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Operando Thermo-Electrochemical Diagnostics with Au, TiO_2 , and $LiFePO_4$ as Reference Electrodes in Li-Ion Pouch Cells

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Thermo-electrochemical monitoring of state-of-the-art rechargeable Li-ion batteries during operation is critical for safety and reliability, yet it remains quite limited, relying on conventional full cell measurements with in situ techniques lagging behind. Here, the feasibility of incorporating Au, LiFePO₄, and TiO₂ electrochemical sensors into commercially available pouch cells, in conjunction with thermocouples to track the cell behavior during galvanostatic cycling at varying operating temperatures is demonstrated. It is found that Au provides the best in operando based electrochemical diagnostics for stable thermo-electrochemical performance via long-term cyclability (>1000 h), differential capacity curves, and at 25, 40, and 60 °C, followed by TiO₂, and LiFePO₄. Furthermore, cell temperature changes are analyzed alongside reference electrode readings, demonstrating the advantages of the complementary nature of these techniques for cell thermodynamics. Collectively, these findings offer deep insight into an improved battery management approach for next-generation lithium-ion energy storage systems.

1. Introduction

Lithium-ion batteries (LIBs) are considered one of the energy storage solutions in today's society due to their wide range of applications from portable electronics to electric vehicles and even space stations.^[1–3] There is high demand for increasing the energy and power density of LIBs due to the interest of researchers and industry in implementing large LIBs in all kinds of electric vehicles (EVs).^[4,5] There remain some key challenges associated with high-performance battery modules, such as the lack of in situ thermodynamic state monitoring.^[6] lowering the thermal and electrochemical safety and performance of these battery systems.

To overcome these challenges, it is beneficial to diagnose and distinguish the individual electrode performance (in addition to

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performance) whole-cell via in-situ instrumented cells.^[7–9] Here we design cells capable of monitoring galvanostatic charge-discharge profile at both cathode and anode. Additionally, we use various reference electrodes^[9] and surface thermal effect monitoring of these cells, which are an advancement when compared with prior studies.^[10,11] In addition to performance and safety optimization, monitoring of internal cell temperature and each electrode potential can be an important asset when trying to minimize polarization effects and battery degradation.[12,13]

We have previously demonstrated evaluating prototype Li-ion pouch and cylindrical cells^[14] with a simple lithium reference electrode. It was observed that there are challenges and limitations intrinsic to working with bare lithium metal, such as acute

moisture sensitivity and handling difficulties, requiring great care and precision. This subsequently limits the stability and feasibility of potential commercial applications. Here we have alleviated these issues by using thin film flexible printed circuit boards as substrates and compatible reference electrode materials.

In this work, we evaluate gold, LiFePO₄, and TiO₂ reference electrodes and thermal variation effects on individual electrode performance. The instrumented cells were tested at 25–60 °C using various electrochemical methods such as galvanostatic cycling cyclic voltammetry (CV) and electrochemical impedance spectroscopy with temperature measurement. The results demonstrated that the instrumented cells provided stable reference electrode readings over 1000 h, and the added reference element had a negligible impact on the Li-ion battery cycle life. In addition, differential capacity curves for individual electrodes were studied at different temperatures to better understand the stability of the reference electrode material in the cell. These techniques can offer a platform for analyzing cell failure mechanisms and improving the safety of Li-ion batteries.

2. Experimental Section

2.1. Reference Electrodes Fabrication

For in-pouch insertion, reference electrode sensors were fabricated using flexible printed circuit boards (PCBs) manufacturing technology, using $25\,\mu m$ flexible polyimide as a substrate with

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copper tracks and gold pad as the current collector material. Electrode inks were prepared for the LiFePO₄ (LFP) and TiO₂ materials and were drop cast or, for split cell testing, cast onto battery-grade aluminum foil using a draw-down coater. A detailed manufacturing procedure is described in our previous work.^[9]

The LFP ink was produced using a disperser mixer in NMP solvent with LFP:carbon black(CB):PVdF in the ratio 90:5:5.The TiO_2 ink was also produced through disperser mixing in water solvent of TiO_2 , CB, carboxymethyl cellulose (CMC) and styrenebutadiene rubber (SBR) in the ratio 90:5:2.5:2.5. The electrodes were dried at 80 °C in an oven for 24 h before being transferred and used in an argon-filled glove box.

