

#### Summary

Use of AWSensors X1 Platform in combination with a compatible potentiostat to perform an electrochemical study of various processes accompanying Li-ion intercalation into battery and supercapacitor electrodes onto the gold surface of 5 MHz QCM sensors.

#### Introduction

LiFePO<sub>4</sub> (LFP) electrode is widely used in Lithium Ion Batteries (LIB) as a practical cathode. It is considered as one of the safest, toughest and most cost-effective cathodes for lithium batteries available today. It possesses a stable electrochemical response, expressed by sharp intercalation and deintercalation peaks during voltammetric cycling. The relatively low working potentials of the LFP provide an electrochemically stable potential window in which only Li insertion/extraction processes take place without the contribution of parasitic processes associated with high operation potentials.

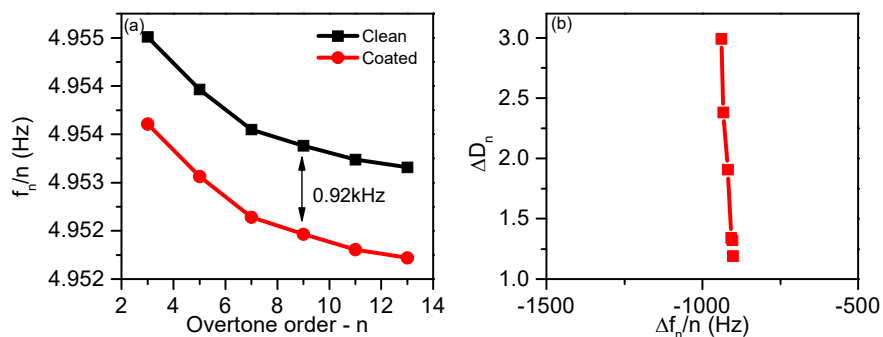
#### Materials and Methods

**Electrode Fabrication.** A commercially available carbon-coated LiFePO<sub>4</sub> powder was mixed with 10% PVDF binder and dissolved in N-methyl pyrrolidone (NMP). The obtained slurry was sonicated for 10 minutes for its better homogenization. The resulted suspension was deposited onto the top gold surface of a 5 MHz quartz crystal using gas-assisted spraying [1]. After the sensor coating the resonance frequency and resonance width values were measured using the AWS X1 platform in air and in 1M Li<sub>2</sub>SO<sub>4</sub> electrolyte solution.

#### Characterization of the electrode in air and in electrolyte solutions.

The bare and coated quartz crystals were introduced in a Quick-lock® EQCM In-batch measurement cell connected to the AWS X1 platform. The X1 Temperature Control Unit was set to 23 °C. Once the temperature stabilized, the admittance spectrum was measured in air for all odd overtones from the fundamental frequency to the 13<sup>th</sup> overtone. As it can be seen from **Figure 1a**, a typical decrease in the frequency shift with the overtone order converging to a fixed value at relatively high overtone orders were observed for both bare and coated sensors. This response gives a preliminary indication of the quality of the tested sensors [1]. Next, in order to validate that the electrode coating is rigid (the necessary condition for application of Sauerbrey equation) the changes in the dissipation factor,  $\Delta D = \Delta W/f_0$  (where  $\Delta W$  and  $f_0$  denote the resonance width and fundamental frequency, respectively), are plotted versus the frequency shift normalized by the overtone order,  $\Delta f/n$ . As shown in **Figure 1b**, the nearly overtone order independent frequency response followed by the relatively small dissipation factor changes was recorded. Note, that at high overtone order, a larger dissipation shift was recognized which may be attributed to the multilayer character of the electrode coating [2].

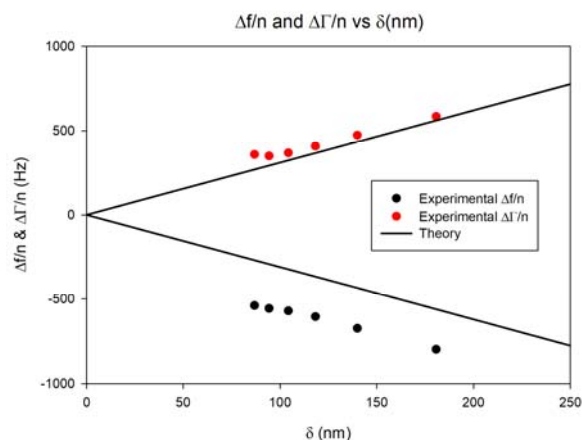
After the initial evaluation of the coating in the air, an electrolyte solution (1M Li<sub>2</sub>SO<sub>4</sub>) was injected into the sensor cell. Both the reference (Ag/AgCl) and counter electrodes (Pt) were inserted in the cell and connected to a Biologic SP-200 potentiostat. An Open Circuit Voltage



