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Title **Calcium-Ion Batteries: Current State of the Art and Future Perspectives**

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Keywords: calcium ion batteries, multivalent ion batteries, ionic mobility, DFT modelling, energy storage

Abstract

Recent developments in rechargeable battery technology have seen a shift from the well-established Li-ion technology to new chemistries to achieve the high energy density required for extended range electric vehicles and other portable applications, as well as low-cost alternatives for stationary storage. These chemistries include Li-air, Li-S and multivalent ion technologies including Mg^{2+} , Zn^{2+} , Ca^{2+} and Al^{3+} . While Mg^{2+} battery systems have been increasingly investigated in the last several years, Ca-ion technology has recently been recognized as a viable option.

In this first comprehensive Ca-ion technology review, the use of Ca metal anodes, alternative alloy anodes, electrolytes suitable for this system, and cathode material development are discussed. The advantages and disadvantages of Ca-ion batteries including prospective achievable energy density, cost reduction due to high natural abundance, low ion mobility, the effect of ion size and the need for elevated temperature operation are reviewed. The use of DFT modeling to predict the properties of Ca-ion battery materials is discussed and the extent to which this approach is successful in directing research into areas of promise is evaluated. The review concludes with a summary of recent achievements and evaluates areas for future research efforts.

1. Introduction

High energy density rechargeable lithium-ion batteries (LIBs) currently dominate the portable electronics market and the electric vehicle market. This technology has been successful due to the relatively high energy density of these batteries and their good cycle life and reliable performance characteristics. However, growth in the electric vehicle (EV) market has been tempered by the limited driving range achievable with lithium-ion technology and there is constant pressure to increase the range by increasing the cell's energy density.^[1] Simultaneously there is a drive to reduce costs to increase the competitiveness with the internal combustion engine. Several countries including China are considering a ban on petrol or diesel powered vehicles in the medium term because of environmental concerns, increasing the urgency for low-cost and high-performance alternatives.^[2]

In addition, large scale energy storage to support the intermittent renewable energy production from solar and wind power is needed to provide the World with reliable and sustainable Green energy. Cost-effective storage is needed to stabilize the energy supply and prevent the variability of the renewable energy from affecting the quality of the power supply from the electricity grid.^[3]

It is widely conceded that lithium-ion technology is reaching the limits of its energy density capabilities and that new “beyond lithium-ion” technologies are required to fill the gap.^[4] This consideration, as well as the drive to reduce costs, has prompted a flurry of research activity in alternative chemistries, for example, Li-air,^[5] Li-S,^[5a, 6] Na-ion and multivalent ion technologies.^[7]

One strategy to enhance the energy density of Li-ion batteries is to replace the graphitic anodes currently employed in commercial cells, with metallic lithium anodes.^[8] However, lithium metal does not plate evenly when deposited from electrolytic solution and forms finger-like, dendritic growths on the anode surface.^[9] This results in a rapidly increasing anodic surface area, increased interaction with the electrolyte and may lead to short-circuit and thermal runaway of cells.^[9b] Despite promising recent advances in this area, no commercial cells with lithium metal anodes are currently produced.^[10]

Li-S cells offer a very high theoretical energy density (potentially 5 times higher than that of lithium ion cells) and require low cost raw materials. There is currently investment in commercial development of these cells by Oxis Energy with the initial commercial offering due in 2019/2020. If they are found to meet practical performance targets, these cells offer a cost effective way to achieve the range targets for EV's in the long term.^[5a, 11]

Li-air cells are at a relatively early stage of development and are attractive for their promised high energy densities, 5-10 times that of Li-ion cells (LICs) and comparable to the specific energy of gasoline.^[12] Although they are being heavily investigated,^[13] there are still major obstacles to their commercialization including problems with cycle life and charging rate. The consensus in the industry is that they are at least 10

years from commercial application. It should be noted that both Li-S and Li-air cells are affected by the tendency of metallic lithium to form dendritic deposits.

In terms of cells based on insertion reactions of alkali metal cations, Na ion technology has developed rapidly. This is largely because sodium ion batteries (SIBs) operate with the same mechanism as LIBs and utilize similar classes of cathode materials, similar electrolytes and similar manufacturing technology, resulting in rapid progress towards commercialization. Na-ion technology however, has an intrinsically lower energy density compared to Li-ion technology due to the larger size and greater mass of Na ions, and is thus better suited to stationary storage applications.^[14] Nevertheless, the abundance and low cost of Na compared to Li makes this technology attractive.

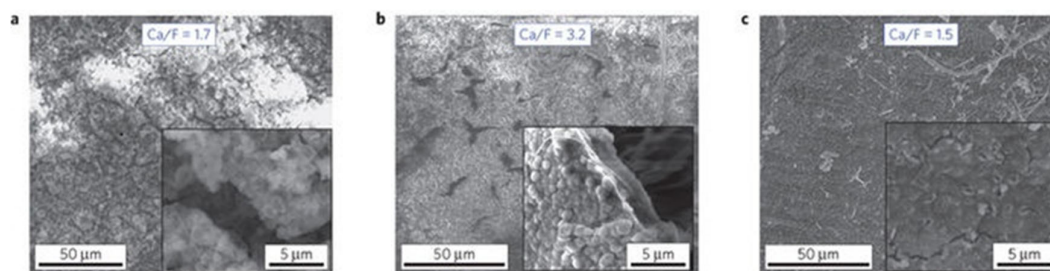


Figure 1. Characterization of deposits obtained in 0.3 M $\text{Ca}(\text{BF}_4)_2$ EC:PC at 1.5 V versus $\text{Ca}^{2+}/\text{Ca}_{\text{passivated}}$. a–c, SEM micrographs at 75 °C for 200 h (a), at 100 °C for 200 h (b), and at 100 °C for 72 h (c). The Ca/F ratios determined by EDX are indicated. Reproduced with permission.^[15] Copyright 2016, Nature Publishing Group.

Several different multivalent ions have been suggested as alternatives to Li^+ and these include divalent^[16] Ca^{2+} ,^[15, 17] Mg^{2+} ,^[18] and Zn^{2+} ^[19] and trivalent Al^{3+} .^[5b] Early work has indicated that, in contrast to lithium, multivalent metals (e.g. Mg and Ca) may be deposited uniformly from appropriate electrolyte solutions, with little or no dendritic growth (**Figure 1**).^[15, 20] This finding makes it feasible to use multivalent metallic anodes in place of the graphite anodes used in lithium-ion batteries, resulting in a significant increase in the anode gravimetric and volumetric capacity. This promises increased energy density for these multivalent battery systems compared to lithium-ion batteries ^[3, 16b, 18b] (**Figure 2**). The use of multivalent ions also leads to a possible increase in the electrochemical capacity of intercalation electrodes and hence to a significant increase in the energy density of cells utilizing these electrodes compared to Li-ion cells. For example, if divalent ions are used (e.g. Mg^{2+} , Ca^{2+}), then only half the number of divalent ions need to be inserted to obtain the same number of electrons transferred, compared to the equivalent monovalent ion intercalation. If a host structure is able to accommodate these divalent ions, then this can theoretically lead to a doubling of the electrode electrochemical capacity compared to that of the same intercalation host with a monovalent intercalating species (e.g. Li^+ or Na^+).^[21]

