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Technical Note

Pt/Polypyrrole Quasi-References Revisited: Robustness and Application in Electrochemical Energy Storage Research

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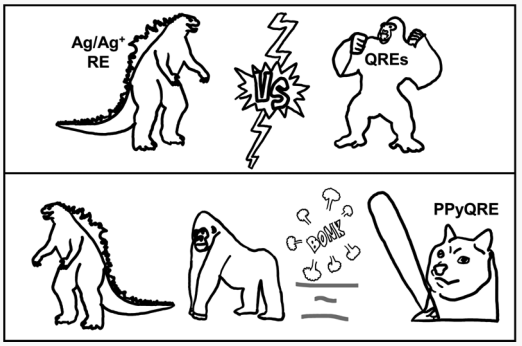
ABSTRACT: Choosing reference electrodes for nonaqueous electrochemical measurements, especially in energy storage research, is challenging due to lengthy experiments (>1 day), the lack of alternatives to the commonly used Ag/Ag^+ reference electrode (RE), the introduction of junction potentials, and the possibility of sample contamination. Often, quasi-reference electrodes (QREs) such as Ag wires and Li metal strips are used. However, small changes in electrolyte composition can cause large potential drifts, and their surfaces may be reactive to the solution. Here, we propose an alternative QRE based on polypyrrole electrodeposited on Pt wire (PPyQRE) encased in a glass tube with the open end sealed with commercial frits. While freestanding PPyQRE wires have been reported in the literature, simple encasing of the PPyQRE overcomes the above-mentioned drawbacks of QREs while providing a reliable reference potential that is closer to the performance of an RE. During cyclic voltammetric and bulk electrolysis testing of a redox mediator in solution, the encased PPyQRE exhibited stable reference potentials over multiple charge/discharge cycles with minimal drift (~5 mV) after ~2.25 days of operation. We also tested the reliability of our reference during the testing of multilayer graphene Li-ion anodes, which often involve cycling samples at highly reducing potentials (<−3 V vs Fc/Fc^+) over long durations (>1 day). In the same testing conditions, the Ag/Ag^+ electrode led to observable Ag deposits on the graphene and large potential drifts (~50 mV), while the PPyQRE exhibited no measurable drift and revealed changes in voltammetric features that were obscured by reference drift when using Ag/Ag^+. Minor reference drifts of ~30 mV over long usage of the PPyQRE (~2 months) can be addressed by calibration with a ferrocene couple at the end of experiments. These results highlight the advantages of using an encased PPyQRE as a simple and practical reference electrode for electrochemical measurements in the field of nonaqueous energy storage research.



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Reference electrodes (REs) enable the measurement or control of the working electrode (WE) potential, which is a cornerstone of any electrochemical experiment. An ideal RE has a stable and well-defined electrochemical potential dictated by the Nernst equation. However, in practice, the potential of the reference can shift, leading to ambiguous and misleading results. Therefore, the choice of REs is often of critical concern in experiment design. While in aqueous media, there are many reliable, well-established reference electrodes such as Ag/AgCl and calomel electrodes,[1−4] nonaqueous electroanalytical measurements commonly utilize Ag/Ag^+ RE[1,3,5] or quasi-reference electrodes (QREs) such as Ag wire.[1,6] In particular, electrochemical measurements in the domain of energy storage technologies such as Li-ion batteries (LiBs) often rely on Li metal strips or Li transition metal oxides as QREs.[5,7,8] Issues associated with the use of QREs include (i) unknown poising reaction (i.e., undefined terms in the Nernst equation) and (ii) drift in reference potential when the solution composition is changed (for instance, upon adding an internal standard such as ferrocene for calibration) among others.[1,2,7] While the Ag/Ag^+ RE avoids these issues, its use in nonaqueous media can lead to the development of junction potentials due to dissimilar solution compositions across the RE frit.[1−3,5] Furthermore, the use of high reactivity REs and QREs such as Li metal limits their use in nonaqueous solvents such as acetonitrile,[9,10] wherein byproducts such as methane gas are generated.[11] Additionally, in our own experience of using the Ag/Ag^+ RE, we have observed dark precipitates forming on the frit upon extended use, possibly due to photoreactivity of Ag^+. Other issues include the possibility of Ag^+ leakage out of the RE, which could lead to reference potential drifting over long experiments, as well as the risk of solution contamination and Ag electrodeposition on the working electrode.[3] Therefore, the

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identification of a robust nonaqueous reference electrode for energy storage research is often a challenge.

