Electrochemical Signatures of Interface-Dominated Behavior in the Testing of Calcium Foil Anodes

To cite this article: Aaron M. Melemed and Betar M. Gallant 2020 J. Electrochem. Soc. 167 140543

View the article online for updates and enhancements.
Fundamental research and practical assembly of rechargeable calcium (Ca) batteries will benefit from an ability to use Ca foil anodes. Given that Ca electrochemistry is considered a surface-film-controlled process, understanding the interface’s role is paramount. This study examines electrochemical signatures of several Ca interfaces in a benchmark electrolyte, Ca(BH4)2/tetrahydrafuran (THF). Preparation methodologies of Ca foils are presented, along with Ca plating/stripping through either pre-existing, native calcium hydride (CaH2), or pre-formed calcium fluoride (CaF2) interfaces. In contrast to earlier work examining Ca foil in other electrolytes, Ca foils are accessible for reversible electrochemistry in Ca(BH4)2/THF. However, the first cyclic voltammetry (CV) cycle reflects persistent, history-dependent behavior from prior handling, which manifests as characteristic interface-derived features. This behavior diminishes as Ca is cycled, though formation of a native interface can return the CV to interface-dominated behavior. CaF2 modification enhances such interface-dominance; however, continued cycling suppresses such features, collectively indicating the dynamic nature of certain Ca interfaces. Cell configuration is also found to significantly influence electrochemistry. With appropriate preparation of Ca foils, the signature of interface-dominated behavior is still present during the first cycle in coin cells, but higher current density compared to three-electrode cells along with moderate cycle life are readily achievable.

Over the past few years, several groundbreaking studies have reported reversible plating/stripping of Ca with high Coulombic efficiencies in select organic electrolytes for the first time. In 2016, Ponrouch et al. demonstrated Ca plating/stripping using Ca(BF4)2/ethylene carbonate (EC):propylene carbonate (PC) at moderately elevated temperatures, with a native SEI found to contain both calcium fluoride (CaF2) and organic compounds.\(^7\) This work was built upon by Biria et al., who reported plating/stripping at room temperature albeit with relatively low areal current densities (<0.5 mA cm\(^{-2}\)).\(^8\) In 2018, Wang et al. reported Ca plating/stripping from Ca(BH4)2/tetrahydrafuran (THF) at room temperature with higher currents (~10 mA cm\(^{-2}\)), high Coulombic efficiency (~95%), and an SEI solely comprising calcium hydride (CaH2)\(^9\); additional studies by Ta et al. and Hahn et al. have further elucidated the role of this electrolyte system by proposing a chemical-electrochemical deposition process\(^10\) and examining the role of Ca(BH4)2 salt in this process.\(^11\) Two independent studies subsequently reported another active ether-based electrolyte, Ca(B(Orf)d3)/1,2-dimethoxyethane (DME), with an SEI that includes CaF2, CaF2, dimethoxyethane (DME), and CaF2 interfaces. This chemical-electrochemical deposition process\(^12\) and the derived interfacial chemistry comprising the SEI on Ca.

The high reactivity of Ca metal, these studies have investigated Ca electrochemical behavior predominantly by plating/stripping Ca onto a Ca-free working electrode (Au, Pt, Cu, stainless steel).\(^13\) This Ca is typically sourced from a counter electrode, with Ca freshly plated and then immediately stripped upon charge. During this process, SEI formation occurs in conjunction with Ca electrodeposition under highly dynamic conditions. This is different from how Ca metal anodes would be used, which inevitably involves significantly longer exposure times to electrolyte; here, some degree of static SEI will be present before electrochemistry begins and can re-form during other periods of cell rest, in addition to dynamically during current flow. While this static SEI may be
formed via chemical reaction with the electrolyte, there is also ample opportunity for interfacial parasitic reactivity to occur well before cell assembly even begins. For instance, Ca foil anodes may be hindered by the tendency to form a stable CaO passivation layer at trace O2 partial pressure, as well as its affinity for reaction with trace solvent vapor and other atmospheric contaminants during processing and cell assembly as noted by others. The nature of these different types of interfaces on Ca metal, and their relative stabilities under electrochemical conditions, is important to understand so that the electrochemical features and performance of Ca foils can be properly interpreted.

