

In Situ QCMD Study of Composite LiFePO₄ Electrodes for Battery Applications

Overview

LiFePO₄ is a widely used cathode material in lithium-ion batteries due to its safety, stability, and cost-effectiveness. It offers a stable electrochemical profile with sharp peaks during intercalation/deintercalation. Operating at low potentials, it avoids parasitic reactions common at higher voltages, enhancing efficiency and longevity.

The BioNavis Quartz Crystal Microbalance with Dissipation (QCMD) paired with a compatible potentiostat, enables advanced electrochemical analysis of processes, for example, during lithium-ion intercalation in battery electrodes. This study focuses on composite LiFePO₄ (LFP) cathodes, utilizing monitoring QCMD sensors for insights into gravimetric Li-ion intercalation/deintercalation (Figure 1), and viscoelastic changes in the electrodes.

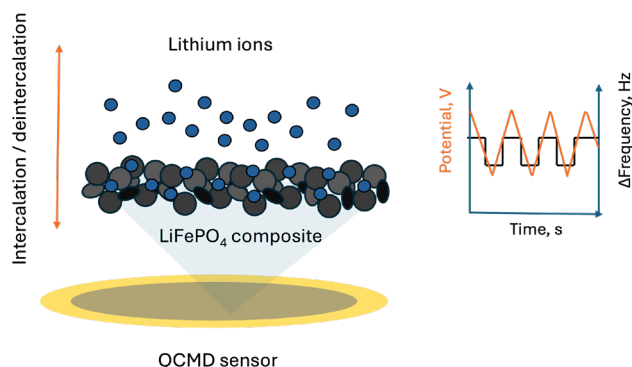


Figure 1. Li-ion intercalation/deintercalation in and out of LiFePO₄ composite when a cyclic potential is applied, and frequency changes are monitored at the same time.

Experimental Methods

A slurry of carbon-coated LFP powder (with 10% PVDF binder dissolved in N-methyl pyrrolidone) was sonicated and applied to 5 MHz gold-coated QCMD sensors via gas-assisted spraying. Coated sensors were characterized in 1M Li₂SO₄ solution using the QuickLock EQCM In-batch measurement cell connected to the BioNavis QCMD 100 system at 23 °C and 13 overtones.

Electrodes (Pt – counter, Ag/AgCl – reference and the gold-coated QCMD surface as a working electrode) underwent cyclic voltammetry (CV) cycling in Li₂SO₄ electrolyte, monitored via the potentiostat. Parameters included initial and final voltages (0.6 V to 0.0 V vs. Ag/AgCl) and a scan rate of 5 mV/s. Theoretical Faraday frequency shifts (calculated by the equation below) were calculated to compare experimental results.

$$\Delta f_{Far} = \frac{MW_{Li} C_{SC} Q}{nFA}$$

where MW_{Li} is Li molar mass (equal to 7 g/mol), C_{SC} is Sauerbrey constant ($56.6 \cdot 10^6 \text{ Hz cm}^2/\text{g}$), Q is the charge transferred during the electrochemical process, obtained by trapezoid integration of the measured current (C), n is the number of transferred electrons per intercalated cation (in this case is equal to 1), F is the Faraday constant (96485.3365 C/mol), and A is the electrochemically active electrode surface (0.78 cm^2).

Results and discussion

During cyclic voltammetry (CV) cycling, the shifts in frequency aligned with theoretical Faraday predictions (Figure 2) at all overtones. Dissipation changes were negligible (Figures 2 and 3), confirming that cycling did not alter the electrode's structural properties or viscoelasticity. Furthermore, when frequency and bandwidth change was plotted against the varied voltage (Figure 3), it was seen that the half-bandwidth is almost zero, indicating that there is no permanent change during the CV scan. These results suggest that the intercalation of Li-ions into LFP happens purely in gravimetric mode (i.e., the weight change of the composite LFP due to inserted Li-ions). Also, the electrode maintained its pristine morphology and mechanical stability throughout the cycling process.