A possible solution to this challenge lies in the use of solid-state QREs. These electrodes have been reported in the literature since the 2000s, and are typically based on conducting polymers.[12] An example from this class of QREs are polypyrrole (PPy) quasi-references (PPyQRE). A detailed investigation into these QREs was reported by Ghilane et al.,[13] and since then, the PPyQRE has been used in several electroanalytical measurements involving electrodeposition, scanning electrochemical microscopy, among others.[14−22] The poising reaction for such polypyrrole QREs is based on the doping reaction of PPy as shown in eq 1, with A^- being the counterion

$$PPy^+A^-(s) + e^- \leftrightharpoons PPy(s) + A^-(soln) \quad (1)$$

The study by Ghilane et al.[13] revealed the unique advantages obtained by using such references in electroanalytical measurements. First, the electrode can be easily calibrated by the ferrocene couple. In addition, since the reference is solid state, there is no issue of junction potentials arising upon its use. Moreover, it was demonstrated that the PPyQRE showed great promise as a stable reference when tested in voltammetric experiments. However, Ghilane et al.[13] also reported that the PPyQRE was unstable in highly oxidizing/reducing solutions as a result of interference with the redox reaction described by eq 1. Such interfering conditions are often amplified in experiments involving dramatic changes in the redox state of the solution, such as those in bulk electrolysis (BE), a technique widely used in redox flow battery research.[23,24] Additionally, by varying the anion in the supporting electrolyte, they revealed shifts in the reference potential. Therefore, it is clear that the identity of the solution controls the reference potential for PPyQRE. To overcome this problem, we propose a simple modification: encase the PPyQRE in a glass tube with its open end covered by a commercial frit (henceforth referred as "encased PPyQRE"). While this simple strategy is often used in many other REs,[25] the scope of this note is to highlight the advantages of such encased PPyQREs, compared to a freestanding PPyQRE, for energy storage research. We show long-term (>1 day) stability of the QRE and its performance during BE experiments where the redox potential of the solution is changed. We further demonstrate the use of such encased PPyQREs in Li-ion battery research.

EXPERIMENTAL SECTION

Chemicals. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 99%), pyrrole reagent (98%), acetonitrile (MeCN, HPLC grade, 99.8%), propylene carbonate (PC, 99.7%, anhydrous), ethylene carbonate (EC, 99%, anhydrous), and lithium tetrafluoroborate ($LiBF_4$, 98%) were procured from Sigma-Aldrich and used as received. 0.5 mm diameter Pt wire (99.99%) was procured from SurePure Chemetals. Ferrocene (Fc, 98%) was procured from Sigma-Aldrich and recrystallized twice out of hexane before use.

Deposition and Assembly of PPyQREs. The deposition of polypyrrole on Pt wire was performed using the same cyclic voltammetry (CV) protocol as described by Ghilane et al.[13] In brief, Pt wire was cycled in 10 mM pyrrole in 100 mM $TBAPF_6$ (dissolved in MeCN) between −0.6 and 1.2 V vs Ag/AgCl for 50 cycles, using a CHI760 potentiostat. The CV was terminated at a potential of 0.45 V (during the anodic sweep) to have part of the electrodeposited PPy doped to PPy^+, as shown in Figure 1a. Subsequently, the Pt wire covered with polypyrrole was gently rinsed in MeCN and allowed to air

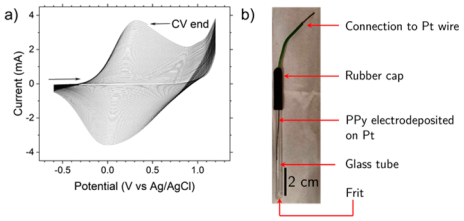

Figure 1. Deposition and construction of polypyrrole quasi-reference electrode (PPyQRE). (a) Voltammogram depicting deposition of polypyrrole (PPy) on Pt wire. (b) Construction of the quasi-reference electrode, with ∼3.5 cm of Pt wire coated with PPy.

dry overnight before use. The use of MeCN as the solvent and rinse is a precaution to prevent water contamination of the box and of experiments where this electrode is used; furthermore, we observed that air drying was key to preventing cracking of the PPy film during vacuum transfer into a glovebox. Finally, the electrode was encased in a glass tube with one end covered by a chemically resistant rubber cap (Product 6448K76, McMaster-Carr, USA), as shown in Figure 1b. The other end of the glass tube was sealed with a glass Vycor frit (Biologic USA, Product 092-VYC4) and PTFE heat shrink (Zeus, Inc.).

