In Situ Acoustic Diagnostics of Particle-Binder Interactions in Battery Electrodes

Tough and brittle characters of the binder in composite battery electrodes stabilize/deteriorate their long-term cycling performance, respectively. Instead of performing conventional long-time cycling tests of battery electrodes followed by their postmortem analysis, the proposed accelerated EQCM-D diagnostic easily distinguishes between the stable and failed cycling modes of strained electrodes by characteristic coupled shifts in the recorded resonance frequency and resonance bandwidth changes on multiple harmonics (EQCM-D signatures).

HIGHLIGHTS

New mechanism of strain accommodation in composite battery electrodes

Very quick screening of optimal binder-electrolyte solution combinations

Stiff binder exhibits small fracture toughness in high-strain composite electrodes

Soft binder with large fracture toughness mitigates high transformation strains

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**SUMMARY**

The high phase-transformation strain developed upon intercalation in the host particles of a composite battery electrode affects the polymeric binder network mechanically, deteriorating the electrode cycling performance. Here, electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) is used to demonstrate a new strain-accommodation mechanism, in high-strain NaFePO$_4$/PVdF electrodes, via relaxation of the binder network surrounding the intercalation particles. Complete mechanical degradation of the polymer network occurs during long-term cycling of NaFePO$_4$ electrodes in aqueous solutions (hard and tough behavior). In contrast, in aprotic solutions, a softened binder easily accommodates the high transformation strain, ensuring excellent electrode cycling performance (soft and tough behavior). Quantification of the high-frequency viscoelastic properties of an operating composite electrode linked to the binder’s fracture toughness ensures fast and facile screening of the optimal polymeric binder/electrolyte solution combinations. This methodology should be extremely important for optimization of cycling performance of Li-Si anodes undergoing huge volume changes during cycling.

**INTRODUCTION**

LiFePO$_4$ (LFP) is one of the most studied battery electrodes in which Li-ion insertion/extraction occurs as a first-order phase transition (two isostuctural phases with different lattice parameters coexist during the intercalation/deintercalation process).$^{1-7}$ The reduction in the volume of the unit cell during Li-ion extraction from a fully lithiated phase, LFP, to form an Li-free phase, FP, is about 5%, reflecting a moderately high misfit of their strain energies.$^8$ However, when an Li-free host, tailored during the synthesis process to accommodate Li ions, is subjected to electrochemical insertion of foreign Na ions of a significantly larger size than the Li ions (0.102 and 0.076 nm, respectively), the resulting phase-transformation strain in NaFePO$_4$ (NFP) electrode is 3-fold larger than that in the LFP electrode.$^9$ It was recently suggested that the large lattice mismatch between the NFP and FP phases can be mitigated, thereby accommodating the high strain of the lattice, by the formation of an intermediate amorphous phase giving rise to an initial stage of a plastic deformation in NFP electrodes.$^{10}$ For more than a 3-fold lower transformation strain in LFP electrodes, the extent of the active mass amorphization is negligibly small. In turn, important and intensively studied Li-Si anodes undergo much more pronounced volume expansion upon lithiation, and the transformation strain thus developed is 20-fold larger in comparison with that for NFP. Crystalline silicon undergoes amorphization during repeated lithiation-delithiation processes.$^{11}$ These
observations indicate that the formation of amorphous phases can serve as a mechanism of strain accommodation on a microstructural level for a variety of intercalation and alloy-type insertion electrodes.

However, a variety of structure-sensitive techniques of high spatial resolution (such as those used in the work reported by Xiang et al.\textsuperscript{10}) that probe local electrode microstructure are often less informative for tracking structural changes in the composite electrodes on a mesoscopic scale. This inspired us to choose LFP and NFP composite electrodes (with commonly used poly(vinylidene fluoride) [PVdF] binder) cycled in both aqueous and non-aqueous electrolyte solutions for a quantitative study of the mechanical electrode/binder interactions using an electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D).\textsuperscript{12–20} This acoustic technique\textsuperscript{12,15,20} is ideally suited for a real-time mesoscopic mechanical characterization of composite batteries electrodes comprising expanding/contracting intercalation particles embedded into a continuous network of a polymeric binder.

