Research has increasingly shifted toward next-generation batteries that are (1) assembled with earth-abundant minerals and (2) work with multivalent ions. These two aspects synergize with the use of post-Li metals as the battery anode (e.g., Na, K, Mg, and Al). Most recently, calcium (Ca) batteries have emerged as a promising next-generation electrochemical energy storage system (Figure 1). When promoting next-generation systems, common figures of merit (FOMs) are used for comparison purposes, including theoretical capacity; theoretical energy density; rechargeable cycles; and, as expected, the performance of incumbent Li-ion or state-of-the-art Li-metal technology to assess possible performance parities (or current disparities). However, often such comparisons use ideal and even unrealistic values that may inevitably favor Li-ion or emerging Li-metal technology or favor one next-generation system while relegating others. Whereas, closer consideration of state-of-the-art metrics can reveal a more practical, realistic comparison and thereby level the playing field to allow proposed Ca battery technology to garner attention. Furthermore, comparisons must acknowledge the nascent level of Ca battery research and anticipate significant advances with continued research. The first part of this Viewpoint discusses some primary metrics to consider for Li and particularly Ca battery systems and shows how a fairer or realistic comparison reveals the clear promise of Ca battery chemistry. The second and final part of this Viewpoint discusses proposed approaches to advance calcium batteries toward becoming a veritable post-Li energy storage technology.

First, it is important to briefly emphasize the benefits of calcium batteries in terms of materials’ supply and cost. Calcium is the most abundant alkaline element and fifth most abundant metal in the Earth’s crust (4.1%), greater than Na, K, Mg, and Li, and the third most abundant metal after Al and Fe. As in the case of other earth-abundant minerals, the future calcium battery industry will benefit from the large world reserves of calcium sources. Combined with large annual production, a clear benefit of calcium batteries, specifically over Li metal, would be its inevitably low cost and adequate supply to meet demand. This is especially the case for the United States which has the greatest level of annual production. Also, from a safety standpoint, the high melting point of Ca metal (∼842 °C) is also an incentive when compared to the lower melting point of Li metal (180.5 °C). Supply and cost metrics affirm the benefits of calcium batteries, as discussed in detail in the Supporting Information.

The first FOMs often considered with regard to battery capability are reduction potentials (for which Li and Ca are comparable) and more importantly theoretical anode capacity, as summarized in Figure 2a,b. Li is a favorite in terms of gravimetric capacity (3861 mAh/g), followed by Al (2980 mAh/g) and then Mg (2205 mAh/g). Likewise, Al, Zn, and Mg show promising volumetric capacities (8046, 5851, and 3833 mAh/L, respectively). Unfortunately, Ca, along with K and Na, do not apparently look as promising. Specifically, while a metallic calcium anode provides a volumetric capacity (2073 mAh/cm3) comparable to that of lithium metal anodes (2062 mAh/cm3), it offers a lower gravimetric capacity (1337 mAh/g). Ca is nowhere close to the FOMs in this regard in comparison to Al, Zn, and Mg, but it outperforms Na.

While suitable for a preliminary assessment of capacity and energy density, such a comparison is far from realistic. First, the dischargeable content for a metal anode is nowhere close to 100% and may differ among metals. Rather, practical discharge capacities must be considered, which can be
significantly lower so as to nullify any differences among metal anodes. Second, discharge/charge capacity is more dependent on the discharge/charge capacity of the cathode (i.e., specifically related to intercalation or conversion processes) rather than the deposition/dissolution at the metal surface. Third, the anode is one of several battery cell components, all of which are considered in calculating the cell weight and/or volume to determine capacity and energy density. Hence, the advantage of certain metal anodes diminishes when considering practical discharge capacities and cell-level capacity and energy density.