**Figure 2. (a) Frequency – overtone order distribution obtained for bare gold (black) and for LFP-coated (red) quartz crystals. (b)  $\Delta D$  vs  $\Delta f/n$  overtone normalized changes.**

(OCV) equal to 0.2 V (vs. Ag/AgCl) was measured while monitoring the frequency and dissipation factor changes as a function of time. When the crystal's baseline stabilized, its admittance spectrum at all the overtone orders were measured. The change in the frequency and resonance widths due to immersion of the coated crystal from the air into the electrolyte solution were calculated by subtraction of the related data measured in the air from that measured in the solution (valid for the rigid coating only). Normalizing the experimental changes of the frequency and the resonance width by square of the fundamental frequency and solution density, the resulting changes were compared with the theoretical Kanazawa plots (see **Figure 2**). The deviation of the experimental points (related to the different overtone orders) from the Kanazawa straight lines implies hydrodynamic solid-liquid interactions between the electrolyte solution and the coated electrode of complex morphology. The use of the appropriate hydrodynamic models provides a unique information about the morphological character of the coating (see *Electrochim. Acta* review and *Energy Materials* review [3]).

**Cyclic Voltammetry characterization.** First the



**Figure 1. Half-bandwidth ( $\Delta \Gamma$ ) and frequency shifts ( $\Delta f$ ) measured for the coated sensor (solid circles) vs theoretical Kanazawa predictions for an ideally flat surface (black lines).**

electrode immersed into the solution was monitored during 1 minute in the OCV mode followed by a cyclic voltammetry (CV) for 10 cycles. Employed CV parameters are summarized in Table 1.

The theoretical Faraday frequency shift was calculated based on the experimentally measured intercalation

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**Table 1. Parameters of the CV measured with composite LiFePO<sub>4</sub> electrode.**

E <sub>i</sub> (V/ vs. Ag/AgCl)	E <sub>i</sub> (V/ vs. Ag/AgCl)	Scan rate (mV)
0.6	0.0	5

charge,  $Q$ , implying 100% coulombic efficiency (i.e. the ratio of deintercalation and intercalation charges was assumed to be equal to 1):

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

Eq. 1

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 ( $96485.3365 \text{ C/mol}$ ), and  $A$  is the electrochemically active electrode surface ( $0.78 \text{ cm}^2$ ).

## Results

The preliminary characterization of frequency and resonance width changes due to immersion of the coated crystal into the electrolyte solution (1M Li<sub>2</sub>SO<sub>4</sub>) from air is presented in **Figure 2** by solid circles. The solid straight lines relate to the Kanazawa-type frequency and resonance width changes for ideally flat surface of the neat crystal (solution density and viscosity used for calculation of Kanazawa plots were  $1098 \text{ kg/m}^3$  [4] and  $1.69 \text{ cP}$ , respectively [2]).

For construction of the plots shown in **Figure 2** the frequency and resonance width changes of the intercalated electrode for all of the overtone orders used were presented as function of the penetration depth of the

acoustic wave in the solution,  $\delta$ . The penetration depth, dependent only on liquid's properties (density,  $\rho$ , and viscosity,  $\eta$ ), fundamental frequency,  $f_0$ , and the overtone order,  $n$ , was calculated by the formula:

$$\delta = \sqrt{\frac{\eta}{n\pi f_0 \rho}}$$

Eq. 2

Due to a complex morphology, the characteristic deviation of frequency and resonance width of the electrode coating from that of the Kanazawa plots for flat surface is mainly due to hydrodynamic solid-liquid interaction of solid matrix of the electrode with the contacting solution. The porous structure parameters of the electrode can be retrieved by the appropriate hydrodynamic modelling [5]. However, for the higher harmonics, the characteristic downward deviation of frequency from the Kanazawa plot is evident of small viscoelastic contribution of the electrode [5].

However, when treating the experimental frequency and resonance width changes on all the overtone orders during consecutive CV cycling of the electrode, we found that the shift  $\Delta f/n$  practically coincides for all  $n$  and with the theoretical Faraday frequency change (see **Figure 3**), whereas the related change in  $\Delta W/n$  appeared to be close to zero (see **Figure 4**). This result clearly shows that insertion of Li-ions into host occurs in a completely gravimetric mode. This, in turn, implies that the change of the electrode potential during the electrode cycling affects negligibly the pristine electrode porosity/roughness and viscoelasticity.

