE) anode and
15 a copper hexacyanoferrate cathode cell [89], but operating voltage and capacity (40 mAh g^{-1}) are still
16 too low for practical energy density. On the other hand, nonaqueous Ca-ion electrolytes can cause
17 current collector corrosion as described by Lipson et al. [106] for stainless steel 304. Therefore,
18 analysis of the chemical resistance of not only the current collectors but also the cell housing material
19 would be required for prototyping.

20 Similarly to Li-based systems, attractive voltages and high theoretical capacities can also be
21 possible for Ca-ion full cells using alloy based anode materials. Unfortunately, as explained above,
22 Ca-Si alloy materials suffer even greater volume changes with Ca^{2+} insertion and extraction so their
23 commercial implementation will be unlikely while similar challenges with Li-Si are yet to be solved.
24 On the other hand, by pairing Ca-Sn with Prussian blue analog cathodes, Lipson et al. [85]
25 demonstrated the first Ca-ion full cell with $\sim 80 \text{ mAh} \cdot \text{g}^{-1}$ that may avoid the surface passivation issues
26 with Ca metal anodes, albeit showing low operating voltage (discharge average $< 1.5 \text{ V}$), likely

1 affected by the high potential (predicted at 0.8V vs. Ca^{2+}/Ca) of the Ca-Sn alloy. Although this will
2 reduce the cell energy density, the potential increase in cycling could make this an attractive strategy.
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4 Meanwhile, for hypothetical Ca-ion battery energy estimations (vide infra), graphite will be used as
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6 anode.
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10 5.2 Techno-economic modelling of Ca batteries

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15 Only very few techno-economic assessments have been carried out so far to provide reliable
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17 quantified values of energy density and potential costs for calcium-based batteries. In fact, most of
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19 the validated techno-economic models developed until now mainly concern the cost assessment of
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21 upcoming LIB chemistries, such as the full material-to-system Battery Performance and Cost
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23 (BatPaC) model by Argonne National Lab [107]. While this model has been comprehensively applied
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25 to Mg batteries [10], the completeness of BatPaC up to full battery pack complexity has hindered its
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27 use for technologies at the very early development stages where many parameters are still uncertain.
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29 Thus, the assessments carried out on Ca-based batteries by Palacin et al. [13,19,108] have applied the
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31 energy-cost model developed by Berg et al. [109], which considers the performance at single
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33 electrochemical cell level. Mainly fundamental parameters (e.g., operating potentials and specific
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35 capacities of the active electrode materials) are employed, avoiding uncertainties and potential
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37 differences in battery cell auxiliaries such as electrical connections, total active area or cell
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39 packaging/housing and their format/dimensioning. Following the details on the unit cell design
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41 provided in the report by Monti et al. [13], we have reproduced the model (cathode capacity limited
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43 to a maximum active layer thickness of 100 μm) to estimate the energy densities at cell level for
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45 hypothetical (virtual) materials with a range of operating potentials (2.0-4.5V vs Ca^{2+}/Ca) and specific
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47 capacities (50-300 $\text{mAh}\cdot\text{g}^{-1}$) and added those calculated for existing materials with experimental data
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49 (Table 3). The validity of these simplifications has been proven in this work with the Li-ion and LiS
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51 data included in Figure 5.
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	Average discharge potential (V vs. Li/Ca)	Specific Capacity _{AM} (mAh g ⁻¹)	Density (g cm ⁻³)	Volumetric Expansion (%)	Porosity (%)	Thickness (μm)
CATHODES						
(NMC) LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂	3.7	170	4.75	–	30	103
(LFP) LiFePO ₄	3.4	160	3.65	–	30	100
Ca ₃ Co ₂ O ₆	3.2	160	4.52	–	30	100
α-V ₂ O ₅	3.03	200	3.36	–	30	100
TiS ₂	2.0	239	3.25	–	30	100
Li ₂ S	2.1	1000	1.66	80	30	100
CaS	1.9	1000	2.59	80	30	100
O ₂ /C (Li ₂ O ₂)	2.96	1168	2.3	75	30	100
O ₂ /C (CaO ₂)	3.28	744	2.95	75	30	100
Hypothetical (Ca) cathode	2.0-4.5	50-300	4.5	–	30	100
ANODES						
Graphite (Li)	0.1	360	2.25	10	35	66-110
Graphite (Ca)	0.272	744	2.25	10	35	45
Li metal	0.0	3884	0.53	50	67	50
Calcium metal (with Al CC)	0.0	1338	1.57	50	67	10-58
Calcium metal (wo/CC)	0.0	1338	1.57	100	50	13-77
OTHER (CC & electrolyte)						
Aluminum CC			2.7			15
Copper CC			8.96			10
Separator+electrolyte			1.02		30 (sep.)	25
ELECTRODE Compositions						
Standard	93 wt% Active material / 4 wt% Carbon additive / 3 wt% Binder					
Sulfur	60 wt% Sulfur / 30 wt% Carbon / 10 wt% Binder					
M-air	60% discharge product / 8% C / 2% Binder / 30 % porosity-liquid electrolyte (volume %)					