Realistic FOMs may be more accurately gleaned from state-of-the-art Li metal batteries. For example, recent Li metal batteries with cell configurations Li//Li2O, Li//Li-Ni0.8Co0.1Mn0.1O2, and Li-MgF2/3D graphene//Li-Ni0.8Co0.1Mn0.1O2 provide energy densities of approximately 500, 765, and 360 Wh/kg, respectively.6–8 These experimental FOMs, rather than theoretical capacities of the metal anode itself, should be emphasized more so in comparisons. It is also possible that theoretical energy densities could conversely favor calcium over lithium, as in the case for a calcium sulfur (Ca//S) battery (3202 Wh/L and 1835 Wh/kg, versus 2800 Wh/L for Li//S).9

While cell-level assessments of Ca metal batteries need to be thoroughly pursued, recent achievements may be initially compared to the energy densities mentioned above. Thus far, several promising Ca-metal battery configurations have been realized: Ca//V2O5, Ca//Ca4Fe9O17, Ca//LiTiO2, Ca//PAQFiber, Ca//TiS2, Ca//FePO4, Ca//Ca3Co2O6, Ca//PAQFiber, and Ca//S.9–17 Figure 2b,c summarizes their capacities, operating voltages (average), and energy densities, including those for Li cells as discussed above. Thus far, Ca battery energy densities can reach as high as 250 Wh/kg, with discharge charge capacities between 60 and 250 mAh/g and operating voltages between 1 and 4 V. Current densities achieved thus far are in the range of 20–500 mA/g, and C-rates from 0.2 C to upwards of >5 C with slightly lower capacities at these rates than Li batteries.9,11,12,16 Promising rechargeable batteries have been realized with Ca//LiTiO2 and Ca//C-fiber, specifically owing to successful electrolyte formulations (Ca(BH4)2 + LiBH4 in THF, and NaPF6 in 1:1:1 by v/v EC-EMC-DMC, respectively) that help sustain Ca redox activity by providing a stable Ca2+-permeable artificial solid electrolyte interface (SEI) to enable long-term cycling or increase cation mobility in the electrolyte. Other systems are rechargeable (as indicated in Figure 2c), but with moderate fading, while the others show significant fading over cycling.

Such comparisons of the experimentally realized cell parameters for Li and Ca batteries (voltages, capacities, and energy densities) show how the latter is not far behind, especially keeping in mind the significant level of advancement opportunities (thus far realized for Li batteries) that have yet to be explored and developed for calcium batteries. With the possibility (or inevitability) of discovering higher-voltage Ca cathodes, energy densities can certainly reach those of Li, and combined with greater capacities that may be achieved with relatively lighter compounds, this could lead to Ca batteries becoming a promising post-Li alternative. Likewise, while Ca//S batteries remain below the capacity and energy density of current state-of-the-art Li//S cells,18,19 the latter has undergone sophisticated materials enhancements20 yet to be explored in Ca/S configurations; hence, improvement in...
capacities and energy densities may also be anticipated. Overall, while indeed Ca battery capacities and energy densities are currently below those for state-of-the-art Li metal batteries, the comparisons made in this Viewpoint based on experimental data highlight a more realistic (and hopeful) perspective and motivate continued research and advancement of Ca batteries.

Total cell weight or the individual weights of electrode components is another FOM considered, especially in the case of portable electronics and, of course, for electric vehicles (EVs). While cell weight is considered in the overall energy density of prototype cells (e.g., reporting the mass the entire cell), often it is the case that the inherently greater molar mass and weight of the electrodes is a factor discriminating away from next-generation batteries. Indeed, Ca metal itself is ~5.77 times heavier than Li metal (on a molar basis), which may be intuited to mean a significantly heavier battery cell. However, the thin anode component (max. 100 µm thickness) is not a significant contributor to battery cell weight; the greater contribution to the weight comes from the cathode.21 Likewise, it has been found that lower calcium salt concentrations are required (1 M vs ~3 M) to achieve similar ion conductivities,22 thereby obviating any concern over a possible increase in electrolyte component weight. The increase in weight with a calcium equivalent intercalation cathode, for example, could also be marginal, especially if lighter transition metals (TMs) are found favorable for Ca cathodes.