The purpose of this study is to investigate the electrochemical effects that several different interfaces—pre-existing interfaces on processed Ca foil, electrolyte-derived native SEI and synthetic inorganic surface films—have on Ca metal foil anodes. Such a study is timely and possible only very recently, given significant progress by the above groups in the identification of electrolytes that form less-blocking interfaces than those reported in early Ca research. This study necessitated, first, a look into the preparation of Ca foil for practical use in order to compare morphologically- and compositionally-consistent electrode surfaces. For electrochemical measurements, we utilized 1.5 M Ca(BH4)2/THF as the baseline electrolyte; the native CaH2 SEI that this electrolyte forms on Ca was found previously to grow over time. This allowed a controlled look into the effects that cell rest, which invites increases in presumed CaH2 thickness, has on subsequent electrochemistry. CaF2 was chosen as the synthetic surface film due to its relevance in Ca SEI phases. Note that CaF2 has been postulated to be an anion conductor, whereas CaH2, which was also thought to be an anion-conductor, has recently been suggested to have a lower Ca migration energy barrier than CaF2, which could allow some degree of cation transport. With the testing of CaF2-coated Ca electrodes, this study also includes a first assessment into the ability of modified SEIs to influence Ca electrochemistry, which would provide a possibly interesting engineering strategy for exploring the use of Ca metal in batteries. Overall, this work shows that as reversible Ca plating/stripping is unlocked in emerging electrolyte; the native CaH2 SEI that this electrolyte forms on Ca was found previously to grow over time.19 This allowed a controlled look into the effects that cell rest, which invites increases in presumed CaH2 thickness, has on subsequent electrochemistry. CaF2 was chosen as the synthetic surface film due to its relevance in Ca SEI phases. Note that CaF2 has been postulated to be an anion conductor, whereas CaH2, which was also thought to be an anion-conductor, has recently been suggested to have a lower Ca migration energy barrier than CaF2, which could allow some degree of cation transport. With the testing of CaF2-coated Ca electrodes, this study also includes a first assessment into the ability of modified SEIs to influence Ca electrochemistry, which would provide a possibly interesting engineering strategy for exploring the use of Ca metal in batteries. Overall, this work shows that as reversible Ca plating/stripping is unlocked in emerging electrolyte systems, the electrochemistry is increasingly limited by addressable concerns such as preparation methodologies and history of Ca foil interfaces.

Experimental
Preparation of calcium electrodes.—All Ca electrode preparation was conducted inside an argon glovebox (H2O content <0.1 ppm, O2 content <0.1 ppm, MBRAUN). Two methodologies were investigated: (1) pressing of Ca dendritic pieces and (2) polishing of pre-rolled Ca sheets. For (1), Ca dendrites (99.99% pure, shipped under Ar, Sigma Aldrich) were simply flattened with a manual mechanical press between plastic sheets. For (2), pre-rolled Ca sheets (99.9% pure, 0.25 mm thick, shipped in mineral oil from ACI Alloys) were cleaned and then mechanically polished in a three step process using a Dremel® grinder with a silicon carbide grinding bit. For step 1, the protective oxide layer was polished off at 5,000 rpm. For step 2, a different, clean silicon carbide bit was equipped and used to further polish the surface at 10,000 rpm. For step 3, ~15–20k rpm was used to smooth the surface, obtaining a reflective finish. The resulting polished Ca was then cut into thin strips or punched into 12-mm diameter circular disks and immediately transferred into a reactor for film synthesis (CaF2) or into cells for electrochemical measurements. For electrochemical measurements in glass cells, ~2min occurred between polishing and the beginning of the measurement. For coin cells, ~10min occurred between polishing and coin cell crimping given required cell assembly times.

Synthesis of CaF2-modified Ca electrodes.—Freshly-polished and -shaped Ca foils were loaded onto a stainless steel mesh and placed inside a homemade stainless-steel reaction vessel sealed using Cu O-rings, which was purged with argon (Ultra-high purity 5.0 grade, Airgas) for one minute and then pressurized to a final gauge pressure of ~15 psi. The reaction vessel was then placed onto a hot plate inside the Ar glovebox and heated to the desired temperature as measured by an embedded thermocouple, after which the reaction vessel was purged with NF3 (99.999%, Electronic Fluorocarbons, LLC) for one minute and then pressurized to a final gauge pressure of ~5 psi. The reaction vessel remained on the hotplate for one hour until it was purged with Ar (UHP 5.0 grade, Airgas) for five minutes, after which the hotplate was turned off until it cooled down to room temperature. The CaF2-covered samples were then removed from the vessel and immediately utilized for chemical/electrochemical measurements or analysis. Formation of CaF2 was separately confirmed by X-ray diffraction and X-ray photoelectron spectroscopy, and typical thicknesses for the reaction conditions used herein were ~100 nm.