Electrochemical and Experimental Measurements. All experiments using PPyQREs were performed in gloveboxes (under Ar atmosphere) with O_2 and H_2O levels less than 0.1 ppm using either a CHI920D bipotentiostat or a CHI760E potentiostat. W cells for bulk electrolysis were procured from Adams & Chittenden Scientific Glass with P5 frits (1.0−1.6 μm pore size). Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were carried out in a Hitachi S4700 SEM equipped with an iXRF EDS detector (Oxford Instruments).

RESULTS

In order to demonstrate the stability of encased PPyQREs, we performed cyclic voltammetry (CV) and bulk electrolysis (BE) measurements. Figure 2a illustrates CVs of a 1 mM ferrocene (Fc) solution cycled for approximately 2.25 days, with a Pt ultramicroelectrode (UME).

Figure 2a reveals only a slight drift after continuous operation during 15,000 CV cycles. $E_{1/2}$ calculations for each cycle, as shown in Figure 2b, reveal the majority of values to lie within a range from 55 to 64 mV (mean, μ = 59 mV, standard deviation, σ = 3 mV). We calculate a small drift of 0.08 mV/h (1.9 mV/day) throughout 56 h of operation. However, one should keep in mind that the diffusion layer generated at such UMEs during voltammetry have characteristic lengths similar to the diameter of the microdisk (25 μm in our case).[2] Therefore, the identity of the solution remains virtually unchanged, especially around the reference electrode. This condition is not met sometimes in electrochemical measurements involving larger electrodes and is clearly not the case in BE.

To prove that the encased PPyQRE assembly maintains a stable reference potential, we compared its performance during BE of Fc with polypyrrole electrodeposited on a Pt wire (referred henceforth as "bare PPyQRE"). We utilized W cell and H cell configurations in the BE experiments. In W cells, the RE, WE, and counter electrodes were separated by P5 frits

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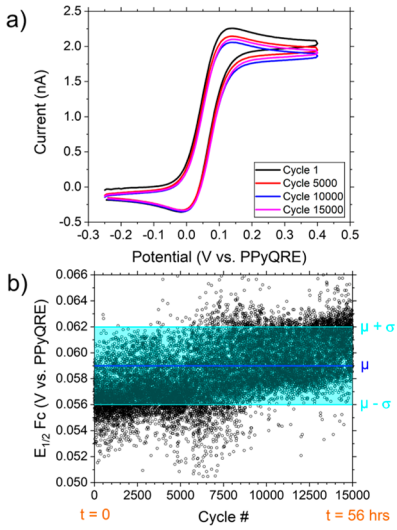

Figure 2. Long-term (>2 days) cycling performance of PPyQRE. (a) Select voltammograms of ferrocene as observed during cycling. (b) $E_{1/2}$ of ferrocene as a function of cycle number. Working electrode: 25 μm Pt UME. Reference electrode: PPyQRE. Counter electrode: graphite. Solution: 1 mM Fc in 0.1 M $LiBF_4$ dissolved in 1:1 PC/EC (by vol). Scan rate: 100 mV/s.

whereas in H cells, the WE and RE were in the same compartment. During BE, we utilized a second working electrode, a 25 μm Pt UME to measure the $E_{1/2}$ of Fc as a function of state-of-charge (SOC; SOC = 0 means all Fc is in the native state; SOC = 1 means all Fc is converted to Fc^+). Figure 3 summarizes the results from these experiments.

The robust performance of the encased PPyQRE is evident from the voltammograms and $E_{1/2}$ data in Figure 3a and b. There is a drift of ±5 mV over the course of the BE measurements, irrespective of whether the reference was tested in a W cell or H cell configuration. In comparison, when we use a bare PPyQRE, we observe a reference shift in the order of ∼200 mV when testing in an H cell configuration and ∼300 mV in a W cell configuration (Figure 3c and d). This result highlights that the frit used in the construction of the encased PPyQRE was able to preserve the identity of the solution inside the glass tube, therefore preventing the reference potential from shifting over the 7 h duration of BE experiments. As in other reference electrodes, the ultimate performance of the PPyQRE might be controlled by the quality and porosity properties of the frit used.[26]