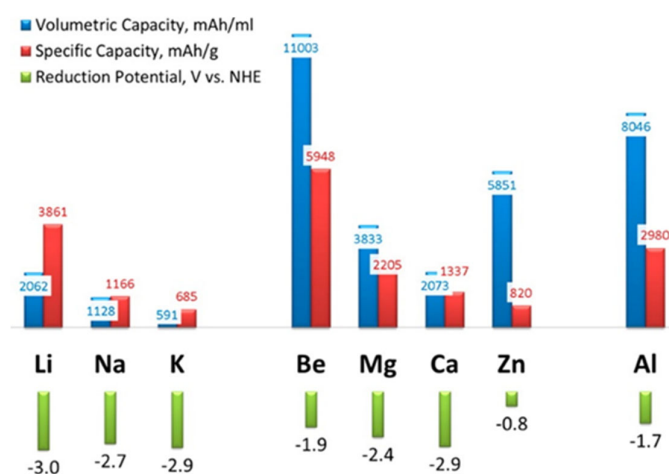


Figure 2. Capacities and reductive potentials for various metal anodes. Reproduced

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Most of the attention in multivalent ion battery development has focused on Mg-ion batteries (MIBs), despite the fact that Mg metal cannot be plated and stripped in conventional electrolyte solutions due to the formation of passivating surface layers.^[5b, 18] A great deal of research effort has been devoted to developing alternative electrolyte systems that do not passivate the Mg metal surface.^[22] The similarity of the size of Mg²⁺ (0.72 Å) and Li⁺ (0.76 Å) means that many of the intercalation hosts used successfully for LIBs are also potential hosts for Mg²⁺. Although these battery systems have been intensively investigated in the last 5 years, there are many issues that still need to be overcome before MIBs are commercially viable. The most significant challenge is the compatibility of high voltage cathodes with advanced electrolytes.^[22a] Current state-of-the-art full-cell MIBs^[18d] still fall short of the energy density of LIBs and significant research effort is required for these systems to fully achieve their potential.

Aluminum ion batteries (AIBs) have also attracted attention as Al is the most earth abundant metal and has a very high volumetric capacity of (8040 mAhcm⁻³). Research in this system is still in the early stages. The major limitation to progress is the lack of suitable electrolytes that are easy to handle and yet allow the reversible plating and stripping of Al metal. Current electrode materials have low voltages (0.6 – 2 V vs Al/Al³⁺), limiting the energy density of cells. However, if high capacity conversion electrodes such as sulphur are used then this system can still deliver high theoretical energy densities of 1200 Whkg⁻¹ suitable for electric vehicle applications.

[23] To date these systems remain impractical due to solubility of polysulphide species in the electrolytes.[23]

Calcium is the 5th most abundant element in the earth's crust, more abundant than both sodium and magnesium, and 2500 times more abundant than lithium. The ready availability of calcium would translate into low materials cost for battery production. Ca is also non-toxic and therefore would not pose an environmental hazard if used in bulk battery manufacture.

In addition, the deposition potential of calcium is only 0.17 V higher than that of lithium and 0.5 V lower than that of magnesium (**Figure 2**), potentially leading to higher cell voltages (determined by the difference between the anode and cathode potentials) and thus higher energy densities compared to MIBs, for example. Even though calcium is a relatively large element, if we consider the mass on a per electron basis then calcium is actually lighter than sodium. The ionic size of Ca²⁺ ions is 1.00 Å which is very similar to that of Na⁺ (1.02 Å) but significantly larger than Li⁺ (0.76 Å) and Mg²⁺ (0.72 Å). Ca²⁺ is therefore an attractive ion to consider for multivalent ion technology. Research into calcium-ion batteries (CIBs) is still in its infancy since the reversible deposition and stripping of calcium in conventional electrolytes was first demonstrated in 2016.^[15] However, parallels with other multivalent ion systems, particularly MIBs, which are relatively well-researched in comparison, should lead to a rapid increase in developments in this area.

In this first review of CIB technology, specific anode and cathode material developments for CIBs are discussed with a focus on the utility of DFT modelling to guide and direct research into areas of promise. The current state of development of electrolytes for CIBs is then evaluated. The review is concluded with a summary of the state of the art developments in this area highlighting areas for future investigation.

2. Anodes for Ca-ion Batteries

2.1 Metallic Calcium Anodes

Metallic calcium anodes are attractive as they offer significantly higher volumetric and gravimetric electrochemical capacities (2072 mAhmL⁻¹ and 1337 mAhg⁻¹, respectively) than the graphitic anodes used in commercial Li-ion battery technology (300-430 mAhmL⁻¹ and 372 mAhg⁻¹) (**Figure 2**). Pioneering work by Aurbach et al.^[24] using common electrolyte solutions including tetrahydrofuran (THF), γ -butyrolactone (BF), acetonitrile (ACN) and propylene carbonate (PC) with calcium, lithium and tetrabutyl ammonium salts (mainly BF₄⁻ and ClO₄⁻ anions), initially indicated that it was impossible to deposit calcium metal from nonaqueous solutions of Ca-ions. They concluded that the electrochemistry of calcium in these solutions was controlled by the surface chemistry of calcium. Passivating films built up on the surface of the calcium electrodes and, in contrast to the case of lithium (but analogous to the case of magnesium), these films did not conduct Ca-ions and effectively prevented the deposition of calcium metal.

In MIBs the limitation of non-conducting surface films in conventional electrolytes has been overcome by the painstaking development of electrolytes

that do not form any passivating films on Mg electrode surfaces. This, however, has resulted in very complex electrolyte systems with limited anodic stability.^[7]

22d, 25]

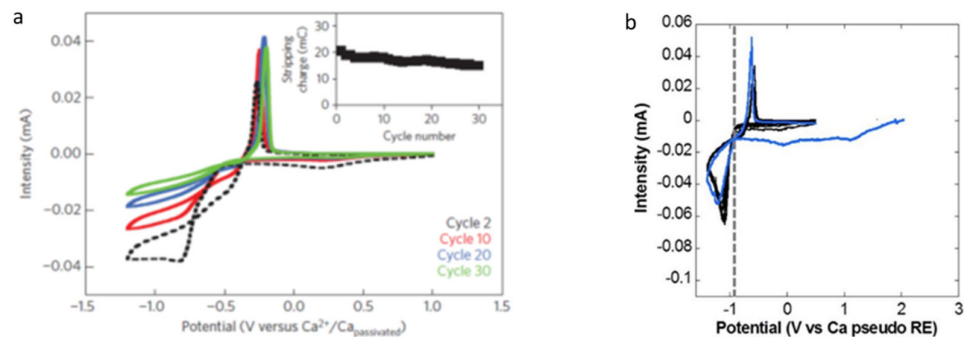


Figure 3. (a) Cyclic voltammograms ($100\text{ }^{\circ}\text{C}$, 0.2 mVs^{-1}) of a calcium deposit (grown by potentiostatic electrodeposition at -1.2 V versus $\text{Ca}^{2+}/\text{Ca}_{\text{passivated}}$, 5 h , $100\text{ }^{\circ}\text{C}$) in $0.45\text{ M Ca}(\text{BF}_4)_2$ EC:PC electrolytes. (b) CVs (0.1 mV/s) obtained in three-electrode Swagelok cells with $0.45\text{ M Ca}(\text{BF}_4)_2$ in $\text{EC}_{0.5}:\text{PC}_{0.5}$ using Ca. Adapted with permission from a)^[15] and b)^[3]. Copyright a) 2016, Nature Publishing Group and b) Copyright 2017, Electrochemical Society.