Table 3: Active materials and their input properties for the battery cell estimations.

In the case of metal-air secondary batteries, the air flow concepts (O₂, open or closed system) introduce other components and full system requirements (e.g. pumps or compressed air cylinders) that introduce gas utilization requirements that lower greatly the metrics, particularly of volumetric energy density. Even for the more studied Li O₂ batteries this is still a work in progress, including several uncertainties and still suffering from low energy roundtrip efficiencies that bring the very high

theoretical energy densities ($3.445 \text{ kWh}\cdot\text{L}^{-1}$ and $3.458 \text{ kWh}\cdot\text{kg}^{-1}$ at materials-only level) to only 35% at cell level and even lower in full systems ($384 \text{ Wh}_{\text{use}}\cdot\text{L}^{-1}$) [110].

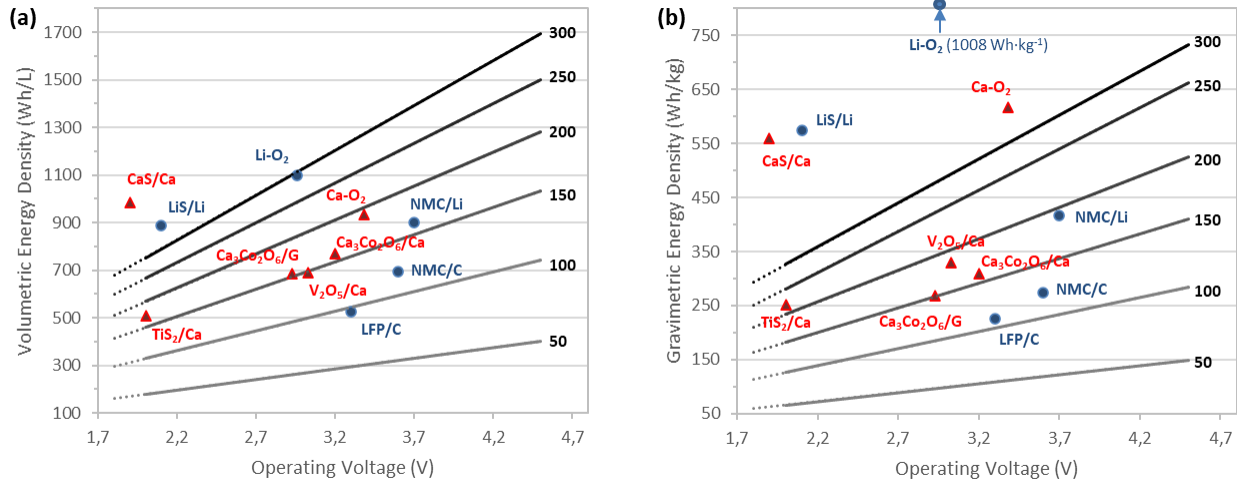


Figure 5: Volumetric (a) and gravimetric (b) energy densities for Li based batteries (blue circles), and considered Ca battery technologies (red triangles). The straight lines are calculated energy densities of hypothetical Ca metal batteries as a function of operation potential and cathode specific capacities (on the right of each line).