2.2. Sensor to Battery Integration

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Sealed multilayered NMC532 versus graphite dry (no electrolyte filled) '575 166' 1 Ah pouch cells were obtained from Li-Fun Technology (China). Before filling, the sensor was slipped into the stack in the middle of the pouch cell. The cells were then injected with 4 g of electrolyte—1 M solution of LiPF₆ mix in EC: EMC 3:7 + 10% fluoroethylene carbonate (Solvionic). After filling, cells were sealed with a compact vacuum sealer (MTI Corp.) and transferred into a temperature-controlled chamber to soak for 24 h at 25 °C to subsequently undergo the formation procedure and test cycling.

2.3. Electrochemical Testing and Evaluations

To understand the behavior of the cells during operation, the cells were cycled through constant-current (CC) followed

by constant–voltage (CV) charge and constant–current (CC) discharge. Galvanostatic charge/discharge (GCD) tests were conducted between 2.5 and 4.2 V at various temperatures of 25, 40, and 60 °C, utilizing their full capacity range.

Galvanostatic intermittent titration technique (GITT) measurements and electrochemical impedance spectroscopy (EIS) were performed to determine the stability of the cells and impedance values. GITT current pulses were applied for 5 min during charge/discharge, followed by a 30 min rest to reach the steady-state/equilibrium potential of the cell. The procedure was repeated stepwise to cover full states of charge/discharge. EIS measurements were conducted at an identical state-of-charge of 0% for all cells for comparability, using a 100 mA amplitude in Galvanostatic mode, with open circuit voltage/rest steps before and after the measurement.

CV experiments were performed using VMP3 multichannel potentiostats (Bio-Logic Science Instruments). All tests were performed in a temperature-controlled chamber (Binder) at 25 °C. For 3 electrode cells, CV was performed with a scan rate of $0.2 \, \text{mV s}^{-1}$. The Au, LFP, and TiO₂ were scanned between 0–1.5, 2.5–4.2, and 1–3.25 V versus Li⁺/Li. A flow diagram for the test protocols and procedures in this article is shown in **Figure 1**. For cross-examining the thermocouples elements implemented within the cells, a 14-bit analog to digital converter PicoLog (Pico) was used. Furthermore, all cells were equilibrated for at least 6 h before experimentation to reduce the effects of measurement error due to thermal variations.



Figure 1. Test protocol and procedure.

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Figure 2. Cyclic voltammetry (CV) curves of: A) Au, B) LiFePO₄ (LFP), and C) TiO₂ at a scan rate of 0.2 mV s⁻¹.

3. Results and Discussion

3.1. Electrochemical Measurements and Stability Monitoring

CV was performed between 0.01 and 4.2 V (vs Li/Li⁺) to better understand the various electrochemical process that occurs during oxidation/reduction on the Au, LFP, and TiO₂ using split three-electrode cells. **Figure 2** shows the CV curves observed at 0.2 mV s⁻¹ for the three cases. For TiO₂ one pair of

anodic/cathodic peaks is present at around 2.1 and 1.7 V in agreement with expected values.^[15–19] This can be attributed to the Ti^{+3}/Ti^{+4} redox reaction, and also related to the removal of Li^+ from different lithium lattice sites in the structure that activates at these relative potentials. The CV (Figure 2A) of Au shows three peaks at 0.15, 0.4, and 0.5 V during an anodic scan and one peak during a cathodic scan at 0.01 V. In agreement with the literature,^[20,21] it is evident from the redox process, specifically the high current peak with the onset above 0 V (vs Li/Li⁺) that there



Figure 3. Anode, cathode, and full cell potential profiles of a pouch cell fitted with a reference electrode. It represents 200 mA (C/5) cycling rate with inserted: A) TiO₂, B) LFP, and C) Au electrodes.

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is bulk lithiation or alloying into Au-Li system. Subsequently, lithium stripping from the gold surface can be seen when the scanning direction is reversed.

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It is observed in Figure 2B,C that anodic/cathodic peak intensity is higher for LFP and TiO₂ during the first cycle. Whereas, Au behavior is observed in Figure 2A during the anodic scan, which exhibits reversible behavior during the first–third cycle. LFP and TiO₂ redox process can be attributed to the initial surface effects such as the electrolyte interface formation (SEI) and further intercalation of Li⁺ into the structure.^[15] This also suggests that only from the second cycle we can observe a full transformation of the anatase TiO₂ to the Li_xTiO₂ phase.^[16] These measurements conform to the theory of two-phase and irreversible transformation after the second peak from TiO₂ to LiTiO₂.^[22,23]

Voltage versus time profiles for cathode, anode, and full cell with respect to Au, LFP, TiO_2 , and Li reference electrodes obtained during prolonged cycling are shown in **Figure 3**. The stability of the data obtained over the extensive cycling test time indicates the long-term capabilities of the reference electrode element. Au and TiO_2 both exhibit long-term stability over 1000 h of 0.2 C cycling, shown in Figure 3A,C.