Electrochemical characterization.—All steps occurred within an Ar glovebox. As-received THF (anhydrous, 99.9%, Sigma Aldrich) and EC (99%, Acros Organics):PC (99.7%, Sigma Aldrich) (1:1 v/v) were dried over 4 Å molecular sieves for over 72 h; water content was determined to be <10 ppm through KF titration. Ca(BH4)2·2THF (Sigma Aldrich) was added to THF and the solution was rested overnight until translucent. Ca(TFSI)2 (99.5%, Solvionic) was vacuum dried at 120 °C overnight in a Buchi apparatus. CaBF3 (95%, Apollo Scientific) was vacuumed dried at 120 °C overnight before mixing with EC:PC and then further drying the solution with 4 Å molecular sieves for several days. A glass three-electrode cell (Pine Research, Low Volume Cell) was used for electrochemical measurements. The Au working electrode was 1.6 mm in diameter and surrounded by a PCTFE shroud (Pine Research, LowProfile). Au foil (0.025 mm thick, 99.99%, Sigma Aldrich) was cut into thin strips or 12 mm disks, soaked in sulfuric acid for 20 min, and rinsed with deionized water before vacuum drying overnight. Freshly-prepared Ca or Au foil working electrodes were affixed in stainless steel holders and submerged in the electrolyte; the submerged area was measured manually for each electrode after testing. Ca reference electrodes utilized the same setup. A Pt wire coil (Pine Research, LowProfile) was used as the counter electrode. 2032-type coin cells were assembled using a coin cell crisper (MSK-160E, MTI Corporation) inside the Ar glovebox with a crimping pressure of 0.81 tons. Whatman glass fiber separators were used for coin cell measurements. A Bio-Lock potentiostat was used for cyclic voltammetry and galvanostatic experiments. Cyclic voltammetry (CV) sweep rates were 25 mV s⁻¹, beginning at the open circuit potential and scanning to −1 and 2 V vs the Ca reference, unless indicated otherwise.

Materials characterization.—Scanning electron microscopy (SEM) imaging was conducted on a Zeiss Merlin high-resolution instrument with an accelerating voltage of 1 kV and a beam current of 100 pA. For SEM measurements performed on post-tested electrodes, samples were first rinsed with THF and then dried under vacuum before being loaded into air-sensitive transfer holders. X-ray diffraction (Supplementary Information) was conducted on a PANalytical X’Pert PRO instrument with a Cu Kα X-ray source. Samples were either put onto glass slides and protected from air using Kapton tape (3 M Company) during measurements or placed inside an air-sensitive holder.

Results and Discussion
Preparing smooth, consistent Ca foil for electrochemical testing is nontrivial due to its reactivity and relative hardness, which makes it significantly less processable than Li metal. All Ca preparation occurred inside an Ar glovebox (<0.1 ppm O2 and H2O). To test different preparation methodologies, Ca was acquired in two forms: so-called dendritic pieces used by some researchers and pre-rolled sheets (99.9% pure, 0.25 mm thick, shipped in mineral oil from ACI...
Alloys)\textsuperscript{10} as shown in Figure 1. The dendritic pieces (Fig. 1a) were flattened with a mechanical press; however, inconsistent shapes and surface morphologies were obtained (Fig. 1b). While certain areas of the pressed Ca were quite smooth microscopically, other areas were rough and inconsistent (Fig. 1c). The pre-rolled Ca sheets could be mechanically polished to remove the protective oxide layer and obtain a more consistent surface morphology (Fig. 1d). The polished foils were then cut or punched into desired shapes (Fig. 1e). Microscopically, these polished foils had a relatively smooth morphology albeit with some unavoidable micron-scale striations inherent to the polishing process (Fig. 1f). Different polishing tools were investigated and were found to affect the remaining surface oxide content, with carbide-based tools preferable to oxide-based tools to minimize imparting any additional CaO under aggressive polishing conditions. It should be noted that the polished Ca surface visibly discolors over several days in the glovebox environment, likely due to contamination with trace levels of solvent; this pre-attened with a mechanical press; however, inconsistent shapes and surface roughness. (d) Ca foil; the dark portion is covered with the as-received oxide layer, and the shiny portion has undergone an initial polish with a silicon-carbide tool. (e) Fully-polished Ca foil following subsequent polishing steps, punched into a 12 mm diameter circle. The inset shows the same sample, angled to minimize reflection. (f) SEM image of the mechanically-polished Ca foil.

Figure 1. Processing calcium metal. (a) Ca dendritic pieces as received. (b) Ca pieces after flattening with a mechanical press. (c) SEM image of a mechanically-pressed Ca piece; the left image shows a smooth area, while the right image shows an area with surface roughness. (d) Ca foil; the dark portion is covered with the as-received oxide layer, and the shiny portion has undergone an initial polish with a silicon-carbide tool. (e) Fully-polished Ca foil following subsequent polishing steps, punched into a 12 mm diameter circle. The inset shows the same sample, angled to minimize reflection. (f) SEM image of the mechanically-polished Ca foil.