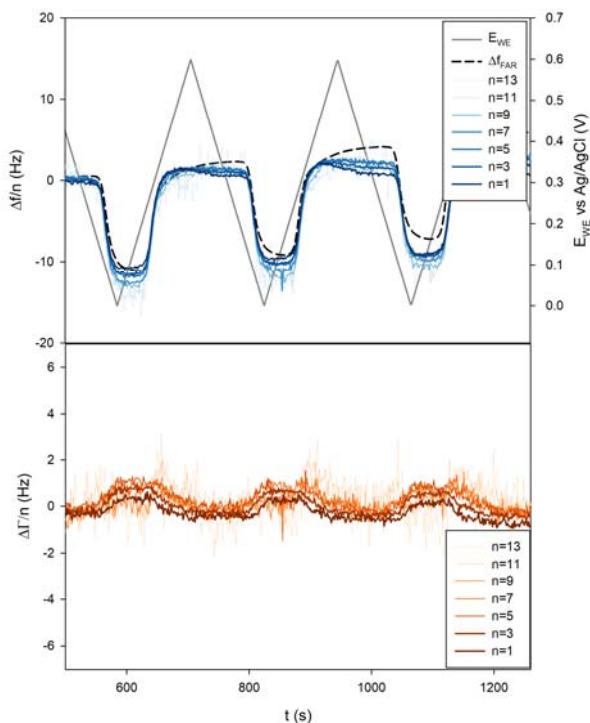
## Conclusions

AWSensor platform provides a very valuable insight into characterization of various processes accompanying Li-ion intercalation into battery and supercapacitor

# Application Note

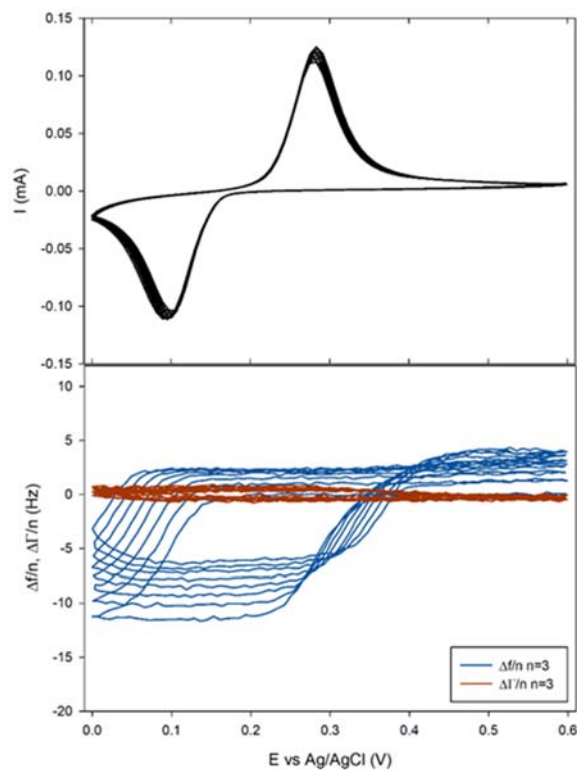
## In-Situ Study of Composite LiFeP<sub>0</sub><sub>4</sub> Electrodes

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**Figure 3.** 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.

electrodes. Although this application note is focused on purely gravimetric aspects of Li-ions intercalation into LFP electrode, the set of the experimental data (resonance frequency and resonance width changes measured at multiple harmonics) can be equally used for quantitative characterization of the electrodes experiencing considerable potential-dependent morphological or viscoelastic changes during their cycling.



**Figure 4.** Electrochemical current (top) and 3<sup>rd</sup> overtone frequency and half-bandwidth (bottom) versus working electrode voltage.

## Acknowledgments

This application note has been prepared with the priceless collaboration of Prof. Michael Levi and Dr. Netanel Shpigel from Department of Chemistry, Bar-Ilan University, Israel.

## References

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# Application Note

## In-Situ Study of Composite LiFeP<sub>0</sub><sub>4</sub> Electrodes

### for Battery Applications

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### Order Information

Product	Quantity	Reference
AWS X1	1	AWS X1 000031 A
AWS X1 Temperature Control Unit	1	AWS X1 000032 A
EQCM in-batch cell for AWS platform	1	AWS CLS+ 000016 Q
AWS 14mm sensor, 5 MHz, Ti/Au, Polished	10	AWS SNS 000043 A

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