In the case of CIBs, Ponrouch et al.^[15] investigated more conventional electrolyte systems based on mixed carbonate solvents (mixtures of propylene carbonate and ethylene carbonate), commonly used for Li- and Na-ion batteries, with $\text{Ca}(\text{ClO}_4)_2$, $\text{Ca}(\text{BF}_4)_2$ and $\text{Ca}(\text{TFSI})_2$ salts. No redox processes were observed for any of the systems at room temperature, in agreement with the findings of Aurbach et al.^[24] At elevated temperatures ($50\text{--}100\text{ }^{\circ}\text{C}$), however, $\text{Ca}(\text{ClO}_4)_2$ and $\text{Ca}(\text{BF}_4)_2$ solutions showed reversible redox processes (**Figure 3a**). The most reversible process was found for $0.45\text{ M Ca}(\text{BF}_4)_2$ solutions at $100\text{ }^{\circ}\text{C}$. Analysis of the electrode deposits confirmed that the redox process occurring was due to the plating and stripping of

calcium metal and that this process was stable over many cycles (**Figure 3b**). Both the salt concentration and the temperature were critically important to the effectiveness of the process. This study aroused great interest as it was the first demonstration of calcium plating and stripping in conventional electrolyte, and even at 100 °C this electrolyte displayed a large electrochemical window (-0.5 V to 3.5 V) vs Ca/Ca²⁺. These findings were recently confirmed by Tchitchekova et al.^[3] in Ca(BF₄)₂ solutions with low voltage hysteresis and good efficiency after the 1st cycle ranging from 40-85% depending on the lower cut-off voltage. These findings introduced a multivalent ion system, relatively free of the metal-electrolyte woes that plagued MIBs, that could operate in the conventional electrolytes developed for LIBs. This finding by Ponrouch et al.^[15] stimulated investigations into compatible high-voltage cathodes for high energy density CIB systems. The need for high temperatures for Ca metal cycling in conventional electrolytes is, however, a practical limitation for commercial application, as high temperature operation is expensive, increases the speed of cell degradation and also increases the likelihood and rate of parasitic side reactions.

Caution is also required in the use of Ca metal (or Mg metal) anodes as they display a significant potential shift and variation in potential over time in non-aqueous electrolytes ^[3, 15, 17]. While there are well established protocols for Li-ion cell testing, similar standard methods are still lacking for multivalent-ion cell testing, especially at elevated temperatures. At present the recommendation is that a 3-electrode system be used for all experimental measurements along with an alternative reference electrode, e.g. Ag/AgCl or an internal redox couple, to monitor the shift of the Ca potentials.^[3]

This finding also has implications for the use of Ca metal as anode in full-cell configurations, as a shifting electrode potential will affect the cell voltage in an unpredictable manner. The origin of the voltage shift and voltage instability is not yet well understood. It has been postulated that several processes may contribute to the voltage shift including a small activity coefficient in the Nernst equation, a junction potential at the cathode surface, an additional redox reaction occurring in the solution or the high electrode impedance. The last mechanism seems likely to be the major contributor.^[3] This implies that surface interactions between the Ca metal and the electrolyte are significant and that some degree of passivation indeed occurs and contributes to the observed high impedance.

2.2 Alloy Anodes

Although the feasibility of metallic calcium anodes has been demonstrated, attractive electrochemical capacities may also be possible using alloy-based anode materials. Ponrouch et al.^[26] investigated the feasibility of using Ca-Si intermetallic alloys as anodes for CIBs with an attractive maximum theoretical capacity of 991 mAhg⁻¹ for the reaction of 1 mol fcc-Si with 2 mol of Ca-ions. As a first step in the examination of the feasibility of Ca-Si alloy anodes, they investigated the commercially available Ca-Si alloy CaSi₂. It was predicted that there would be a 306 % volume change in going from fcc-Si to CaSi₂ at an average voltage of 0.37 V with a theoretical capacity of 557 mAhg⁻¹. Experimental investigations confirmed the electrochemical extraction of Ca²⁺ from CaSi₂ but the resulting product was amorphous (probably due to the very

large volume change) and re-insertion of Ca^{2+} only occurred with a very large overpotential, likely due to the collapse of the structure.

Despite attractive voltages and high theoretical capacities, the very high volume changes associated with Ca^{2+} insertion and extraction from Ca-Si alloys will likely make commercial implementation of Ca-Si alloy anodes difficult. Similar challenges with Li-Si alloys have been studied for many years resulting in complex nanomaterial architectures to mitigate the negative effects of the large volume variations. However, no commercial cells with Li-Si alloy anodes have yet been produced.^[27]

Lipson et al.^[17] reported the use of a Ca-Sn alloy anode in full cell testing of Prussian blue analogue cathodes with non-aqueous electrolytes. Thermodynamic calculations predicted a voltage of 0.8 V vs Ca/Ca^{2+} for the reaction of Ca and Sn but no details of the alloy were given in this study. Capacity loss in the full cells tested by Lipson et al. were speculatively attributed to possible delamination of the anode and dissolution of the Sn.^[17]

Alloy anodes offer an attractive area for the development of practical full cell CIBs as they avoid the issues of surface passivation associated with Ca metal anodes. Further studies of Ca-alloy anodes are required to fully evaluate their potential.

2.3 Defective Graphene Anodes

The anode of choice for LIBs is graphite but it has a very low capacity for Ca-ion insertion.^[28] Lower dimensional materials such as graphene have been shown to have a higher Li-ion capacity than graphite. First-principle calculations performed by Datta et al.^[29] have demonstrated that pristine graphene cannot adsorb Ca-ions but defective graphene can and the capacity increases with the increase in defect density. For example, for divacancy defects (i.e. the absence of a C-C dimer) at 6.25 % defect density, the capacity is 297 mAhg⁻¹, compared with 2900 mAhg⁻¹ for a 25% defect density. Cations are adsorbed preferentially in the region of a defect due to charge transfer from the ion to the graphene sheet.

2.4 Practical anodes for half-cell testing

Even though Ca metal anodes are attractive for high energy density full-cells, the voltage instability and high impedance of Ca metal anodes discussed in 2.2, makes it important to define alternative anodes that can be used easily to evaluate potential Ca-ion cathode materials. Several options have been used to date.