Voltammetry (CV) in 1.5 M Ca(BH₄)₂/THF with a sweep rate of 25 mV s\textsuperscript{−1}, a commonly-used scan rate in Ca plating/stripping measurements.\textsuperscript{19,20,22} Ca foil was used as reference electrode (RE) and a Pt coil was used as counter electrode (CE). It should be noted that there have been reported issues with Ca as RE, wherein the reference can shift by hundreds of millivolts positive to the nominal Ca/Ca²⁺ redox potential in Ca(BF₄)₂/EC:PC,\textsuperscript{17} likely arising from chemical passivation on the Ca RE surface.\textsuperscript{31} In spite of these limitations, such dramatic shifts have not been observed in previous studies in ether-based electrolytes.\textsuperscript{19,22,23} so a Ca RE was used herein. Figure 2b shows the CV behavior using a gold disk working electrode (WE), which was performed first to validate our setup vs the initial study on this electrolyte system by Wang et al.\textsuperscript{19} Upon the cathodic scan, Ca deposition began at an overpotential of −0.25 V vs Ca/Ca²⁺, reaching a maximum plating current density of approximately −11 mA cm\textsuperscript{−2} at −1 V. Next, the plated Ca was oxidized, with the anodic current density reaching approximately 13 mA cm\textsuperscript{−2} at 1 V and then dropping down to zero by 1.3 V. Comparing the charge passed during stripping vs plating, the Coulombic efficiency of this first scan was 93.9%. These results agree well with the current densities (∼10 mA cm\textsuperscript{−2}) and Coulombic efficiency (∼95%) from the original study.\textsuperscript{19} This electrochemical behavior is also reasonably reversible over subsequent cycles. By scan 25, the general CV shape is similar to that of scan 1, with a relatively minor decrease in maximum oxidative current density (∼10 mA cm\textsuperscript{−2}) and a more significant decrease in Coulombic efficiency (86.5%).

The same CV scan was next conducted with Ca foil as the WE, which is shown alongside the Au disk WE in Fig. 2c. To calculate areal current density for these electrodes, the submerged surface area was measured after each trial; a typical area was ∼0.3 cm\textsuperscript{2} (compared to 0.02 cm\textsuperscript{2} for the Au disk WE). With these relatively small areas, rounding error in area calculation could approach ±10%. The current densities of Ca foils were highly reproducible across trials; however, the plating voltage-current slope with the Ca WE was significantly more resistive than that of the Au disk. Consequently, the maximum current density of the Ca WE was nearly an order of magnitude smaller than with the Au WE (1.4 vs 11 mA cm\textsuperscript{−2} at −1 V vs Ca/Ca²⁺). In addition, the onset plating potential of the first cycle was −0.4 V for Ca, larger than the −0.25 V onset plating potential on Au. The origin of these disparities will be discussed in detail later.

To more closely examine the origins of unique CV features on the Ca WE, several CV measurements were conducted on Ca foil subjected to either “plating first” or “stripping first” cycles. CVs of freshly-polished Ca foils are shown in Fig. 2d. When extensive efforts were taken to eliminate any possible exposure of the fresh Ca to contaminants such as trace solvent—by extensively purging the glovebox before each measurement and minimizing Ca handling time to <2 min prior to electrolyte immersion—the “freshly-polished” Ca foil (green scans) exhibited quasi-linear behavior

\[ \text{Ca}_{(s)} + 2\text{e}^- \rightarrow \text{Ca}^{2+} \]
an oxidation onset occurred at 0.1 V, followed by a local maximum above 0.7 V vs Ca/Ca²⁺. No local maxima or minima were observed. The voltage-current response, which apparently oxidizes at lower overpotentials, was particularly evident upon oxidation: for the first cycle, as shown in the red scans in Fig. 2d. These features were particularly evident upon oxidation: for the “plating first” CV, an oxidation onset occurred at 0.1 V, followed by a local maximum in current density near 1 V vs Ca/Ca²⁺ and subsequent local minimum at 1.2 V. This local minimum, or “inflection point,” corresponded to 74.6% of the plated capacity. However, it is cautioned that this value should not be interpreted as Coulombic efficiency because of the large amount of underlying Ca and thus dissimilarity of the measurement conditions from those typically used for Coulombic efficiency quantification. In contrast to Au, the current density did not drop back to zero for the Ca electrode upon continued forward scan, and instead began to increase again there-after, reaching 2 mA cm⁻² at 2 V. During this completion of the forward scan, the CV reverted to linear behavior with a slope similar to that observed on the preceding plating scan. This unique stripping feature involving local maxima/minima only occurred when samples were not subjected to the rigorous procedure outline above and are thus attributed to an interface-dominated effect. Notably, this particular interface-dominated effect arises from the past processing history of the Ca foil and not the electrolyte-derived interface (discussed below).