This kind of limitations also difficult a reliable estimation of practical battery performance for metal-air systems and hence, only theoretical values are usually reported for multivalent metal-air batteries such as Mg-O₂ ($14 \text{ kWh}\cdot\text{L}^{-1}$ and $3.9 \text{ kWh}\cdot\text{kg}^{-1}$, based on MgO products) most recently [111]. Despite these drawbacks, we have applied the simplified calculation model to a hypothetical Ca-O₂ cell based on CaO₂ discharge product ($2515 \text{ Wh}\cdot\text{kg}^{-1}$ and 3.28 V vs Ca^{2+}/Ca [30]) and compared it to Li-O₂ (based on Li₂O₂ discharge product and data reported by Gallagher et al. [110]). Due to the higher density of Ca and CaO₂, Ca-O₂ batteries may not compete in energy density but the lower cost and abundance of calcium could be advantageous for stationary applications.

The overall results indicate that the estimated energy densities for calcium batteries could surpass the state-of-the-art lithium-ion batteries (LIBs) while most likely having lower cost (see also Introduction section). Moreover, calcium metal based cells with moderate operating voltages of 2.1-

2.5 V and cathode capacities between 250-200 mAh·g⁻¹ would yield higher energy densities than state-of-the-art LIBs, although Li metal based cells such as Li-S and NMC|Li (901 Wh·L⁻¹; 417 Wh·kg⁻¹) would still present higher energy density due to the lower weight of lithium. Moreover, the energy densities of a Ca-S battery, similarly to Li-S, are higher than for any other technology except Li-O₂, since both anode and cathode have very high capacities. However, Ca being denser than Li results in Ca-S showing lower gravimetric energy density (560 Wh·kg⁻¹) but higher volumetric energy density (985 Wh·L⁻¹), which can be preferred for large-scale stationary applications.

In case of other cathodes, such as Ca₃Co₂O₆ with relatively high voltage (3.2 V vs Ca²⁺/Ca) and specific capacity (160 mAh·g⁻¹), V₂O₅ (3.03 V / 239 mAh·g⁻¹) or TiS₂ (2.0 V / 239 mAh·g⁻¹), they cannot compete in gravimetric energy density with the sulfur cathode. However, the estimations show that combinations of 3.0 V / 250 mAh·g⁻¹ or 3.5 V / 200 mAh·g⁻¹ can yield gravimetric energy densities above the 400 Wh·kg⁻¹ targeted by the Strategic Energy Technology (SET) Plan for year 2030 [112] and high volumetric energy densities >1000 Wh·L⁻¹, even higher than any of the estimated sulfur-cathode-based battery technologies and exceeding the 750 Wh·L⁻¹ target in the SET Plan. For the gravimetric energy densities, 3.5 V/300 mAh·g⁻¹ or 4.0 V / 250 mAh·g⁻¹ combinations are necessary to exceed Li-S and Ca-S.

In terms of power capability, current densities applied to calcium battery materials studied so far are low (typically 0.1C) and only few instances have been found where higher current rates have been analyzed: Vanadium-based cathodes such as VOPO₄·2H₂O (2.8 V/100 mAh·g⁻¹) [68] appeared to withstand 2C rate delivering 43 mAh·g⁻¹ and 1D-CaV₆O₁₆ (205 mAh·g⁻¹ at 0.3C) discharged 117 mAh·g⁻¹ at the exceptionally high rate of 12C [47]. With this last instance as example (calculated nominal 612 Wh·L⁻¹ and 330 Wh·kg⁻¹), it would be possible to achieve 4.9 kW·L⁻¹ and 2.6 kW·kg⁻¹. Otherwise, expecting that 2C current rates are feasible without energy loss, most of the estimated Ca metal based batteries estimated here could achieve > 1500 W·L⁻¹ and >700 W·kg⁻¹ (SET Plan targets).

Overall, taking into account also the abundance and lower cost of Ca (Calcium metal costs foreseen between 5-50 $\text{\$}\cdot\text{kg}^{-1}$ [13]) in comparison with the relatively high price (100 $\text{\$}\cdot\text{kg}^{-1}$) of Li metal (in addition to production and resource/mining issues), cost and resources advantages are also expected for Ca metal based full batteries. Indeed, calcium batteries would have comparable cost-effectiveness of state-of-the-art NMC/graphite LIBs (110 $\text{\$}/\text{kWh-cell}$ [10]) even for very high hypothetical cathode material costs ($>80 \text{\$}\cdot\text{kg}^{-1}$ vs $33 \text{\$}\cdot\text{kg}^{-1}$ of reference NMC). Considering the high potential energy density, particularly volumetric, of Ca metal-based batteries, this low cost would be particularly attractive for large-scale stationary energy storage applications.