As an experimental tool, Au and/or TiO₂ is a preferred option due to no additional formation step required (unlike for LFP) minimizing the complexity and preparation time required, when used as a reference electrode. Finally, for comparison, Li-strip as a reference electrode in the same set-up (shown in Figure S1, Supporting Information), and non-modified benchmark (BM) pouch cells were also tested to provide baseline readings (shown in Figure S2, Supporting Information)—no significant deviation in the cycling behavior was observed.

Coulombic efficiency (CE) comparison of benchmark and reference electrode integrated cells was also used as a quantifiable indicator for the reversibility of the cells at various temperatures. The results are shown in **Figure 4**. The CE achieves over 99.8% for all reference electrodes at 25, 40, and even 60 °C in line with the benchmark cells. The CE of all other integrated cells having LFP, Au, TiO2, and benchmark cells demonstrated similar behavior at 25, 40, and 60 °C. The above-mentioned experimental results indicate that the inserted sensor has a negligible impact on the cycling stability of the pouch cells at standard as well as elevated temperatures, in favor of adding the functionality of the integrated reference electrode sensors in pouch cells for various applications.



Figure 4. Coulombic efficiency versus cycle number of cells with RE (Au, TiO₂, LFP, and benchmark cells) for initial ten cycles each at C/5, A) 25 °C B) 40 °C, C) 60 °C, with D) showing the overall long-term Coulombic efficiency (CE) over 1000 h.

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Differential capacities as a function of cell potential were analyzed for the first and tenth cycles as shown in Figure 5. Additional observations of in situ phenomena can be made thanks to the presence of the reference electrodes. Conversely, the quality of reference electrodes can be confirmed.

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First, dQ/dV analysis indicates that there is a slight decrease in capacity following an increase in the temperature from 25 to 60 °C. Initially, charge peaks at \approx 3.65 V (smaller) and \approx 3.75 V (larger) were observed. However, initially minor shoulder peak at 3.65 V becomes a major feature in the charging step. This indicates that the loss in charging capacity occurs primarily at higher potentials, corresponding to a loss of storage capacity of the graphite that is present in the anode, as the graphite fully lithiates at high cell potential.

LFP reference electrode indicates cathode peak shifts to a higher potential at a higher temperature, in contradiction to the complementary readings with Au and TiO₂ references. This is associated with higher polarization as compared to Au, and TiO₂ at a higher temperature, indicating LFP instability in this application. The corresponding discharge peaks at \approx 3.6 V



Figure 5. dQ/dV curves measurements taken from instrumented cells for: A–C) full cell and D–F) cathode at 25–60 °C.

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Figure 6. EIS of the evaluated pouch cells with LFP, TiO₂, Au, as reference electrodes at temperatures of: A) 25 °C, B) 40 °C, and C) 60 °C.

are consistent with those observed for the first discharge at 25, and 40 °C. In addition, additional discharge peaks were recorded at \approx 3.4, 3.5, and 3.6 V at a higher temperature of 60 °C.

These results demonstrate that both TiO_2 and Au are suitable for high-temperature cell diagnostics. These stable high-temperature reference electrodes can be used for battery degradation mechanism identification, given that separate electrode and full cell values are obtained with these enabling analysis of distinct potential curve features.^[24–26]

As illustrated in Figure 6A-C, EIS spectra exhibit contraction of the semi-circle as the temperature increases. This contraction of the semi-circle at high temperatures implies that the impedance and ohmic resistance, charge transfer resistance decrease.^[27–29] One of the reasons for impedance drops at a high temperature can be a decrease in internal resistances, also resulting in a decrease in voltage drop under load. Furthermore, a decrease in charge transfer resistance with a rise in temperature suggests that the Li-ion insertion/deinsertion process at the electrodes becomes easier.^[27,28] In addition, the first semicircle grows while the second diminishes, which suggests that the SEIrelated effects are the main cause of the decrease in impedance at high temperatures.^[27,28] The reduction of the second semicircle may be associated with the depletion of Li-ion from the cathode.^[28] The presence of all three reference electrodes is shown to have a negligible impact on the EIS response of the cells, with the possible exception of LFP, suggesting instability at elevated temperatures in line with the differential capacity (Figure 5) analysis.