Amatucci et al.^[30] used a Ag/Ag⁺ quasi-reference electrode in the evaluation of vanadium oxide cathode materials for calcium insertion. They reported a stable potential for this quasi reference of 0 V vs S.H.E. \pm 100 mV. This was incorporated into an asymmetrical cell using an activated carbon capacitive electrode as the counter and the V₂O₅ as negative electrode. Ca-ion insertion into the working electrode was accompanied by the simultaneous formation of an

electrochemical double layer at the counter electrode by adsorption of anions. On discharge the Ca-ions were removed from the lattice and the anions desorbed from the double layer. All the Ca-ions for intercalation originated from the cell electrolyte. Although electrolyte oxidation on the surface of the electrode led to a small voltage drift, this proved to be an effective way to quickly evaluate polyvalent cation insertion. A similar approach was described by Bervas et al.^[21] using a capacitive carbon cloth electrode with a very high surface area ($2000 \text{ m}^2 \text{ g}^{-1}$) as the counter electrode. Capacitive counter electrodes have also been applied in Mg^{2+} intercalation research^[31] and in the work of Lipson et al. in CIB studies.^[32]

Possibilities also exist for the development of Ca-ion insertion anodes that exhibit a low constant potential over a wide compositional range, analogous to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for LIBs.^[3, 33]

Problems with current collector corrosion in Ca-ion electrolytes have been described by Lipson et al.^[32] For stainless steel 304 current collectors, spurious peaks in cyclic voltammograms for C-coated current collectors are observed which could easily be misinterpreted as redox peaks resulting from insertion or extraction of Ca-ions from an insertion electrode. The use of graphite foil current collectors is recommended as an alternative free of side reactions.

In summary, there are several possibilities for half-cell testing for CIBs. The most commonly used is a three electrode system with a capacitive carbon counter electrode coupled with the working electrode of the material under test and a

separate reference electrode. While calcium metal can be used as a quasi-reference electrode, it should be recognized that its potential may not be stable and should be calibrated against Ag/AgCl or an internal redox couple such as ferrocene/ferrocinium. In these systems, flooded cells with large electrolyte volumes are typically used with the electrolyte as the source of the Ca-ions for insertion, distinct from commercial cells where the electrolyte volume is minimized.

3. Cathodes for Calcium-Ion Batteries

3.1. Density Functional Theory (DFT) Modelling: Predictions for Ca²⁺ ion Cathodes

DFT modelling has recently proved to be a powerful tool in predicting the likely success of multivalent intercalation in a variety of materials and in directing research to explore novel materials as multivalent ion hosts.^[32, 34] In this section we will discuss the general predictions of DFT modelling for multivalent ion intercalation with particular relevance for CIB technology.

3.1.1 General Ionic Mobility Considerations

Despite the potential advantages, multivalent ion batteries have their own challenges. The most critical is the relatively sluggish kinetics resulting from the slow diffusion of multivalent ions in intercalation host structures due to their increased charge which increases the strength of the cation-cation repulsions and the cation-anion attractions as the ions diffuse through the host structure. DFT modelling has been applied, in

particular, to investigate the limitations in multivalent ion mobility in insertion electrodes, as sufficient ionic mobility is essential for the application of electrodes in battery systems.

Decreasing the ionicity (charge localization) in the host decreases the coulombic interactions with the diffusing species. For example, in transition metal sulphides, the M-X bonds are less ionic than in oxides and the diffusion of multivalent ions is facilitated^[22a]. However, although the use of transition metal sulphides has been successful in improving the kinetics of multivalent ion diffusion compared to that in oxide hosts, the voltage obtainable with sulphides is lower than that of their oxide analogues which compromises the energy density of cells with sulphide electrodes.

Liu et al.^[35] estimated the effect of the calculated migration energy barriers on ionic diffusion in insertion compounds and found that, if the migration barrier was 525 meV, this corresponded to an ionic diffusivity of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at room temperature. This allowed a discharge time of 2 h for micron sized active particles, representing a practical lower limit. In the case of nanoparticles, a lower diffusivity can be tolerated with an estimated upper limit of the diffusion barrier of 645 meV for 100 nm particles. Although the ionic diffusivity can be predicted and used to direct research efforts towards the most promising materials, there remains the possibility of other mechanisms not accounted for in the modelling that may limit the practical charge and discharge rate of the material, e.g. instability of the chosen phase or poor electronic conductivity.

3.1.2 Predictions of Ionic Mobility in Host Materials

Rong et al.^[36] used multivalent ion mobility predictions to develop general guidelines for the selection of potential multivalent ion intercalation hosts by investigating four structures widely used for Li ion batteries: spinel Mn_2O_4 , olivine FePO_4 , layered NiO_2 , and orthorhombic $\delta\text{-V}_2\text{O}_5$. Multivalent ion mobility in these hosts was lower than that of Li-ions, as expected. However, the most significant finding was that particular hosts were better suited to one multivalent ion compared to another and a structure well-suited to one could perform very poorly for another. Contrary to previously held opinions, the ionic size or the “openness” of the structure was not the determining factors in the ionic mobility. Instead, the multivalent ion mobility was predicted to be best for structures in which the intercalating ions were initially inserted into sites that were not of the preferred co-ordination for that ion. The ions were then more inclined to migrate from these initial “unstable” sites into the neighboring more favored positions, enhancing ion mobility. Ion diffusion pathways with small changes in ion coordination number were favored. Ca^{2+} in the Mn_2O_4 spinel lattice was given as an example of this with a predicted migration barrier near to the 525-650 meV quantitative limit for successful battery operation (**Figure 4a**).

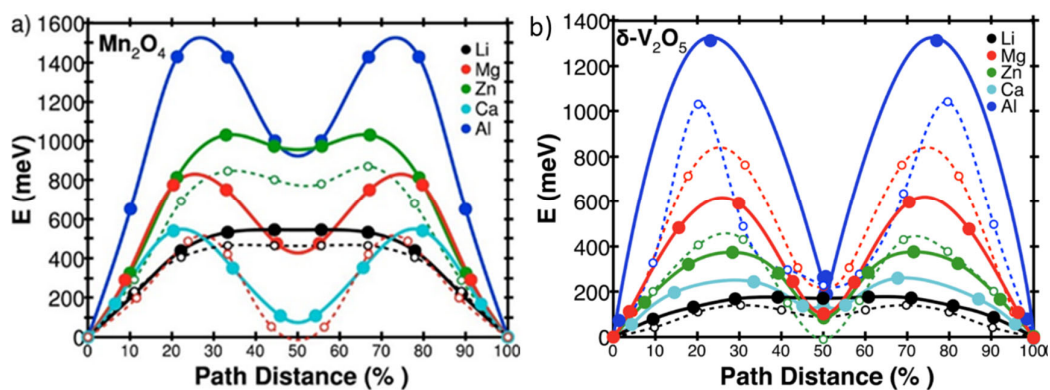


Figure 4. Li and multivalent ion migration energies plotted along the diffusion paths in a) spinel Mn_2O_4 and b) $\delta\text{-V}_2\text{O}_5$ in the empty lattice (solid) and dilute vacancy (dashed) concentration limits. Reproduced with permission.^[36] Copyright 2015, American Chemical Society.