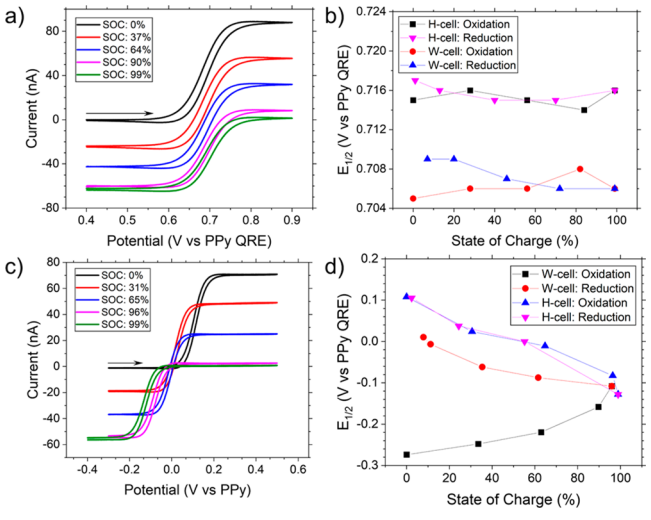

Figure 3. Bulk electrolysis of ferrocene in different configurations. (a) UME CVs during Fc to Fc^+ oxidation in an H -cell configuration. (b) $E_{1/2}$ during Fc oxidation and Fc^+ reduction with an encased PPyQRE. (c, d) Same as panels (a) and (b), respectively, but with bare PPyQRE. Initial solution composition: 8 mM Fc in 0.5 M $TBAPF_6$ dissolved in MeCN. Pt flag electrodes were used as working and counter electrodes for the BE of Fc. Scan rate in voltammetric experiments was 100 mV/s.

Now that we have demonstrated the stability of PPyQRE in nonaqueous electrochemical measurements of CV and BE concerning redox species in solution, we highlight two examples illustrating their performance in Li-ion battery research. We targeted experiments using multilayer graphene (MLG) electrodes as Li-ion battery anodes.[27−30]

A first experiment compares the use of an Ag/Ag^+ RE vs encased PPyQRE in a potentiostatic intermittent titration (PITT) measurement to characterize solid-state Li-ion diffusion in MLG. In brief, PITT experiments involve characterizing the current−time behavior of electrodes over small potential increments, leading to the quantification of diffusion coefficients with respect to applied potential on the electrode.[31] The current−time measurements need to be run until equilibrium, and therefore, a PITT experiment runs for a long duration (around 10 h in our case). In practice, we run multiple PITT experiments while running voltammograms of Li^+ (de)intercalation in between. Figure 4a and b illustrates these CVs with the Ag/Ag^+ RE and encased PPyQRE, respectively. As observed in Figure 4a, over the course of the PITT measurement, there is a reference potential drift of 50 mV when we use an Ag/Ag^+ RE. This can be explained by

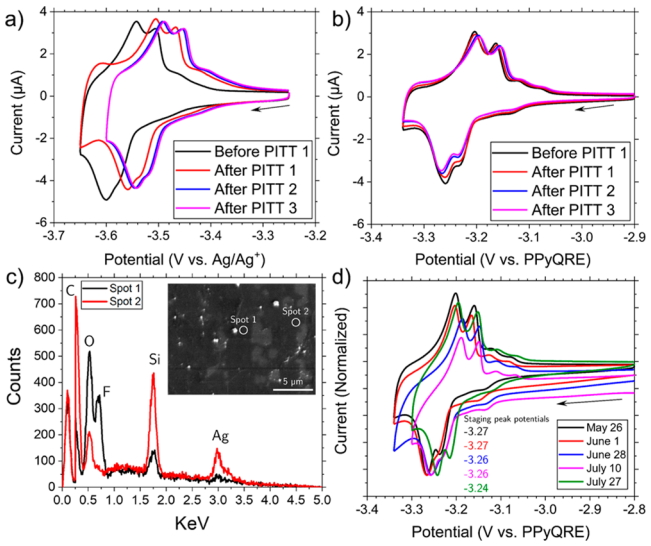

Figure 4. Performance of Ag/Ag^+ RE and encased PPyQRE characterized with Li^+ (de)intercalation experiments; macro-disc MLG working electrode (area, 7.1 mm^2); scan rate, 1 mV/s. (a) CV using a Ag/Ag^+ RE ($[Ag^+]$ = 0.1 M) and (b) using a PPyQRE after three PITT measurements (denoted as PITT1, PITT2, and PITT3). (c) SEM-EDS measurement of the MLG surface after CV and PITT measurements with the Ag/Ag^+ RE. (d) Li^+ (de)intercalation CVs obtained with different MLG electrodes across two months. The potential corresponding to the highest current peak in the cathodic sweep is reported in the inset (current axis is normalized to this peak value).