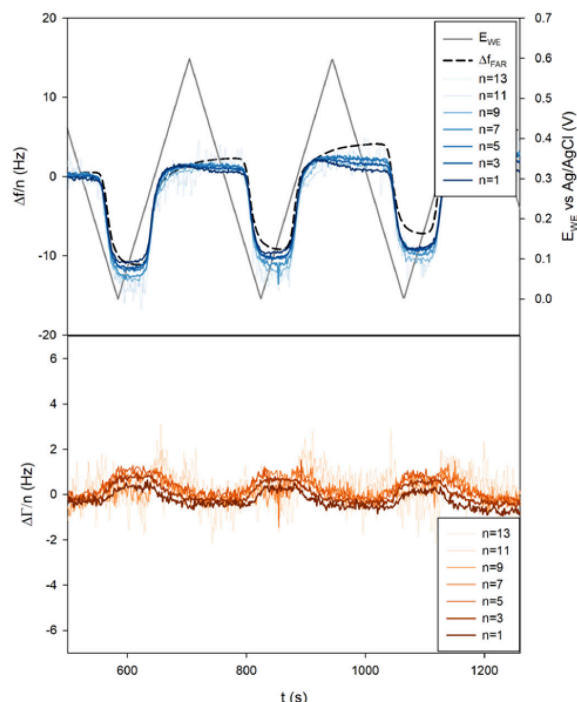
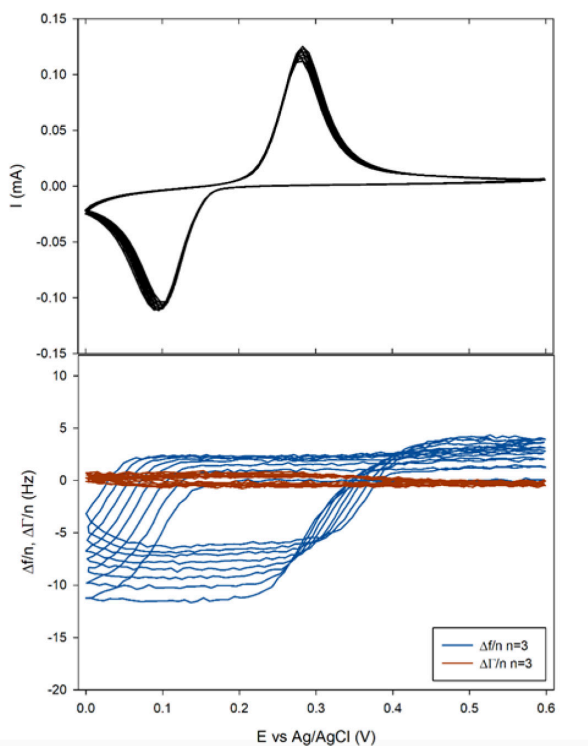


Figure 2. Frequency (top) and half-bandwidth (bottom) shift registered during CV technique. Theoretical Faraday frequency has been added to the top graph as a dotted black line. This illustrates the Li-ion intercalation/deintercalation process when a cyclic potential is applied.



Conclusions

The BioNavis QCMD platform is a robust tool for analyzing Li-ion intercalation/ deintercalation in battery electrodes. This study confirmed that LFP electrodes maintain structural and electrochemical stability under cycling, with purely gravimetric intercalation behavior. The platform also offers potential for other application areas such as *in situ* electrodeposition, electropolymerization, enhanced functionalization of surfaces, etc.

Recommended instrumentation for reference assay experiments

BioNavis QCMD 100

Sensor surface: Au sensor with Ti adhesion layer

Software: BioNavis Control

Figure 3. Electrochemical current (top) and 3rd overtone frequency and half-bandwidth (bottom) versus working electrode usage, showing that no permanent morphological or viscoelastic changes occur during the cycling.