The preparation of phases without the intercalating ion initially present, was proposed as likely the best strategy for preparing materials with high ionic mobility, as ions could then be inserted into meta-stable positions electrochemically or by soft-chemistry routes. $\delta\text{-V}_2\text{O}_5$ was identified as an example for the application of this strategy, with migration energies below the threshold for several of the multivalent ions considered, including Ca^{2+} (**Figure 4b**). This was a result of the flexibility of the structure which results in minimal coordination changes for the migrating ions along the diffusion path.

Two ways of improving the mobility of multivalent ions in insertion electrodes are the use of nanostructured materials to reduce the diffusion length from the electrode surface into the bulk and the elevation of the cell operating temperature. The use of elevated temperature cycling proved essential to the demonstration of reversible magnesium cycling in TiS_2 ^[26] and thiospinels^[22a] and also in the demonstration of reversible Ca plating in conventional electrolytes^[15]. However, the increased

temperature of cell operation unfortunately also increases the kinetic of parasitic side reactions such as current collector corrosion and electrolyte breakdown [37].

3.2 Specific Cathode Materials: DFT Modelling and Experimental Results

3.2.1 Layered compounds

V_2O_5

V_2O_5 has a corrugated layered structure and therefore has scope for expansion and contraction to accommodate the intercalation of large multivalent cations such as Ca^{2+} (**Figure 5 a, b**). The rhombohedral structure undergoes several transitions to other phases with cation intercalation resulting in steps in the cell voltage.

Recently the stability of different V_2O_5 polymorphs and their barriers to Ca- and Na-ion diffusion have been investigated in detail by DFT simulations [38]. The authors found that while α - V_2O_5 and α - CaV_2O_5 are more stable than δ - V_2O_5 and δ - CaV_2O_5 , significantly lower barriers for Ca-ion diffusion exist in bulk δ - CaV_2O_5 compared to α - CaV_2O_5 . This was ascribed to the smaller changes in ion coordination number along the diffusion paths implying that a better rate performance may be achieved by cycling Ca-ions in δ - CaV_2O_5 than in α - CaV_2O_5 .

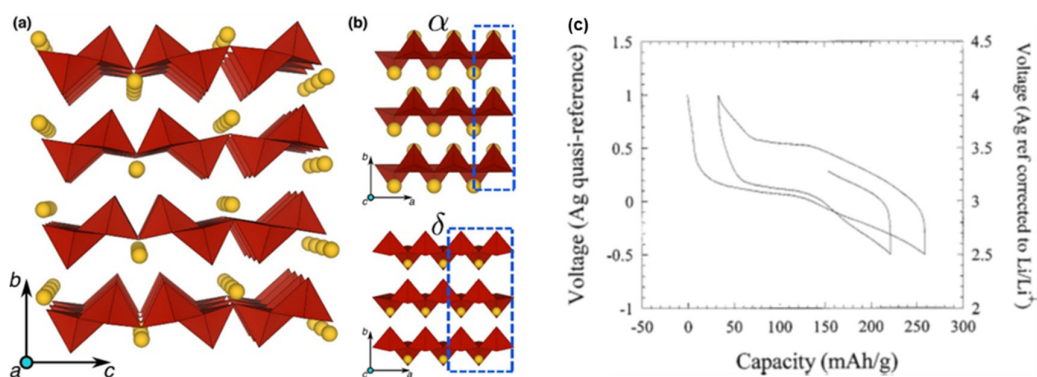


Figure 5. a) Displays the structure of orthorhombic V_2O_5 , with the red pyramids indicating VO_5 polyhedra and the yellow spheres corresponding to the intercalant atoms. b) Illustrates the difference between the alpha and delta polymorphs of orthorhombic V_2O_5 . Reproduced with permission.^[39] Copyright 2015, Royal Society of Chemistry. c) Reversible electrochemical insertion of Ca^{2+} into nano-crystalline V_2O_5 . Reproduced with permission.^[40] Copyright 2001, Elsevier.

The authors also compared the surface and bulk diffusion of Ca-ions in the two V_2O_5 polymorphs and found significantly lower barriers to Ca-ion diffusion at the (010) surface compared to the bulk. This surface dominates the equilibrium morphology of this compound and this finding explains the significantly improved performance of nanostructured V_2O_5 cathodes compared to bulk structures for Na^+ and Mg^{2+} intercalation and implies that the same improvement may be expected for Ca^{2+} insertion in nano-crystalline electrodes.

Amatucci et al.^[30] were the first to experimentally investigate the intercalation of multivalent cations into V_2O_5 . They used nano-crystalline α - V_2O_5 in a 0.5 M $Ca(ClO_4)_2$ in propylene carbonate (PC) non-aqueous electrolyte in an asymmetrical cell with activated carbon as counter electrode and a Ag/Ag^+ quasi-reference electrode. The nano-crystalline nature of the material reduced the diffusion lengths and improved the performance of the material. They reported reversible Ca^{2+} insertion for 3 cycles with a capacity of 200 mAhg^{-1} at ambient temperatures (**Figure 5 c**), but the large polarization between charge and discharge curves indicates the sluggish movement of the Ca-ions in the lattice. Extended cycling in this material has not yet been reported. Although there was limited evidence of intercalation, they checked

carefully for the presence of proton insertion as the source of some of the increased capacity, compared to their experiments with Li^+ intercalation in the same material. They concluded that the contribution of proton insertion was negligible. However, Sa et al.^[41] investigated Mg^{2+} insertion into $\alpha\text{-V}_2\text{O}_5$ in wet (2600 ppm H_2O) and dry (15 ppm H_2O) electrolytes and found clear evidence for proton intercalation in the wet electrolytes from solid state NMR, which resulted in increased capacity. Although there was evidence for Mg^{2+} intercalation in the dry electrolyte (XAS and EDX), the capacity was significantly reduced. Caution is therefore required in assuming that the observed Ca^{2+} capacity in V_2O_5 is all due to Ca^{2+} intercalation and further investigation is required to exclude proton intercalation as a contributor to the measured capacity.

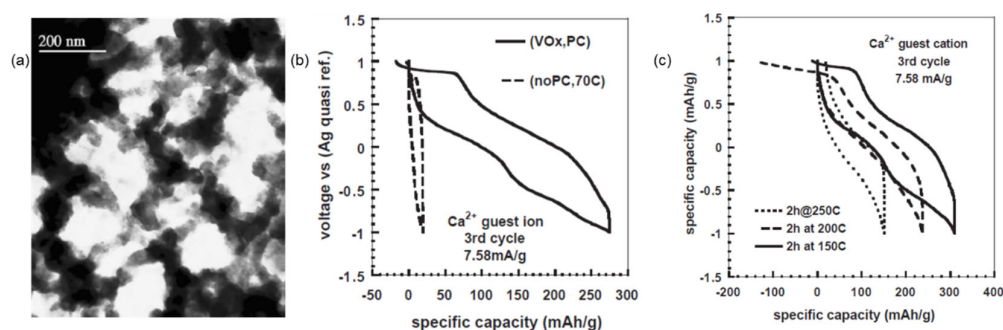


Figure 6. a) Bright Field Transmission Electron Microscope of the (VO_x,PC) nano-composite annealed half an hour at 150 °C, b) The 3rd cycle in $\text{Ca}(\text{ClO}_4)_2$ electrolyte of a) the (VO_x,PC) nanocomposite and of the pure vanadium oxide xerogel dried three weeks at RT and 1 week at 70 °C in vacuum. c) the (VO_x,PC) nano-composite annealed 2 h at 150, 200 and 250 °C. The three-electrode cells were cycled at RT in a dry room at a current density of 7.58 mA g^{-1} . Reproduced with permission.^[21] Copyright 2005, Elsevier.

Solvent co-intercalation has been flagged as a possible means of improving the mobility of multivalent ions in insertion electrodes. The use of hydrated host structures partially shields the coulombic interaction between the multivalent cations and the host structure and improves the kinetics of ion migration.^[42] While this strategy is important in understanding the kinetic limitations, it should be noted that hydrated cathodes are incompatible with alkaline earth metal anodes such as Mg and Ca in full cell configurations. However there is scope to explore solvent co-intercalation effects with anhydrous solvents^[5b].

Bervas et al.^[21] formed V_2O_5 xerogels from alkoxide precursors which yielded a typical 2-dimensional structure. They then prepared nanocomposites of crystalline V_2O_5 and propylene carbonate (PC) by prolonged soaking of the xerogel in PC and then heat-treated the composites at various temperatures to decompose or partially remove the PC. The resulting product was an aerogel mesoporous network of amorphous or poorly crystallized vanadium pentoxide particles with the mesopores filled with PC (**Figure 6a**). The (VO_x, PC) nanocomposites gave specific capacities in excess of 270 mAhg^{-1} when Ca-ions were intercalated and in excess of 350 mAhg^{-1} when the composites were heat-treated to less than $200 \text{ }^\circ\text{C}$ (**Figure 6 b and c**). A dried xerogel without any PC gave capacities of only 20 mAhg^{-1} by comparison, indicating that the PC insertion dramatically changed the Ca^{2+} insertion properties of the material, possibly by partially shielding the Ca-ions' electrostatic interactions with the crystal lattice. The presence of structural water may have also contributed to the good electrochemical performance in a similar way.

Hewettite, $\text{CaV}_6\text{O}_{16}\cdot x\text{H}_2\text{O}$

A recent abstract detailing reversible Ca^{2+} insertion and extraction in hewettite has been published. Hewettite has a 2-dimensional layered structure of V_3O_8 layers with hydrated Ca-ions inserted between the layers and was prepared electrochemically by ion exchange with the sodium analogue.^[23] Reversible intercalation was found by CV and galvanostatic cycling. Full details of this investigation have yet to be published.

3.2.2 3-Dimensional Tunnel Structures

Spinel

Liu et al.^[35] performed an ab initio study of a series of spinel structures as potential multivalent ion electrodes. In the case of Ca-ion electrodes, reasonably high voltages for Ca^{2+} intercalation were predicted although the voltages were lower than those for the analogous Li compounds. For example, CaMn_2O_4 was predicted to be a potential Ca^{2+} electrode based on the calculated stability of the charged and discharged forms of the electrode, with a predicted voltage of approximately 3.1 V vs Li/Li^+ , a potential energy density of 1000 AhL^{-1} and a gravimetric capacity of 250 mAhg^{-1} . However, there was also a large calculated volume change with Ca^{2+} intercalation of $>25\%$ which is an indication of instability in the lattice during insertion and extraction of the Ca-ion. Calculated Ca-ion mobilities were also predicted to be favorable in these compounds. However, CaMn_2O_4 normal spinels, have never been reported experimentally probably due to the fact that Ca-cations prefer to occupy high coordination sites rather than the tetrahedral sites in normal spinels. In fact, no structures with Ca-ions in tetrahedral sites have ever been reported^[43]. The possibility of forming the normal CaMn_2O_4 phase

has been investigated theoretically by Dompablo et al.^[34b] and found to be impractical from solid state routes involving the heat treatment of post-spinel phases, requiring temperatures > 3000 K. The preparation of normal spinel CaMn_2O_4 by soft chemistry routes is, however, not excluded. However, the instability of Ca^{2+} in tetrahedral coordination is likely to result in inverse spinels with manganese in the tetrahedral sites, blocking the potential Ca-ion migration pathways.

Arroyo et al.^[44] also investigated theoretically the stable marokite CaMn_2O_4 structure as a potential Ca-ion electrode. They found high barriers to diffusion of the Ca-ions from the initial stable 8-coordinate sites compared to the favorable ion mobility predicted for the normal spinel with low-coordinate site occupation initially. This is in agreement with the findings of Rong et al.^[36] Experimental results showed no electrochemical activity of Ca^{2+} in marokite, in agreement with the theoretical predictions.

Perovskites

DFT modelling of perovskite CaMO_3 ($M = \text{Mo}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co},$ and Ni) compounds as Ca^{2+} electrodes has been reported by Arroyo et al.^[44] Results showed large volume changes $> 20\%$ for calcium perovskites with Ca^{2+} insertion and de-insertion, too large for practical battery applications. The exception here was the case of Mo where the predicted volume changes were close to 10% with an average predicted voltage of 2.5 V, good electronic conductivity, and several stable phases with intermediate calcium content. However, the predicted barriers to Ca^{2+} mobility in this structure were found to be high (2 eV) and intrinsic to the structure, such that they could not be reduced by

changes in composition. This prediction was confirmed experimentally as no electrochemical extraction of Ca^{2+} from CaMoO_3 was observed.^[44]

3.2.3 Chevral Phases

Smeu et al.^[34c, 34d] investigated the use of CaMo_6X_8 (X= S, Se, Te) Chevral phases as possible Ca^{2+} ion electrodes. A favorable voltage of 1.4 V was predicted for X=S vs Ca/Ca^{2+} . The barriers to the ionic mobility of Ca-ions were found to be significantly higher than those for Mg-ions indicating that Ca^{2+} diffusion would be slower than Mg^{2+} diffusion in these compounds. The selenides gave lower diffusion barriers than the sulphides for both Mg- and Ca-ions. Barriers for Ca^{2+} diffusion in Mo_6S_8 were 780 meV and in Mo_6Se_8 520 meV compared with 270 and 180 meV for Mg-ions in the same two compounds. This should be compared with the 525-650 meV quantitative limit for successful battery operation. However, no experimental investigations of Ca-ion insertion in Chevral phases have been reported to date.

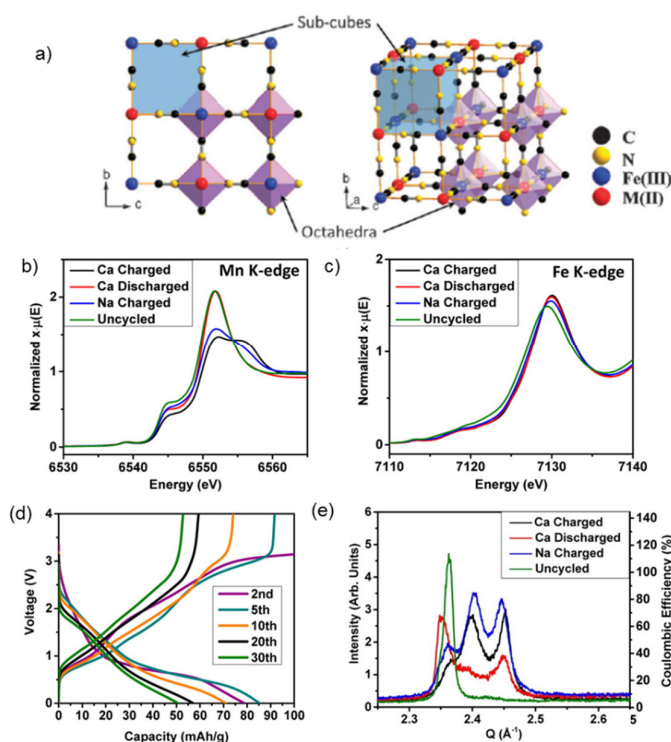


Figure 7. a) Framework of PB analogues, Normalized b) Mn K-edge and c) Fe K-edge ex situ XANES for MFCN after different stages of electrochemical cycling, d) Charge and discharge curves for the galvanostatic cycling of a cell with de-sodiated MFCN as the cathode, calciated tin as the anode, and 0.2 M $\text{Ca}(\text{PF}_6)_2$ in a 3:7 EC:PC electrolyte e) Ex-situ XRD patterns of MFCN after different stages of electrochemical cycling. The 2θ values have been converted to what they would be if measured using $\text{Cu K}\alpha$ X-rays. a) Reproduced with permission.^[45] Copyright 2012, Royal Society of Chemistry. b)- d) Reproduced with permission.^[17] Copyright 2015, American Chemical Society.

3.2.4 Prussian Blue (PB) Analogues

PB analogues are an example of Metal Organic Framework structures and have been investigated widely recently as insertion electrodes for batteries.^[17, 46] These

materials have the general formula $A_xMFe(CN)_6 \cdot yH_2O$ where $A=Li,Na,Mg,Ca$ etc. and $M=Ba,Ti,Mn,Fe,Co$ or Ni . They have a cubic framework (space group: $Fm-3m$) with $M(II)$ and $Fe(III)$ on alternate corners of a cube of corner-shared octahedra bridged by linear cyanide anions which expand the faces of the cubes (**Figure 7a**). PB analogues have recently been explored as electrodes for monovalent ion batteries (Li^+ , Na^+ , and K^+) and have shown excellent cycling rates with good capacity retention and cycle life for K^+ and Na^+ using nickel and copper hexacyanoferrate^[43, 45, 47] and in both aqueous and non-aqueous electrolytes. They can be synthesized in bulk from aqueous solutions of metal salts and hexacyanometallate precursors by co-precipitation. This synthesis can be performed at room temperature and in aqueous solution so the production of these materials is potentially cheaper than the conventional oxide insertion hosts used for batteries.^[47]

Following the success with monovalent cation insertion, Lipson et al.^[17] explored the possibility of Ca -ion insertion in the PB analogue $NaMnFe(CN)_6$. The material was initially desodiated electrochemically and then cycled in a non-aqueous Ca^{2+} electrolyte. A capacity of 75 mAhg^{-1} was recorded for 3 cycles in $0.2 \text{ M } Ca(PF_6)_2$ in a 3:7 EC:PC electrolyte using a BP2000 carbon anode and a rate of 10 mVs^{-1} . They demonstrated unequivocally the insertion and extraction of Ca -ions using EDX spectra and ex-situ XRD at different states of charge (**Figure 7 e**). XANES spectra of the Mn K-edge clearly show a shift of the oxidation state of manganese with charge and discharge confirming Ca^{2+} insertion and extraction. However similar shifts in the Fe K-edge were not observed indicating that only the $Mn^{2+/3+}$ couple is active during the cycling (**Figure 7 b and c**).

Pairing the PB analogue cathode with a calciated Sn anode Lipson et al.^[17] demonstrated the first full-cell CIB with an initial capacity of approximately 80 mAhg⁻¹ (**Figure 7 d**). Initial coulombic efficiency was poor but stabilized after 3 cycles due to the formation of a passivating surface layer. Capacity retention after 35 cycles was only 50%, however, due to possible delamination of the anode, dissolution of the Sn and an increase in cell resistance caused by surface film formation (**Figure 7 d**).^[17] Despite this promising proof of concept demonstration, there is clearly much work to be done to achieve a practical, reversible CIB.

In a follow-up study with nickel hexacyanoferrate Lipson et al.^[46a] found that this material could also reversibly intercalate Ca-ions electrochemically from nonaqueous electrolytes although the initial capacity was only 60 mAhg⁻¹ at a voltage of 2.6 V vs Ca/Ca²⁺ and capacity retention with cycling was poor. These capacities are still too low for practical battery applications.

Padigi et al.^[48] investigated potassium barium hexacyanoferrate as a Ca-ion electrode. The inclusion of the large Ba cations in the lattice further expanded the lattice of the PB analogue to allow easy inclusion of the large Ca-ions. Interestingly they found no electrochemical activity in dry acetonitrile electrolytes but, with the addition of 17% water in the Ca(ClO₄)₂ electrolyte, reversible peaks appeared in the CV. They reported a charge capacity of 62.2 mAhg⁻¹ and a discharge capacity of 55.8 mAhg⁻¹ after 30 cycles (80% of the theoretical capacity of K₂BaFe(CN)₆) although no direct evidence of intercalation was given. The charge transfer resistance was shown to decrease with increasing water content in the electrolyte. The enhancement of polyvalent ion intercalation with water addition has been reported previously.

Kuperman et al.^[49] investigated potassium iron hexacyanoferrate in non-aqueous CIBs and reported reversible capacities of 150 mAhg^{-1} at $23 \text{ mA} \cdot \text{g}^{-1}$ current density. However the charge/discharge curves lack well-defined plateaus and instead are typical of the triangular curves that indicate capacitive behavior. Thus, despite the apparent good performance, there is no concrete evidence of Ca-ion intercalation in this case.

4. Electrolytes

4.1 Non-aqueous electrolytes

The development of electrolytes for Ca-ion batteries is in the very early stages. As discussed in 2.1, it was only in 2016 that the reversible deposition of calcium was demonstrated in non-aqueous electrolytes^[15]. However, the fact that this is only possible at elevated temperatures limits the practical application of this system. Prior to this, detailed studies by Aurbach et al.^[24] had indicated that the formation of passivating surface layers in tetrahydrofuran (THF), γ -butyrolactone (BF), acetonitrile (ACN) and propylene carbonate (PC) with calcium salts (mainly BF_4^- and ClO_4^- anions) showed that deposition of calcium metal from nonaqueous solutions of Ca-ions was not possible at ambient temperatures.

A thorough evaluation of non-aqueous Ca-ion electrolytes by Tchitchekova et al.^[3] concluded that mass transport in these electrolytes is compromised by significant ion-pairing (particularly at high salt concentrations) as well as stronger interactions between the ions and the solvent molecules compared to similar monovalent ion

(Li⁺/Na⁺) electrolytes (**Figure 8**). This difference becomes less marked at high temperatures, becoming insignificant at 100 °C. Ca-based electrolytes also have higher viscosities at ambient temperature than the corresponding lithium and sodium analogues; ion mobility varies inversely with viscosity. For example, for electrolytes based on Ca(ClO₄)₂, viscosities vary from 3 cP at ambient temperature for a 0.1 M solution to 70 cP for the 1 M analogues. Viscosity decreases with increasing temperature.

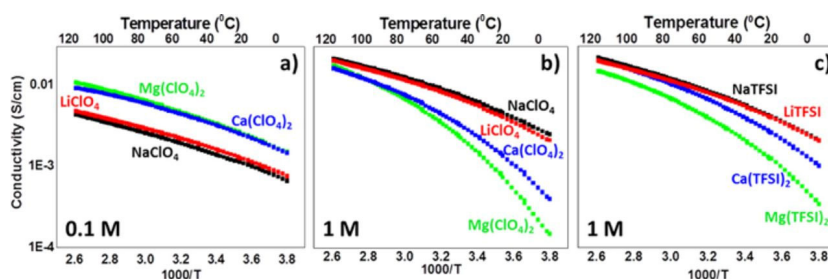


Figure 8. Arrhenius plot of the electrolyte ionic conductivities. Reproduced with permission^[3]. Copyright 2017, Electrochemical Society.

Tchitchekova et al.^[3] concluded that the kinetics of CIBs is limited, not only by the limited mobility of the Ca-ions in the solid state lattice, but also on the slow ion mobility in the non-aqueous electrolytes and issues associated with breaking the cation-electrolyte bonds at the electrode/electrolyte interface (desolvation effects), evidenced by the high impedance of calcium electrodes. This implies that development of electrolytes for Ca-ion systems needs to focus on increasing cation mobility and limiting ion-electrolyte interactions. The use of anion encapsulation and complexation of cations was suggested as a possible avenue to improve the mass transport of Ca-ions in solution.^[3]

4.2 Aqueous Electrolytes

Super-concentrated electrolytes have recently emerged for lithium ion batteries as they have been shown to have significantly different properties compared to the 1 M solutions used traditionally.^[50] Lee et al.^[51] demonstrated that Prussian Blue analogue cathodes (CuHCF) gave different electrochemical performance in super-concentrated aqueous solutions of $\text{Ca}(\text{NO}_3)_2$ compared to dilute solutions. Electrochemical capacities were increased slightly but, most remarkably, the capacity retention with electrochemical cycling was enhanced significantly. When cycled for 150 cycles at a 2 C rate, the cell using dilute electrolyte retained only 58% of its original capacity compared with 97% in the super-concentrated electrolyte. The origin of this improved

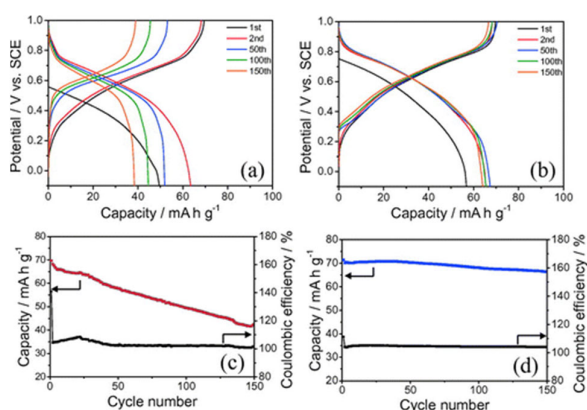


Figure 9: Charge/discharge and cycling performance curves in (a), (c) 1 and (b), (d) $8.37 \text{ mol dm}^{-3} \text{ Ca}(\text{NO}_3)_2$ dissolved aqueous electrolyte during 150 cycles at 2°C .

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performance is not yet well understood but XRD data showed that the CuHCF cathode retained its crystallinity in the super-concentrated electrolyte whereas the dilute electrolyte cathode showed a reduced crystallinity after cycling. It was suggested that lower availability of water molecules may have reduced the extent of hydration of the

Ca-ions and thus reduced their ionic radius in the concentrated solution, facilitating insertion and extraction from the lattice. This is, however, yet to be firmly elucidated. Super-concentrated aqueous electrolytes therefore offer a new avenue for exploration for CIBs with potentially improved performance compared with dilute electrolyte cells.

5. Summary and Future Outlook

The recent demonstration of the cycling of Ca metal in conventional non-aqueous electrolytes at elevated temperatures initiated research into CIBs. However, the use of Ca metal anodes remains problematic. Significant capacity drift and high electrode impedance complicate their application. Alternative, stable, easy to use anodes for Ca-ion studies, for example, alloy anodes or Ca^{2+} insertion anodes with low stable potentials, are required for cathode screening. Preliminary reports of Ca-Sn anodes are interesting and suggest the possibility of similar systems using other metals that are used for Na-ion battery anodes e.g. Bi and Sb.

Ion-pairing and de-solvation issues have been highlighted as problematic for non-aqueous Ca-ion electrolytes at ambient temperatures and electrolyte development is required to address these issues and lower the temperature of cell operation. Suggested strategies include anion encapsulation and cation complexation.

First principle modelling studies have revealed that reasonable Ca-ion mobility can be expected in layered materials such as V_2O_5 where the cations have a high coordination

number which varies only slightly along the diffusion paths. The diffusion rate can be optimized by appropriate selection of host structure, elevated temperatures, co-intercalation of solvents, e.g. PC, or partial hydration of the host to reduce the electrostatic interactions. The investigation of co-intercalated hosts using non-aqueous solvents is an area for possible exploration. The advantages of the presence of the solvent in the host can be obtained without the negatives of, for example, water which would preclude the use of calcium metal anodes. The exploration of other layered host structures such as birnessite and hewettite is also suggested.

Despite indications from DFT modelling suggesting high mobility for Ca-ions in close-packed structure such as the Mn_2O_4 spinel network, no practical demonstration of this has been possible due to the difficulty of synthesizing compounds with Ca-ions in low coordination tetrahedral sites. Soft chemistry routes to form calcium-containing manganese oxides remain to be explored.

To date the best performing cathodes for CIBs are the molecular organic framework structures of Prussian Blue analogues. However, in the studies reported so far, they have low capacities and poor capacity retention in non-aqueous electrolytes. The best reported reversible Ca-ion insertion has been for CuHCF cathodes in super-concentrated aqueous electrolytes with excellent capacity retention at 2 °C and a capacity of 65 mAhg^{-1} . This capacity is, however, still too low for practical application.

Multivalent ion batteries are undoubtedly an attractive prospect for increasing battery energy density. The relatively new field of CIB development can be expected to benefit

from the knowledge base accumulated both in the investigation of other multivalent ion batteries such as Mg^{2+} batteries, and also in the development of Na-ion batteries since the ionic sizes of Na^+ and Ca^{2+} are very similar. There is a need for investigation across all major components of cell design: anodes, cathodes and electrolytes. This represents an opportunity for researchers to initiate studies to increase the pace of development in this important technological area.

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