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possible Ag^+ leakage and development of junction potentials across the frit in the RE. The leakage also modifies the concentration of Ag^+ in contact with the Ag wire, thus modifying its Nernst potential. Additionally, it is a concern in the electrochemical measurements at the MLG electrode, which is biased to strongly reducing potentials for Li^+ intercalation, therefore leading to the possibility of Ag plating. We have observed such Ag contamination arising from plating on the surface of MLG anodes after CV and PITT measurements when analyzing them ex situ using SEM-EDS. Figure 4c illustrates the EDS spectra at select points of a sample, which revealed significant Ag metal presence, thereby proving that Ag metal plating is realistically expected when using the Ag/Ag^+ RE in such Li^+ intercalation measurements in anodes. On the other hand, there are no major concentration gradients across the ends of the frit when using an encased PPyQRE since the solutions inside and outside the glass tube are the same. This fact, combined with the low-reference drift characteristics of the PPyQRE results in excellent long-term control over working electrode potentials as shown in Figure 4b. In fact, the improved voltammograms in Figure 4b exhibit a small but clear peak splitting as the sample ages during operation, suggesting changes in the kinetics of charge transfer during the experiment. These details are largely obscured by the uncertainty introduced by reference potential drifts when using Ag/Ag^+ RE.

A second example highlighting the applicability of the PPyQRE with MLG samples is shown in Figure 4d, consisting of Li^+ (de)intercalation behavior captured via CV on various MLG samples at different times over two months, with the same encased PPyQRE. We expect the intercalation potentials to be consistent across measurements since it is a thermodynamic parameter. Kinetic complications are not expected, especially with our recent evidence of Nernstian behavior being observed with the staging peak potentials on such MLG electrodes.[27] Therefore, the fact that we are able to see consistent cathodic staging peak potentials in Figure 4d vs PPyQRE attests to the robustness of the encased setup. It should be noted that the peak splittings in such electrodes depend heavily on factors such as cycling history and charge transfer kinetics, and therefore, we do not utilize the anodic staging peaks for estimating reference potential drift.[32] The minor drifts observed between these experiments (~20−30 mV) could be easily solved via calibration to Fc/Fc^+. In these experiments, we performed such calibrations after each run and verified that within each measurement the reference potential does not drift significantly, consistent with the data reported above. This observation has also been consistent with the use of various PPyQREs in our laboratory over the past two years.

We have successfully used the PPyQRE in a variety of nonaqueous solvents: propylene carbonate, ethylene carbonate, acetonitrile, diethyl carbonate, dimethylformamide, and tetraglyme. Supporting electrolytes used in some of these solvents were $LiBF_4$, $TBAPF_6$, KPF_6, $NaPF_6$, and $LiPF_6$. The reference potential of the encased PPyQRE does not drift when exposed to oxygen, whereas the presence of dissolved oxygen has been previously reported to affect the potentiometric response of freestanding PPyQRE wires.[33] In any case, the lack of dissolved oxygen in most nonaqueous electrochemical energy storage measurements is an added support for the stability of PPyQREs. Additional experimental literature detailing the use of PPyQREs are described in many papers which cite ref 13 (some of which have been highlighted earlier). It is also to be noted that there remain unidentified challenges in the use of such PPyQREs. For example, we have observed in our experiments that the construction of a PPyQRE in a solution containing lithium bis(trifluoromethanesulfonyl)imide immediately results in the polypyrrole flaking off the Pt wire, therefore rendering it ineffective in the presence of such salts.

CONCLUSIONS

We proposed the use of a Pt/polypyrrole electrode within a glass tube with a fritted end to make a stable quasi-reference electrode for electrochemical energy storage research. Our results clearly prove the advantages of using such a RE for measurements wherein the bulk solution redox potential changes significantly, for example, in bulk electrolysis. Practical electroanalytical measurements on Li-ion battery materials also highlight the utility of the encased PPyQREs. We hope that the work reported here aids the energy storage research community to address the challenge of identifying a suitable nonaqueous reference electrode for electroanalytical measurements.

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Notes

The authors declare no competing financial interest.

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