To further investigate the origin of the unique stripping features, a measurement was conducted in a fresh cell by reversing the scan direction such that Ca was stripped, rather than plated, first. A significantly larger overpotential of ~0.7 V (compared to 0.1 V for “plating first”) was required before significant Ca oxidation occurred. We interpret this to reflect the absence of freshly-plated Ca, which apparently oxidizes at lower overpotentials. No local maximum or minimum were observed. The voltage-current response above 0.7 V vs Ca/Ca²⁺ nearly overlapped with the higher-voltage oxidative portion of the “plating first” sample (Fig. 3). This indicates that the linear behavior above 0.7 V vs Ca/Ca²⁺ corresponds to stripping of Ca through the pre-existing interface in both samples, i.e., it reflects oxidation of “bulk” Ca within the foil. The following plating scan exhibited a lower overpotential of ~0.25 V, akin to Ca nucleation onto the Au disk (and compared to ~0.4 V for “plating first”). These results collectively indicate the presence of a pre-existing interface layer on the Ca WE that influences initial plating/ stripping. The interface layer is not fully blocking, however, such that initial plating or stripping can occur, and interface-dominated effects disappear on the second scan for either plating- or stripping-first cases (Fig. 2d), indicating that they are altered by active electrochemistry. Specifically, plating creates interface deposits that are more electrochemically accessible than the underlying bulk Ca on subsequent charge; stripping up to high potentials, meanwhile, serves as an activation process that makes subsequent plating more facile.

This electrochemical behavior of Ca foil in Ca(BH₄)₂/THF electrolyte contrasts with the CVs of the original study by Aurbach et al. that investigated Ca electrodes (of size 0.125 cm²) in several inactive electrolytes including carbonates and THF with non-borohydride salts. In those cases, the initial reduction scan typically showed negligible current density (<0.5 mA cm⁻²) at large cathodic potentials (~1.5 V), and reduction currents at these large overpotentials were attributed to electrolyte decomposition as opposed to active Ca plating. The subsequent oxidation scans showed negligible current density due to electrode passivation until ~1 V vs Ca/Ca²⁺, for Ca-based salts, after which significant stripping current densities could occur between 1–2 V vs Ca/Ca²⁺ (~1–10 mA cm⁻², depending on the electrolyte). With Ca(BH₄)₂/THF, on the other hand, higher current densities (~1 mA cm⁻² in this cell configuration) for both reduction and oxidation are observed within a narrower voltage window (~0.5 V); yet-higher current densities are presented later on.

Ca(BH₄)₂/THF has been reported to continuously react with exposed Ca metal, forming a CaH₂ interface that increases in thickness over a timeframe of ~20 h. Cross-sectional SEM measurements of a soaked Ca foil (several days) enable visual estimation of this surface layer to be ~20 nm thick (Fig. S1 is available online at stacks.iop.org/JES/167/140543/mmedia). To examine the electrochemical penalty of this native, dynamic CaH₂

Figure 2. First-cycle behavior of calcium foil working electrodes. (a) Schematic of the three-electrode glass cell used for cyclic voltammetry measurements. CV scans were performed with 1.5 M Ca(BH₄)₂ in THF at 25 mV s⁻¹ for all panels, with reference and counter electrodes of Ca and Pt, respectively. (b) 25 CV cycles of a gold disk WE, with the Coulombic efficiency of the first cycle indicated. (c) The first CV cycle of a Au disk WE and Ca foil WE overlaid. (d) The first and second cycles, both “plating first” and “stripping first,” of freshly-polished vs interface-dominated Ca foil WEs.
The objective of this experiment was to introduce an interface was intentionally imparted to the Ca foil prior to cell assembly. The objective of this experiment was to introduce a synthetic interface prior to Ca coming into contact with significant trace solvent (to the extent possible) or electrolyte, in contrast to the two previous examples of pre-existing and natively-derived SEI. CaF₂ was selected for this task as it has been found in the SEI of electrolyte systems reported previously.17,22,23 It was important to keep the synthetic interface as thin as possible to avoid complete ionic deactivation. Through fine-tuning of synthesis conditions, we succeeded in fabricating nanoscale-thickness, conformal, single-composition CaF₂ interfaces on Ca by reaction with nitrogen trifluoride (NF₃) gas using a technique reported previously for Li,29 yielding ~100 nm thick polycrystalline CaF₂ layers with minimal porosity (Fig. S3–S5). The first CV cycle at 25 mV s⁻¹ exhibited a plating overpotential of −0.4 V, comparable to that without CaF₂ present, and achieved comparable reduction current (approximately −1 mA cm⁻²) on the first scan. Upon stripping, compared to previous samples, a more-pronounced inflection point was observed at 1.3 V, indicating a heightened presence of a Ca foil interface, and consistent with understanding developed so far on the origin of this feature. Beyond this point, and in contrast to previous samples, the current density remained below 0.5 mA cm⁻² for the remainder of the oxidative scan, indicating that the artificial CaF₂ interface more thoroughly suppressed access to the underlying bulk Ca than the pre-existing or CaH₂ interface. In comparison, the second cycle had a higher-magnitude plating current density (−2.2 vs −1.4 mA cm⁻²), a smaller onset plating overpotential (−0.25 vs −0.4 V), and larger currents over the entire oxidative range, indicating that both interface-dominated and bulk Ca stripping became more electrochemically active. Further cycles approached quasi-linear behavior, with the inflection points gradually becoming less pronounced. It should be noted that CaF₂ films became chemically unstable after several days of soaking in Ca(BH₄)₂/THF; however, the films were resilient to the short timescales (<2 h) required of CV testing. SEM images post-cycling (Fig. S6) indicated nodule-like deposition morphologies, separated by areas of smooth CaF₂ film.

The combined inflection points and observed Ca morphologies appear to be a consistent phenomenon when Ca plating/stripping occurs through an inhibitive Ca interface. Although the post-cycling Ca WE (Fig. S7) had deposition structures that were relatively smooth and interconnected in comparison with the separated nodules through CaF₂, the Ca WE surface still exhibited distinct
generally led to lower attainable currents. To measure the inverse of similar size (Fig. 5a), repositioning of Ca plating onto this Au foil was nearly the same as for the Ca foil, with similar current densities and resulting potentials. The resulting current density increased somewhat by several mA cm$^{-2}$ for both sizes—possibly resulting from increased Ca$^{2+}$ availability within the cell—although did not approach the values of the smaller-area WE, suggesting additional limitations beyond just the CE. Additionally, we observed a high degree of inhomogeneity of surface utilization when larger areas are used, for Ca (Fig. 6a) as well as Au, as indicated by preferential plating/stripping at the edges of the foil electrodes, reflecting non-uniform current distribution. Although the underlying links between cell geometry, CE behavior, transport, and ionic resistance are complex to disentangle, these insights indicate that it is critical to carefully consider electrolyte and cell configuration in evaluating the behavior of foil electrodes in emerging electrolytes. Regardless, 3-electrode beaker-type cells are not ideal for testing the intrinsic behavior of Ca where true performance metrics are concerned.

To address this limitation and further test the performance of Ca foils prepared using the presented polishing methodology, we also constructed coin cells in which cell geometry could be better-controlled and electrode separation distance minimized. Two-electrode coin cells were constructed in either asymmetric Ca-Au or symmetric Ca-Ca configurations (Fig. 7a). Whatman glass fiber separators were wetted with 180 $\mu$L of 1.5 M Ca(BH$_4$)$_2$/THF; Celgard 2325 polymer-based separators were also examined but had issues with cell shorting. In coin cells, the first plating/stripping cycle onto Au foil (black trace in Fig. 7b) looked qualitatively similar to that of the Au disk from the glass cell setup; however, there was an additional onset plating overpotential of 100 mV ($\sim0.35$ vs $\sim0.25$ V). This likely results from the additional barrier of directly sourcing Ca$^{2+}$ through the pre-existing interface of the Ca foil anode, in contrast to sourcing Ca$^{2+}$ from the relatively large electrolyte volume of the glass cell with a Pt CE. However, the current-voltage slopes were higher (less resistive) in the coin cell, resulting in slightly higher magnitudes of plating/stripping current compared to the glass cell, consistent with the expected decrease in ohmic resistance with closer electrode placement. When the positive electrode was changed from Au foil to a second Ca foil, the first CV reverted to exhibiting interface-dominated effects. In this configuration, coupled plating/stripping with two Ca electrodes expectedly resulted in yet-higher reduction onset potentials ($\sim0.45$ V).

Figure 5. The effects of cell configuration on electrochemical activity of Ca plating/stripping. (a) First CV cycles of Au or Ca working electrodes of different submerged surface areas. (b) Uncompensated solution resistance vs the distance between working and reference electrodes for different CVs. “3E” indicates a CV performed in a three-electrode glass cell.

![Figure 5](image-url)
reflecting compounded limitations through both interfaces, though the attainable current remained large (in excess of $\pm 10 \text{ mA cm}^{-2}$). This significant improvement in plating behavior compared to the glass cell is attributable to more homogeneous utilization of the Ca electrode surface in the coin cell configuration, which could be confirmed by SEM of a galvanostatically-plated Ca electrode (Fig. 6b). Upon the positive scan, the interface-to-bulk stripping transition again occurred; in this instance, the maximum attained currents reached as high as $\sim 25 \text{ mA cm}^{-2}$, exceeding those attained in the 3-electrode cell and again indicating a mitigation of the resistance limitations experienced in the latter. A "stripping-first" experiment was again conducted in which the scan direction of the symmetric Ca-Ca cell was reversed (Fig. 7c). Because the upper voltage window in these measurements was asymmetric (2.0 V vs Ca/Ca$^{2+}$ on charge vs $-1.0 \text{ V vs Ca/Ca}^{2+}$ on discharge), this had the effect of subjecting the positive electrode to an initial activation step that exceed the depth-of-oxidation experienced in the "plating-first" scan (where oxidation of one electrode only proceeded to $+1.0 \text{ V vs Ca/Ca}^{2+}$). Once the bulk Ca became more strongly activated during the asymmetric oxidative scan to 2.0 V vs Ca/Ca$^{2+}$, the subsequent plating currents reached as high as $-20 \text{ mA cm}^{-2}$. Cell shorting routinely occurred during subsequent cycles for this particular scan window (1 to 2 V) which we interpret to arise from the asymmetric conditions, imposing an imbalanced plating capacity, as well as high current densities.

Subsequent measurements tested Ca-Ca coin cells within a limited, symmetric voltage window ($\mp 0.5 \text{ V}$) to mitigate the above issues, and they showed significantly improved cycle life (more than 100 cycles, Fig. 7d). The CV shape evolved, as expected, from one that is interface-dominated in Cycle 1, to one fully symmetric in Cycle 3, and then finally to one reflecting stabilized, and thus intrinsic, plating/stripping behavior with maximal moderate current densities ($\pm 8 \text{ mA cm}^{-2}$) in Cycle 20. Current densities were still consistent by Cycle 100, but onset overpotentials increased slightly ($\pm 0.15 \text{ vs } \pm 0.1 \text{ V for Cycle 20}$), reflecting continued electrolyte reactivity with Ca over time. Ca-Ca coin cells could also be cycled galvanostatically for more than 50 cycles at a rate of $1 \text{ mA cm}^{-2}$ and capacity of $1 \text{ mAh cm}^{-2}$ as shown in Fig. S10; following an initial overpotential of 1 V to break through the passivation layer, stable cycling occurred at potentials of approximately $\mp 0.2 \text{ V}$.

While more work is needed to improve Ca electrode preparation and cell construction, the electrochemical testing of Ca symmetric coin cells appears promising for examining emerging electrolyte formulations, especially those that minimize surface-blocking effects such that intrinsic Ca performance can be measured with increased accuracy. Figure 8 shows the CV behavior of Ca-Ca coin cells comparing two additional electrolytes—Ca(BF$_4$)$_2$/EC:PC$^{17,18}$ and Ca(TFSI)$_2$/THF$^{19}$—at room temperature. In this configuration, we observed minimal reduction currents ($<0.1 \text{ mA cm}^{-2}$ at $-1 \text{ V}$) for Ca(BF$_4$)$_2$/EC:PC as reported previously, and only slight oxidation currents at high potentials ($>1.2 \text{ V vs Ca/Ca}^{2+}$). Ca(TFSI)$_2$/THF was inactive in this configuration, further underscoring the unique role played by the Ca(BH$_4$)$_2$/THF combination. Further detailed research utilizing less-reactive solvents and salts, such as Ca(B(Ohfip)$_3)_2$/DME$^{22,23}$ in similar coin cell configurations will be informative to test the performance and feasibility of these emerging electrolyte systems in practical cells.

**Conclusions**

We investigated the electrochemical behavior of Ca foil, having both native and synthetically modified interfaces, with a focus on Ca(BH$_4$)$_2$/THF electrolyte. Key cyclic voltammetry features were identified on the stripping portion of the scan that serve as clear indicators of interface-dominated electrochemistry. Such interface features can arise from the prior history and handling of Ca anodes, from dynamic evolution of a CaH$_2$ interface during testing, or from intentional ex situ surface modification by CaF$_2$. Ca interfaces, at least those examined here, are dynamically modified by cycling, resulting in a transition from surface-dominated electrochemistry to one that reflects more intrinsic plating/stripping behavior of Ca metal. We believe that the non-fully-blocking and impermanent
nature of all three types of interfaces studied herein presents an optimistic outlook for the use of Ca foil electrodes in coin-cell testing, particularly if improved electrochemical methodologies such as electropolishing or suitable formation cycles can be identified to effectively remove undesired surface layers at the outset of testing. This work also found that the electrochemical cell configuration and geometry significantly influence interpretation of the electrochemical performance and are thus equally as important as the interface to understand. By minimizing electrode separation distances and increasing the geometric alignment of electrodes as can be achieved in coin cells, high plating/stripping current densities (~20 mA cm\(^{-2}\)) are readily attainable using Ca foils. We hope that this work helps to identify a path forward for the use of Ca metal in routine electrochemical testing, relaxing a requirement to rely on plating/stripping on foreign—and often precious-metal—substrates as in many prior studies.

Acknowledgments

The authors gratefully acknowledge financial support from an MIT Energy Initiative SEED Fund award. For A.M.M., this work was supported by a NASA Space Technology Research Fellowship. The authors would like to thank Dr Eric C. Darcy at NASA-JSC and Dr Ratnakumar Bugga at NASA-JPL for their perspectives throughout the NSTRF project. This work made use of the Materials Research Science and Engineering Center Shared Experimental Facilities at MIT, supported by the National Science Foundation under Award DMR-14-19807.

ORCID

Aaron M. Melemed © https://orcid.org/0000-0001-7646-3130
Betar M. Gallant © https://orcid.org/0000-0002-4586-2769

References

1. J. W. Choi and D. Aurbach, Nat. Rev. Mater., 1, 16013 (2016).
2. W. M. Haynes, D. R. Lide, and T. J. Bruno, CRC Handbook of Chemistry and Physics (CRC press, Boca Raton, FL) 97th ed. (2014).
3. A. Ponrouch and M. R. Palacin, Curr. Opin. Electrochem., 9, 1 (2018).
4. R. J. Gummow, G. Vamvounis, M. B. Kannan, and Y. He, Adv. Mater., 30, 1801701 (2018).
5. M. E. A-D Dompablo, A. Ponrouch, P. Johansson, and M. R. Palacín, Chem. Rev., 120, 6331 (2019).
6. A. M. Melemed, A. Khurram, and B. M. Gallant, Batteries Supercaps, 3, 570 (2020).
7. Y. Liang, H. Dong, D. Aurbach, and Y. Yao, Nat. Energy, 5, 646 (2020).
8. D. Aurbach, R. Skaletsky, and Y. Gofer, J. Electrochem. Soc., 138, 3536 (1991).
9. S. J. Richard Prabakar, A. B. Ikhe, W. B. Park, K.-C. Chung, H. Park, K.-J. Kim, D. Ahn, J. S. Kwak, K.-S. Sohn, and M. Pyo, Adv. Sci., 6, 1902129 (2019).
10. R. Verrelli, A. Black, R. Dugas, D. Tchitchekova, A. Ponrouch, and M. R. Palacín, J. Electrochem. Soc., 167, 070532 (2020).
11. M. Cabello, F. Nacimiento, J. R. González, G. Ortiz, R. Alcántara, P. Lavela, C. Pérez-Vicente, and J. L. Tirado, Electrochem. Comm., 67, 59 (2016).
12. D. S. Tchitchekova, C. Frontera, A. Ponrouch, C. Krich, F. Bardé, and M. R. Palacín, Dalton Trans., 47, 11298 (2018).
13. R. Verrelli, A. P. Black, C. Frontera, J. Oto-Solé, M. E. A-D Dompablo, A. Fuertes, and M. R. Palacin, ACS Omega, 4, 8943 (2019).
14. M. S. Chae, H. H. Kwak, and S.-T. Hong, ACS Appl. Energy Mater., 3, 5107 (2020).
15. R. Dugas, J. D. Forero-Saboya, and A. Ponrouch, Chem. Mater., 31, 8613 (2019).
16. X. Liu, G. A. Elia, and S. Passerini, J. Power Sources Advances, 2, 100008 (2020).
17. A. Ponrouch, C. Frontera, F. Bardé, and M. R. Palacín, Nat. Mater., 15, 169 (2015).
18. S. Brita, S. Pathreker, H. Li, and I. D. Hosein, ACS Appl. Energy Mater., 2, 7738 (2019).
19. D. Wang, X. Gao, Y. Chen, L. Jin, C. Kuss, and P. G. Bruce, Nat. Mater., 17, 16 (2017).
20. K. Ta, R. Zhang, M. Shin, R. T. Rooney, E. K. Neumann, and A. A. Gewirth, ACS Appl. Mater. Interfaces, 11, 21536 (2019).
21. N. T. Hahn, J. Seil, T. J. Seguin, D. M. Driscoll, M. A. Rodriguez, M. Balasubramanian, K. A. Persson, and K. R. Zavadil, J. Mater. Chem. A, 8, 7235 (2020).
22. A. Shyamsunder, L. E. Blanc, A. Assoud, and L. F. Nazar, ACS Energy Lett., 4, 2271 (2019).
23. Z. Li, O. Fuhr, M. Fichtner, and Z. Zhao-Karger, Energy Environ. Sci., 12, 3496 (2019).
24. H. J. T. Ellingham, J. Soc. Chem. Ind., 63, 125 (1944).
25. P. Molaiyan and R. Witter, Mater. Des. Process. Commun., 1, e76 (2019).
26. M. C. Verbraeken, E. Suard, and J. T. S. Irvine, J. Mater. Chem. A, 19, 2766 (2009).
27. J. Forero-Saboya, C. Davoine, R. Dedryvere, I. Youssef, P. Canepa, and A. Ponrouch, Energy Environ. Sci., 13, 3423 (2020).
28. S. D. Pu et al., ACS Energy Lett., 5, 2283 (2020).
29. M. He, R. Guo, G. M. Hobold, and B. M. Gallant, Proc. Natl Acad. Sci. USA, 117, 73 (2020).
30. K. A. See, J. A. Gerbec, Y.-S. Jun, F. Wudl, G. D. Stucky, and R. Seshadri, Adv. Energy Mater., 3, 1056 (2013).
31. D. S. Tchitchekova, D. Monti, P. Johansson, F. Barde, A. Randon-Vitanova, M. R. Palacin, and A. Ponrouch, J. Electrochem. Soc., 164, A1384 (2017).
32. J. G. Connell, B. Genorio, P. P. Lopes, D. Strmcnik, V. R. Stamenkovic, and N. M. Markovic, Chem. Mater., 28, 8268 (2016).
33. A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications (Wiley, New York) 2nd ed. (2001).