As illustrated in Figure S1, the polymeric binder in a composite electrode binds together neighboring intercalation particles that are arranged naturally in layers. From electrochemical and mechanical points of view, this porous multilayer active mass can be regarded as an interphase between the quartz crystal surface and the contacting electrolyte solution. The bottom layer of the electrode is rigidly attached to the Au-coated quartz crystal surface serving as a current collector (“no-slip” condition at the crystal/bottom layer interface).\textsuperscript{12–20} The top layer of the multilayered assembly is bound to the rest of the active mass by the same binder, which forms a continuous network throughout the entire electrode depth. The multilayered assembly on the quartz crystal surface is probed by the transverse acoustic waves generated by the crystal oscillating in MHz-range frequency on multiple odd harmonics (overtone orders, \(n\), from 3 to 13); both intercalation-induced gravimetric and viscoelastic changes in the battery electrodes can be sensitively tracked.\textsuperscript{16–19}

EQCM-D produces two coupled output responses, the resonance frequency \(f/n\) and the resonance bandwidth \(W/n\) or, equivalently, the dissipation factor \(D = W/f_o\); all the output responses are functions of \(n\); \(f_o\) stands for fundamental frequency. Quantification of the viscoelastic changes in the electrodes is reached via fitting a suitable acoustic load impedance model to the experimental frequency and dissipation factor changes (\(\Delta f/n\) and \(\Delta D\), respectively).\textsuperscript{15,18–21} All the applications of the EQCM-D method in the energy storage and conversion field reported so far (including theoretical and experimental backgrounds of the method) have been recently reviewed by us.\textsuperscript{18} The challenging issue of the electrochemical/mechanical coupling in high-strain intercalation hosts has never been discussed in either the available literature or our previous EQCM-D studies.

This work is focused on recording and quantification of the effect of moderate and high transformation strains on the viscoelastic properties of composite LFP/PVdF and NFP/PVdF electrodes, respectively, cycled in both aqueous and non-aqueous electrolyte solutions. A mesoscopic view of the different transformation strains in LFP/PVdF and NFP/PVdF electrodes caused by the related microstructural changes in the lattice parameters (atomic-scale view) is shown schematically in Figures 1B and 1A, respectively. We believe that successful quantification of the viscoelastic properties of the high-strain NFP/PVdF electrode (the highest transformation strain among the topotactic intercalation hosts) can promote this methodology for speedy and facile optimization of the binder/electrolyte solution combinations in order to significantly improve the cycling performance of extraordinary high-strain anodes.

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RESULTS

Electrode Viscoelasticity in Air and Neat Binder Films in the Electrolyte Solutions

Figure 2 presents the morphology and structure of the LFP/PVdF electrodes used for this study, obtained by scanning electron microscopy (EM), atomic force microscopy (AFM), and scanning EM-focused ion beam (SEM-FIB) measurements. Tilted images of the electrodes (Figures 2A and 2E) and especially the cross-section of the FIB-cut electrodes (Figures 2B and 2D) clearly show the individual layers of intercalations particles bound together and to the quartz crystal surface (Figure 2B) by PVdF binder. Figure 2F gives an impression of flexibility of the multilayered electrode assembly. The various images of the composite electrode shown in this figure were used for a schematic presentation of the multilayered electrode structure shown in Figure S1.

Comparing the images in Figures 2B and 2E, we conclude that the top layer (facing electrolyte solution) may contain less strongly bound intercalation particles compared with the bottom layer (facing quartz crystal surface). The implication is that the top layer is more compliant than the bottom layer (see the sloping versus vertical displacement profiles schematically shown in Figure S1). This is further proved by direct measurements of $\Delta f/n$ and $\Delta D$ changes for the coated versus uncoated (neat) quartz crystal using the acoustic multilayer formalism$^{15}$ (a special
Figure 2. Scanning EM Images of Pristine Composite LFP/PVdF Electrode Attached to a Quartz Crystal Surface

(A) The electrode attached by the binder to a flat Au-coated quartz crystal (inset: AFM image of the external surface).
(B) Scotch-tape peeled backside of the electrode (facing the crystal surface).
(C) Sectioning and cutting off the bottom surface of the electrode coating by FIB.
(D) Cross-sectional scanning EM image of the cut electrode layer showing its multilayer structure.
(E) Tilted scanning EM image of composite electrode layer showing the LFP particles embedded within the (continuous) matrix of the PVdF binder.
(F) A piece of the composite electrode layer pulled off the quartz surface.