To provide meaningful comparisons of Li and Ca cells, a cell configuration model21 was employed to consider weights of different incumbent Li-ion, Li-metal, and Ca-metal battery cell configurations (Figure 3a). Cathodes present in the literature, described herein, as well as theoretically studied perovskite (CaMnO₃) and spinel structures (CaM₂O₄) with different transition metal centers for which predicted open-circuit voltages are available²³,²⁴ are used for this comparison. There is an ~20 mg/cm² increase (or greater) in the cell weight for calcium batteries, with the lowest (experimental system) being Ca//V₂O₅, which also provides a cell weight similar to that of incumbent Li-ion technology. Ca//S is also ~20 mg/cm² greater in weight than Li/S. Nevertheless, cell weights provide a far more practical picture in comparison to the exaggerated values based on a comparison between the Li and Ca metals themselves. In terms of cell capacities (Figure 3b), Ca/|TiS₂, Ca/V₂O₅, and Ca/LTO cells all have comparable but slightly lower capacities than state-of-the-art Li batteries. The theoretical binary metal oxides (perovskite and spinel) can provide increases to gravimetric capacity and significant increases to volumetric capacity, owing to their greater material densities. The Ca//CaFeO₁₇ and Ca//FePO₄ cells are significantly heavier (178 and 100 mg/cm²), yet owing to their relatively large cell potentials, they become potentially competitive for volumetric capacity. With further research and development, it may be possible to optimize cell weight toward light yet energy dense calcium battery cells, for example, by using suitable calcium lanthanide oxide cathodes. Synthesis and electrochemical studies have already begun in perovskite cathodes, such as CaMnO₃.23 Some calcium battery cells also provide reductions in cost performance ($/kWh) as discussed in the Supporting Information.

Calcium batteries still present vast opportunities for discovery, exploration, and research toward proposing battery architectures that build on current achievements or those which propose novel approaches toward greater capacities, cell potentials, and energy densities. The remainder of this Viewpoint discusses pathways to further development that can lead to both strategic steps forward and even leaps in calcium battery technology. Indeed, with such advances, Ca batteries can become a competitive post-Li alternative.

To begin, transitioning from monovalent (+1) to a multivalent system (+2) in the case of calcium presents several challenges centered on three issues: (1) redox activity at the metal anode, (2) mobility in electrolytes, and (3) intercalation–deintercalation in cathodes. The larger ionic radius (100 pm for Ca²⁺ vs 76 pm for Li⁺), higher valency, and greater charge density result in slower processes, such as transport through the SEI, electrolyte, and cathode. Thus far, the approaches to electrolyte and cathode development generally seek to employ Ca-equivalents from other metal systems, such as Mg owing to its valency (2+) and Na for its similar ionic

Figure 3. Predicted areal weight and capacities for experimental and theoretical battery configurations spanning Li metal, Li–S, Ca metal, and Ca–S cells, including both experimental and theoretical calcium cathodes. (a) Pouch cell weights on a per cm² basis for battery cell configurations. Cells weights are the summative combination of separator + electrolyte, anode, and cathode. All amounts and assumptions are in accordance to the parameters provided by the reported cell model.²¹ (b) Predicted capacities of the respective pouch cell configurations.
radius (102 pm). Examples include Li- and Mg-inspired salts such as Ca(TFSI)\(_2\) and Ca(B(Ohf)\(_2\))\(_2\) and cathodes such as sodium vanadate, magnesium vanadate, and sodium vanadium phosphates.\(^{26-30}\) Other examples explored in Ca-ion batteries (some of which are aqueous) include calcium manganate, layered vanadium phosphates, and potassium copper hexacyanoferrate.\(^{31-33}\) While trying Ca analogues among others has provided some headway, more fundamental understanding of the unique coordination and transport properties (in electrolytes, cathodes, and SEI) will be needed to inspire more out-of-the-box thinking to discover material systems better tailored to the unique properties of Ca\(^{2+}\).

Redox activity at a Ca metal interface has seen significant advancement over the past few years,\(^{14,26,27,34,35}\) specifically through greater understanding and proper selection of suitable electrolytes. Nevertheless, electrolytes remain a key area of study. In particular, unlike with Li metal, the even stronger reductive capacity of Ca metal renders many electrolytes unstable, and their decomposition products can passivate the Ca metal interface or create an SEI that presents sluggish Ca\(^{2+}\) transport. In-depth studies of a wider range of electrolytes (solvent and salts) should be explored, particularly to establish correlations with resultant SEI composition and Ca\(^{2+}\) permeability. A promising area of study is the use of mixed cation salts, whereby the SEI composition as well as electrolyte properties can be engineered to be more suitable for Ca\(^{2+}\). Examples include the use of NaPF\(_6\) whose decomposition forms a stable Na\(_2\)O SEI layer permeable to Ca\(^{2+}\) ions,\(^{12}\) and the use of Li salt to reduce the strength of solvent coordination to Ca\(^{2+}\) to enable faster kinetics.\(^{11}\) Use of solid and gel polymer electrolytes also opens possibilities to stabilize the Ca anode.\(^{36-38}\) These alternatives are important should challenges persist with native Ca electrolytes being unable to provide stable SEI formation and competitive mobilities. Beyond suitable electrolytes, there are also opportunities for engineering the anode structure. For example, porous metal anodes may be explored to enable faster rates (via increased surface area) and to mitigate dendritic growth at high current densities,\(^{39}\) as is the case for Ca at high deposition rates.\(^{40}\) These aspects are critical should calcium ever be considered for portable electronics and are critical for electric vehicles. Combined with electrolytes that enable long lifetime cycling, this may be a path toward enabling higher battery currents and greater cycle lifetime. Electrolyte interactions at the cathode interface are also critical. Key to insertion–deinsertion kinetics is the capability for the cathode to induce, even possibly catalyze, the desolvation of Ca\(^{2+}\) from its coordinated solvent complexes.

Critical to the establishment of high energy density calcium batteries is the development and demonstration of high-voltage cathodes, combined with good transport kinetics to enable high current densities. This entails host materials suited for the large size of Ca\(^{2+}\) ions that also yield low migration energy barriers. However, beyond available lattice sites for Ca\(^{2+}\) in the host cathode, the capability to drive the transition metal center to realistic oxidation states will be a greater determinative factor in the realizable capacity. Hence, examining the material hosts with transition metals with different redox couples is essential. Some candidate TM s and their redox couples suggested as possibly exceeding Li cathode capacities are V\(^{3+}/V^{5+}\), Mn\(^{2+}/Mn^{4+}\), Cr\(^{3+}/Cr^{6+}\), and Mo\(^{3+}/Mo^{6+}\).\(^{41}\) In addition to the importance of a reliable redox couple is the redox stability of the intercalation compounds over the range of TM oxidation states, which is critical to avoiding undesirable and irreversible phase transformations. The use of binary and even ternary transition metal compounds to mitigate the dependence of intercalation–deintercalation on the redox couple of a single transition metal is one option. Work continues on the study of calcium transition metal oxides, focusing on crystal structures with transition metals such as Mn, Co, and V, among others.\(^{5,25,28}\)

With regard to mobility, Ca cathode materials need to provide an open framework with loosely coordinating sites that form a connected network for the transport of Ca\(^{2+}\) ions. Furthermore, the anionic framework of the material must be easily polarizable, which in turn allows the electron distributions to be “soft”, to amply support the multiple transition state configurations that Ca\(^{2+}\) must assume to move from one lattice site to a neighboring one. Theoretical predictions indicate this through reductions in the migration energy barriers of the transition states, with \(\sim 100\) meV being a benchmark from Li systems, and Ca migration barriers thus far calculated are above 250 meV, with the smallest values calculated for hosts with Mn, Cr, Ti, and Mo transition metal centers.\(^{42}\) Use of transition metal sulfides (Ca\(_2\)S\(_2\)) can introduce a S\(^2-\)-based anion framework that provides a greater “softness” for Ca\(^{2+}\) transport, however, at a slight penalty to cell voltage compared to its O\(^2-\) counterpart parts. Another approach is to employ layered materials, thereby enabling faster diffusion through storage and transport in the van der Waals gap, as opposed to diffusion via 3D hopping between lattice sites. While this can increase transport kinetics, it may also come with a slight reduction in cell voltage, a trade-off that may be optimized via tuning the composition. For example, layered TiS\(_2\) provides smaller migration energy barriers when the layer spacing is adjusted,\(^{43}\) and further reductions can be achieved when sulfur is replaced with Se (i.e., TiSe\(_2\)).\(^{42}\)

Finally, issues with intercalation–deintercalation hosts can be circumvented by exploiting conversion cathodes, such as sulfur (Ca–S batteries), combined with solutions to mitigate polysulfide dissolution.\(^{20}\) Other options include the use of organic cathodes with redox-active centers. Polymer cathodes have proven promising for Mg batteries,\(^{43}\) and anthraquinone and benzoquinone groups can provide theoretical Ca battery energy densities of 400 and 941 Wh/kg.\(^{10}\) In addition, metal–organic frameworks (MOFs)\(^{44}\) are an attractive materials platform to consider, owing to their rich chemistry providing a parameter space to tune Ca\(^{2+}\) migration, capacity, and energy density. MOFs have already shown promise for Na as well as Zn batteries\(^{45}\) but are yet to be thoroughly explored for Ca batteries.

Based on the above considerations, this Viewpoint proposes calcium transition metal oxides and sulfides, and particularly layered structures, as potential cathode candidates to be pursued, with possibly better performance with binary or ternary transition metal centers in the host lattice. Such materials can also provide benchmarks for further advances. A trade-off may have to be accepted between cathode voltage and kinetics, with a preference toward lighter compounds to optimize for greater specific capacities. There are also great opportunities in the continued exploration of MOFs or organic materials, for which the balance between better kinetics, lower weight, yet comparable capacities could enable Ca batteries to attain competitive performance. The combination of a Ca metal anode with a suitable electrolyte that combines high cation conductivity with a stable SEI and a high-capacity, high-
voltage cathode shows enormous potential to finally reach or exceed the FOMs of Li metal batteries. Of course, cycling lifetime, examination of cell failure, and reaching commercial grade efficiencies will need to be achieved, the work for which will naturally follow fundamental advances.

In the exploration of new cathodes and electrolytes, beyond battery level studies, rigorous characterization will be necessary to arrive at unambiguous conclusions on the transport, kinetic, and electrochemical processes. X-ray diffraction (XRD)\(^{46}\) combined with high-resolution transmission electron microscopy (HRTEM)\(^{47}\) are critical to correlate Ca\(^{2+}\) intercalation with changes in the cathode phases and structure. Inductively coupled plasma mass spectrometry (ICP-MS),\(^{48}\) high-energy X-ray spectroscopies (XAS and XANES),\(^{30}\) X-ray photoelectron spectroscopy (XPS),\(^{49}\) and solid-state NMR\(^{50}\) are key to understanding the oxidation and coordination environment under both intercalation and deintercalated states. These characterization techniques must also be combined with quantitative spatial analysis of composition, such as through mapping with energy dispersive X-ray spectroscopy (EDS) or electron energy loss spectroscopy (EELS).\(^{49}\) With regard to electrolytes, cyclic voltammetry and other voltage/current scanning techniques must be followed by careful spectrometric (Raman, FTIR, and EDS)\(^{54,49}\) and elemental analyses to elucidate decomposition products and the composition of the solid electrolyte interface. Likewise, assessment of the bulk Ca anode surface morphology\(^{44,45,50,51}\) during plate/strip cycles will be critical rather than analysis on single deposits. In situ techniques employed to further understand all processes will prove indispensable to these efforts.

The aim of this Viewpoint is to provide a fresh perspective with regard to the potential of calcium metal batteries in the context of other systems, specifically Li, using better figures of merit that are more realistic, thereby providing a more balanced and fair comparison. There are presently several Ca battery configurations that provide promising capacities and energy densities, combined with low cost and cell weights. With further research and development, calcium batteries may become an asymptote post-Li technology. The aim herein is for calcium metal batteries to be viewed as having significant, competitive potential; hence, they should garner attention for research and exploration and consideration as a next-generation energy storage technology.

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## ASSOCIATED CONTENT

*Supporting Information*  
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c00593.

Discussion on the availability, supply, and cost metrics for metal anodes and metal resources; cost performance of experimental and theoretical calcium batteries (PDF)

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