6. Summary and Outlook

Considering the much larger abundancy on earth crust of calcium minerals, the much smaller costs of calcium-containing industrial commodities compared to the corresponding lithium ones (i.e., 20 to 40 times cheaper) and the almost unexplored landscape of calcium electrochemistry, Ca-based batteries may disclose remarkable innovations and technological breakthrough, either from a fundamental science point of view or from an application perspective.

The choice of active electrode materials and their coupling with the electrolyte sets the theoretical limits in voltage and energy density but also affects the kinetics (power), cycle life and safety.

Recent advances in Ca electrolytes have enabled reversible Ca plating/stripping at room temperature. While Ca metal is by far the most promising anodic material, its electrochemistry is rather complex (e.g., a very stable calcium oxide is formed) and, due to low coulombic efficiency, it is still far from meeting the expectations for commercial applications. As a possible alternative to calcium metal, tin has attracted interest and Ca-Sn alloy anodes are considered a viable strategy towards the new family of Ca-ion batteries.

Room-temperature electrolytes, stable against high-voltage cathodes, are currently looked for as a necessary requirement for high-energy density Ca batteries. Size and charge of the Ca^{2+} cation

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complicate the realization of classical intercalation cathodes with electrochemical performance similar to the state-of-the-art Li-based positive electrodes. Among the limited practical studies on positive active materials, based on calcium intercalation chemistry, layered oxides, in particular V_2O_5 and MoO_3 , proved to be promising. As an example, low cost synthesis route and use in aqueous systems, made 1D $CaV_6O_{16} \cdot 7H_2O$ an interesting possible candidate. Also, calcium cobaltite materials have shown exciting results, due to the 1D crystal structure, which may facilitate cation migration along with the inter-chain spaces. However, the use of cobalt-based materials will challenge the recycling process beyond them.

Intercalation limitations can be circumvented through alternate electrochemical mechanisms such as conversion or coordination. Some preliminary tests, employing both types of reactions, using sulfur and organic cathodes, respectively, performed by some of us and currently under consideration for publication, provide promising results for the implementation of these kinds of cathode chemistry. Both types of cathodes show relatively good electrochemical performance with reversible electrochemical mechanism, confirming interaction of discharged cathode material with Ca^{2+} . Thus, we think that new cathode concepts might offer viable practical alternative to more renowned inorganic cathodes.

Among other possible positive materials, O_2 is certainly an intriguing solution to achieve low-cost, safe and environmentally friendly calcium batteries, even though important issues associated with its chemistry are still a challenge for Sodium and Lithium systems. As demonstrated by our simplified calculation model, applied to hypothetical $Ca-O_2$ and $Li-O_2$ cells, the former may not compete in energy density. $Ca-O_2$ batteries could only be advantageous for large-scale stationary applications, due to lower cost and abundance of calcium.

The same model applied to many other calcium- and lithium-based cell configurations, revealed in our study that the estimated energy densities for calcium batteries could surpass the state-of-the-art LIBs, while most likely having lower cost. Particular voltage/capacity combinations, associable to realistic Ca-cell materials, would provide both gravimetric and volumetric energy densities higher

1 than targeted values at cell level for the year 2030. Given a 2C current rate, not easy to achieve, due
2 to the sluggish diffusion of the bivalent calcium ion, but already demonstrated by few examples in
3 literature, also power density performances, expected by 2030 at cell level, would be surpassed.
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7 Based on the above considerations, despite technical aspects concerning the implementation
8 and upscaling of this technology, as discussed in Section 5, we envisage calcium batteries a research
9 avenue worth pursuing. By mainly addressing the cycle life issue, it is considered a future emerging
10 technology particularly advantageous from a techno-economic point of view for large scale stationary
11 applications.
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HIGHLIGHTS:

- Properties of anode, cathode and electrolyte materials for Ca-batteries
- Estimates of key performance indicators for future development
- Techno-economic aspects for technology upscaling

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: