Misreported non-aqueous reference potentials: the battery research endemic.

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**Energy Storage in Non-Aqueous Systems**

Electrolytes are an essential component of electrochemical energy storage devices (ESD), which are usually composed of non-aqueous (NA) solvents. Much of current research into such devices surrounds maximizing energy densities by enhancing operating voltages, to meet increasingly demanding applications. In lithium-ion batteries (LIBs), electrolyte reduction is well documented at the anode, contributing to the formation of the invaluable solid electrolyte interface (SEI) layer. At high positive voltages, however, electrolyte oxidation can often limit the device’s lifetime and electrochemical performance. Thus, evaluation of the electrochemical stability window (ESW) is important to ensure the use of sufficiently stable electrolytic compositions. The rapidly emerging field of NA redox flow batteries (NARFB) comprising redox organic molecules (ROMs) is another energy storage space that routinely uses organic solvents. In this case, it is critical to establish the redox potential of the ROMs with respect to both the electrolyte potential window and with respect to each half-reaction, as their potential difference governs the cell voltage and indicates electrolyte stability. Progress to expand the operational window of a ROM-based NARFB has been substantial in recent years but accurate assessment of scientific developments and meaningful comparison of published literature in this field is a real challenge owing to the range of reference electrodes being used and inconsistent experimental conditions.

While traditionally batteries operate as two-electrode devices, reliable voltammetric measurements require three electrodes: a working electrode (WE), counter electrode (CE) and reference electrode (RE). A reference electrode is an important diagnostic tool to decouple and characterize electrode behavior, which is especially critical under fast charging conditions. The high energy and power requirements of electric vehicles that employ LIBs mean that degradation and safety monitoring is more important than ever. With increased charging rates, lithium deposition at the anode becomes more favorable, where subsequent formation of dendrites can lead to cell shorting (a significant safety concern), and degradation at the cathode can lead to increased cell impedance.

Good reference electrodes should be non-polarizable and provide reliable and reproducible potentials. This is achieved through fast electrode kinetics, high surface area and stable conditions and composition.1 While robust reference electrodes for use in aqueous systems are well established (*e.g.,* Ag/AgCl), they are unsuitable for use in NA systems because of high liquid junction potentials between the internal and external solutions, resulting in large potential drifts, contamination of the external electrolyte, and frit pore plugging due to the insolubility of aqueous salts (*e.g.,* KCl) in organic solvents.2 Thus, bespoke reference electrodes are required for NA applications.

**The Problematic Silver Reference**

The Ag/AgCl RE maintains a stable electrode potential by establishing a stable equilibrium with the chloride ions in the aqueous RE electrolyte, in accordance with the Nernst equation. Correspondingly, the RE potential relative to the standard hydrogen electrode is dependent on the activity of the chloride ions, a detail often underreported, even in aqueous three-electrode chemistry. A well-known and stable chloride concentration is critical to the potential-determining equilibrium. In NA media solid AgCl is unstable as the presence of excess chloride ions rapidly forms the soluble AgCl2− species.3 Ideally, one would implement a silver RE coated with a silver salt containing the anion that corresponds to the supporting electrolyte (*e.g.*, PF6−). Unfortunately, these silver salts are also soluble in NA solvents, such that modifying the surface with PF6− or BF4− anions akin to the AgCl surface of aqueous systems renders an electrode surface that continually erodes upon prolonged solvent exposure, causing potential drift. One possible alternative is an Ag2S coated silver wire, which was recently reported to show no variation in RE potential and stability when testing both LiPF6andLiTFSIbased electrolytes (Figure 1) and a series of ionic liquids.4,5 Unlike the aforementioned silver salts, Ag2S is insoluble in most solvents. Thus, Ag/Ag2S is perhaps an understudied but more versatile NA RE, allowing helpful comparison across battery research. However, the nature of the potential-determining equilibrium is unclear given that sulfide ions are not necessarily present. A notable commercial venture has been the Ag/AgCl leakless electrode (*e.g.,* eDAQ). Manufacturers claim that the leakless Ag/AgCl RE is tolerant to and stable in a wide range of NA solvents. Yet, their application is not seen in the literature, and again, there is a lack of understanding as to how these REs form their half-cell potentials.

Instead, commonplace NA REs are based on the Ag/Ag+ redox pair. Various Ag/AgNO3 or Ag/AgClO4 configurations are reported with varying concentrations of AgNO3/AgClO4 and tetraalkylammonium salts of *e.g.,* perchlorate or hexafluorophosphate in organic solvents such as acetonitrile, dimethylsulfoxide, methanol, ethanol, and tetrahydrofuran. These REs display acceptable stability for short-term use. However, their potentials are very sensitive to electrode/electrolyte composition and the preparation of the silver wire. They must be carefully stored between experiments and regularly renewed and recalibrated to avoid the potential drifting with time, limiting their suitability for long-term use (*i.e.* over 8 hours). Lee and Tang evaluated potential REs for sodium ion batteries and found a well-maintained commercial Ag/Ag+ RE containing AgNO3 that experienced a drift of 0.21 mV hr−1 in acetonitrile.6

A fritted NA RE, however, is not always a suitable RE for a battery experiment, due to the added impedance of the frit, the challenge of inserting such a design into the battery cell, and the problematic diffusion of Ag+ and NO3− ions through the frit into the test solution and their corresponding electro and photoactivity. This frequently forces researchers to employ a silver wire quasi-reference electrode (QRE), typically immersed directly in the electrolyte under investigation. The exact composition of QREs, however, is unknown and can vary significantly between electrodes. Consequently, potential drifting between scans and with time is all but expected due to differing surface layers (*e.g.,* Ag2O) and electrolyte composition. The QRE potential is easily influenced by trace impurities (*e.g.,* water and oxygen).1 Isolation of the QRE in a self-contained fritted capillary filled with the test solution can improve short term stability. However, long term stability is still limited (*ca*. 24 mV shift over 12 h in 0.1 M TBAPF6/MeCN.

**Internal Standards**

As silver reference potentials can vary significantly, directly reporting potentials *vs* the Ag/Ag+ pair is unwise; instead, a more robust standard should be reported against such as an internal redox reference system (IRRS). In essence, an IRRS is an electrolyte independent redox system that provides a known reference point from which to calibrate measured potentials. To encourage standardization, IUPAC recommended the adoption of the ferrocene/ferrocenium (Fc/Fc+) and bis (biphenyl)chromium(I)/(0) redox couples.7 Most commonly, Fc is the IRRS of choice throughout NA literature. This creates further pitfalls however, as care should be taken when converting measured potentials between different reference scales since variations in concentration, salt and solvent can significantly alter the reference potential, as detailed in a critical study by Pavlishchuk and Addison (essential reading for anyone embarking on NA electrochemistry).2

Such IRRSs are typically added to the test solution at the end of the experiment, disregarding any potential drifting that may occur during a series of measurements. Thus, frequent calibration or incorporation of the standard into the solution throughout the experiment is recommended. Unfortunately, the standard may interfere with redox processes under investigation, so the choice of standard should be carefully considered. Fc is found to irreversibly oxidize at potentials similar to those of the cathode oxidation window for lithium batteries.8 A further problem to acknowledge is the apparent solvation effect on the standard (Fc and cobaltocene in particular), making their redox potentials solvent dependent.9 Unlike the two aforementioned IRRSs, the metal center in decamethylferrocene (DmFc) is protected by methyl substituents, resulting in weaker solvation interactions, providing a stable reference potential and avoiding unwanted interactions with the study solution.10 While this makes DmFc a preferable candidate, its practicality as a widely-used standard is limited by its high cost (£527/5 g DmFc vs £12.70/5 g Fc. Sigma Aldrich, November 2021).

**The Misused Lithium Reference**

In the case of LIBs, ESW measurements are dominated by three-electrode cells consisting of a platinum WE and lithium CE and QRE. Measured potentials are then reported *vs* Li/Li+. While this approach may mitigate issues in reference potential conversions, the initial potential and potential drift when using a Li QRE is highly dependent on electrolyte composition and Li+ concentration, due to differences in the degree of adsorbed species (**Figure 2**). SEI layers that form at the Li QRE differ with electrolyte composition, altering the nature of the QRE. Thus, the potential is better considered as measured against Li/SEI rather than Li metal.9 As the exact composition and potential of such references cannot be defined with confidence, direct comparisons of ESWs measured in different electrolytes are inaccurate and significant conclusions from such comparisons should not be made. Furthermore, contaminants can be produced during these reactions, potentially interfering with measurements. Variations in mechanical treatment and cleaning of Li also have considerable influence on the reference potentials, yet these procedures are often omitted from experimental details.

As alternatives, lithium alloys (*e.g.,* LiySn) provide stable potentials over several weeks, after which they require additional lithiation.4 Some insertion materials (*e.g.,* lithium titanate (LTO) and lithium iron phosphate (LFP)), on the other hand, offer further improvements to stability as they show a long plateau at a specific voltage which is not affected by minor changes in composition. Such REs, however, are complex to prepare as they require the construction of a preparation cell to lithiate the insertion material which is then extracted and placed into the working cell.12 In the case of post-Li batteries (such as Na, K, Mg and Ca), where corresponding metal REs are used, more significant potential drifts are observed yet analogous alloys and insertion materials have been barely explored.4

LIB research has resulted in a problematic legacy in terms of referencing other NA electrochemical systems under development. Frequently, the Li/Li+ reference potential is used to correct the potential when an alternative QRE has been used, or where it has no bearing on the study being undertaken. This has unfortunately spilt over into the NARFB field and as a result, comparing ROM redox potentials from one study to the next is a real challenge due to inconsistency in referencing. Much of the early work in this field evaluates ROMs vs Li, but the composition of the electrolytes was ever-changing. Other works have then directly compared the redox potentials of derivatized ROMs such as TEMPO to systems employing QREs.13 The persistence in trying to relate all battery research to lithium systems is resulting in none of the systems being relatable or reliable. Recently, standardization has been attempted within NARFB research, with recommendations to use the ferrocene couple routinely, but none regarding the actual RE to be used.14

**Electrochemical Set-Ups**

Two-electrode cells are routinely used in LIB research due to the assumption that the electrochemical response of the CE is *‘negligible’*, having minimal effect on the working potential. However, best practice would be to use a three-electrode cell to account for failure of this assumption. For example, this assumption is invalid in post-Li systems and so the use of a RE is mandatory.4 Within battery research, several three-electrode cells are employed including beaker cells, Swagelok cells, coin-cells (Figure 3) and the commercial El-cell (www.el-cell.com), the design of which is of critical importance in NA media to limit uncompensated resistance and further misreporting of WE potentials. A more detailed comparison is outlined by Dugas et al.4, but in brief, the use of beaker cells limits airtightness, and thus practicality for long-term measurements, as well as providing an unrealistic comparison to Li- and post-Li batteries due to the large excess of electrolyte. They do, however, allow the use of large, fritted REs. In stark contrast, the coin-cell, El-Cell and Swagelok-cell offer a sealed testing system but are limited to thin wire QREs. The small electrolyte volumes used may lead to more significant interference from an IRRS, limiting their implementation in such set-ups. The discovery of more reliable and stable REs is therefore of utmost importance.

When considering sealed systems, the differences in electrochemical arrangement can also influence data outputs, which are often incomparable. In the case of the El-cell – a premium commercial cell that offers a range of single-use REs including various metals (*e.g.* Li, Na, Mg) as well as LTO and LFP – the high long-term data quality and consistency is at a high cost with limited comparability to literature. This issue extends to Swagelok-type cells. Homemade three-electrode coin cells, whilst cheap and comparable, limit consistency. A three-electrode coin-cell that mimics the standard C2032 two-electrode coin-cell, developed and patented by General Motors, has been commercialized by Arbin Instruments, in which the use of a Li, LTO of LFP reference electrode is recommended.15 Such a consistent, affordable, and comparable set-up may be the answer to standardization across Li and post-Li battery testing.

Further errors beyond RE type and electrochemical set-up exist in the form of measurement artefacts, causing RE potentials to deviate from true values. In the case of LIBs, such deviation, caused by inhomogeneous lithiation currents due to RE blocking effects, has been shown to result in the failure of predicting Li plating.16 Such effects could be minimized by reducing the width of the RE or increasing electrolyte diffusion.16 We reiterate the conclusions of Li *et al.* and encourage that sufficient attention be paid to possible errors in RE potentials, from RE materials and preparation to cell-set-up and RE geometry.

**Recommendations For Reference Electrode Best Practice**

It is not possible to indicate a specific RE for NA chemistry, and a summary of the options discussed above is given in the SI (Table S1) along with a crude assessment of their strengths and weaknesses. While establishing standardised NA REs is a complex and challenging issue, it is evident that more consistency and care is required in the literature when reporting on electrochemical systems in which redox potentials and/or potential windows are critical to the development being described. For the lithium-air battery, such an approach to referencing was outlined by Mozhzhukhina & Calvo.11 But this advice extends to all NA systems. While there is general agreement across the field that an ideal RE is yet to be identified, being aware of sources of errors that can lead to misreporting is vital for progress. Through a compilation of important literature, this commentary aims to highlight the considerations that must be given sufficient attention when embarking on NA electrochemical research. As such:

* Three-electrode cells should be employed when studying NA electrolytes. In the case of three-electrode coin-cells and Swagelok cells, we recommended the procedures outlined by Minter et al12 and Solchenbach et al17, respectively.
* In beaker cells, an Ag wire should be employed in a self-contained fritted cell and referenced against an IRRS. IRRS stability with cycling and time should be ascertained.
* Ideally, IRRSs should be present throughout the experiment and selected so as not to interfere with the electrochemical measurements, which may require the use of alternatives to Fc, such as DmFc which are stable in a wider potential window and unaffected by solvation effects.
* In the case that such an IRRS is not feasible, the potential of the QRE should be measured vs an IRRS in an equivalent test solution, both before and after the experiment.
* Details of data calibration should be reported alongside IRRS measurements. The stability of a given RE should be evaluated using time dependent IRRS potential measurements prior to undertaking electrochemical testing. Such data should be supplied in the SI.
* When setting out to fully evaluate novel RE/QREs, it would be beneficial to perform such measurements in a range of electrolyte compositions vs a sufficiently stable IRRS to determine its versatility.
* Above all, procedures for RE preparation and voltage determination should be *explicitly* reported. This includes the nature, purity, enclosure, and supplier of the (Q)RE. Also, experimental conditions, the concentration of supporting electrolyte and IRRS, the scan rates, and the application of any resistance compensation.
* Due to solvent specificity of many NA REs, reported potentials should include the solution of study (*e.g. vs* Li+/Li in 0.1 M TBAPF6 in MeCN).
* Conversion between reference potentials should be done with care and should be sufficiently reported alongside raw data to aid with reliable comparisons.
* Li QREs should be avoided and replaced with more stable alternatives, such as lithium titanate in the case of LIBs. In post-Li batteries, research should endeavor to evaluate analogous materials for implementation as REs.

While somewhat obvious, the above suggestions are scarcely observed in the literature, and this becomes problematic when trying to ascertain if advances are being made. Electrochemistry in NA media is challenging, but NA batteries are ubiquitous in society and so we implore researchers to adopt the highest possible standards in their work, and peer-reviewers to demand as such from inadequate contributions during publication. Joule’s ‘Battery Checklist’ is an important guideline that outlines protocols for reporting battery assembly and electrochemical results. Further guidelines to this existing document regarding the reporting of REs, experimental arrangement and protocols would prove invaluable to encourage transparency and comparability in results. Beyond the requirements for publication in Joule, such a meticulous approach to data reporting should be adopted across the field. This would require combined efforts and advocacy from PIs, journal editors and funding agencies to bear noteworthy influence on the widespread community.

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**AUTHOR CONTRIBUTIONS**

B.M and K.T conceived the manuscript outline. C.A made significant contributions to figure drawing and editing of the manuscript. D.S. and N.T contributed to the final editing of the manuscript.

**DECLARATION OF INTERESTS**

The authors declare no competing interests

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**FIGURE LEGENDS**

**Figure 1. The Ag/Ag2S reference electrode**

Time-dependent potential of Ag (a) and Ag2S (b) QREs from cyclic voltammetry (20 mV/s) performed in a solution containing 5 mM ferrocene and either 1 M LiPF6 or 1 M LiTFSI in EC:DMC. WE: stainless steel, CE: activated carbon. Reproduced with permissions from ref [4] (permission related to this material should be directed to the ACS).

**Figure 2. Lithium as a quasi-reference electrode**

IR drop corrected cyclic voltammetry (100 mV/s) performed in a solution containing 10 mM ferrocene and 0.1 M LiBF4 in ACN (acetonitrile), DMSO (dimethyl sulfoxide), MP (1-Methyl-2-pyrrolidinone) or PC (propylene carbonate). WE: Pt, CE: PT mesh, QRE: Li. Reproduced with permissions from ref [11].

**Figure 3. Three-electrode set-ups**

Simplified schematic illustration for the assembly of conventional three-electrode cells; beaker cell, ‘Swagelok cell’ and adapted coin cell. An Ag/Ag+ QRE submerged in a separated solution of electrolyte is shown calibrated against a Fc internal standard solution.