The surface temperature evolution during galvanostatic charge/discharge (GCD) was monitored in parallel on both instrumented and pristine pouch cells. To further investigate the temperature impact and electrochemical measurements correlation, both current and potential profiles were plotted alongside temperature readings, as shown in **Figure 7**. This way we compare three different reference electrodes; Au, TiO₂, and LFP displaying potential profiles of cathode, anode, and full cell in relation to the changing temperature. A similar kind of thermo-electrochemical analysis is usually attempted^[12,13] only for full cell values. In our previously published work, such measurements were attempted either electrochemically^[10,11,14] or thermally, e.g., using fiber-optic sensors for commercial cylindrical cells.^[30]

The shape of the measurement profiles in Figure 7 shows that at each evaluated temperature (25, 40, and 60 °C) the maximum value was reached at the very end of each discharge cycle. This can be associated with an increase in impedance at the cell discharged state. The temperature returned to the baseline temperature when the cells were allowed to rest for 30 min after each cycle. In addition, with high accuracy monitoring, two peaks can be clearly defined in the constant current (CC) phase of the cycles, which could be correlated to the dQ/dV phase change around 3.65 and 3.75 V identified in Figure 4. The instrumented cells provide a consistent, repeatable, and continuous monitoring of change in potential and temperature, which correlates well with the state of charge (SOC) throughout the cycling program. The experimental data presented earlier also illustrates, in conjunction with Figure 6, that the integrated sensors have no impact on the cells' cycling performance.

4. Conclusions

In this study, various reference electrodes were successfully integrated into commercial 1 Ah lithium-ion pouch cells and evaluated alongside thermocouples for real-time thermoelectrochemical monitoring. The electrochemical performance of such instrumented cells was evaluated over 25–60 °C and was found promising in realizing in situ monitoring of individual cathode, anode, and full cell electrochemical potentials by using Au, LiFePO₄, and TiO₂ as the reference electrode materials. In contrast to our previous work utilizing lithium metal reference electrodes in commercial cells, herein used materials and methodology alleviate intrinsic handling difficulties and enable flexible co-location of other sensing elements.

All integrated cells had shown a stable galvanostatic chargedischarge cycling and Coulombic efficiency over 1000 h. It proves that the embedded reference electrode element has had a negligible impact on the cyclic performance of the cells. CV was performed on the reference electrodes Au, LiFePO₄, and TiO₂ for evaluation of their redox process versus Li in threeelectrode electrochemical cells. dQ/dV plots curves pronounce the differential capacity loss and polarization/voltage shift in cathode/anode to higher potential from first to tenth cycle only



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Figure 7. The full cell, anode, and cathode potentials, alongside current and temperature profiles for cells fitted with an example of the reference electrodes Au and benchmark. Each cycle were done at C/5 at 25, 40, and 60 °C A–C) Benchmark and D–F) Au, respectively.

for LiFePO₄ reference electrode, as a comparison to Au, and TiO_2 showing stable performance from 25 to 60 °C, made evident with the use of reference electrode in-situ electrochemical measurements.

The temperature sensor can relate internal charge-discharge cycling in a real-time scenario by comparing it with the distribution of temperature data, which together with the voltage data obtained from the integrated reference electrodes can be supportive of continuous monitoring for the state of charge (SOC) estimation. Furthermore, EIS and Coulombic Efficiency data obtained at the various temperatures further proves that reference electrode insertion has no impact on the overall impedance of the evaluated commercial lithium-ion pouch cells.

Overall, the in situ cell sensing methodology developed here can support the design, research, and rapid prototyping of new cells and smart battery systems. Further studies will explore multipoint-based in-situ temperature monitoring at various temperatures alongside herein devised reference electrodes to further monitor and improve models' accuracy of internal thermodynamic behavior for rapid charging, aging, and SoX estimation of lithium-ion pouch cells.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Z.A. and T.A. performed the experiments and data analysis with the assistance of A.R. All authors wrote the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

battery diagnostics, electrochemistry, gold, LFP, lithium-ion batteries, pouch cells, reference electrodes, thermodynamics, titanium oxide

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