Scale bars, 500 nm (B, D, and E), 5 μm (A and C), and 15 μm (F).
rule for the combination of acoustic load impedances of the individual layers, formally resembling in-series and in-parallel combinations of the elements of equivalent electrical circuits analogs of the electrochemical impedance of composite electrodes).

As expected, composite electrodes with a multilayer structure have a larger dissipation factor $D$ than the uncovered crystal (see Figure S2), and the specific overtone order dependence of $D$ reflects the particular mechanism of the oscillation-energy dissipation, which is linked to the multilayer electrode structure. Previously, we described in detail how this analysis is performed.22,23 For the electrodes used in this work, the experimental frequency and dissipation changes of the electrode measured in air are presented in Figure S2, whereas the extracted model viscoelastic parameters are indicated in Table S1 (see also comment following Figure S2).

Viscoelastic diagnostics of neat PVdF films in aqueous and non-aqueous solutions were performed to characterize the intrinsic viscoelastic properties of the binder, which are affected neither by the multilayered structure of the pristine electrode nor by the strongly expanded/contracted intercalated/deintercalated electrode particles. The details of this simple test have been reported previously.22,23 The data for neat PVdF films in contact with 2 M aqueous solutions of Li$_2$SO$_4$ and 1 M solutions of LiPF$_6$ and NaPF$_6$/EC + DMC (with related comments) are presented in Figure S3. The major conclusion is that PVdF binder is stiff in both aqueous solutions, but swells and softens in the aprotic solutions we used (swelling and softening of the binder is easily recognized by this EQCM-D test).18,22

**Single-Layer (Thin) Electrodes in Aqueous and Non-aqueous Solutions**

The behavior of single-layer (further termed thin) electrodes with a loading mass $\sim 35 \mu g/cm^2$ is remarkably simple in all the four relevant electrolyte solutions used. Cyclic voltammetry (CV) curves for both LFP and NFP electrodes in aqueous and aprotic solutions (Figures 3A and 3D, respectively) are strictly quasi-reversible. Due to the quasi-Nernstian behavior of LFP with respect to Li ions in the solution,24,25 the anodic peak potential during Li-ion extraction in pure Na$_2$SO$_4$ solution is shifted toward a more negative potential with respect to the extraction peak potential in the Li$_2$SO$_4$ solution. In contrast, the potential of Na-ion insertion is shifted toward much more negative potentials compared with that of Li-ion insertion, and the extraction of Na ions occurs in two well-separated steps. The shape of the CV curves characterizing Na-ion insertion/extraction into/from the FePO$_4$ host is in excellent agreement with previous reports.24–26 The existence of two anodic peaks for Na-ion extraction and only one cathodic peak for Na-ion insertion is explained by formation of the intermediate phase Na$_{0.7}$FePO$_4$, with related volume changes,26 in contrast to the direct transformation between the LiFePO$_4$ and FePO$_4$ phases.27

EQCM-D signatures of the thin LFP and NFP composite electrodes in both aqueous and aprotic solutions (Figures 3B, 3C, 3E, and 3F, respectively) are amazingly simple. During both Li- and Na-ion insertion/extraction the dissipation factor remains constant. Thus, $\Delta f/n$ does not depend on $n$ and practically coincides with the frequency change (designated $F_{\text{Faraday}}$); $\Delta f/n$ is then transformed into the related mass-density change due to the inserted (intercalated) Li ions ($\Delta m$) using the Sauerbrey equation

$$\Delta m = -C \cdot \Delta f/n,$$

(Equation 1)

where $\Delta f/n$ is the change in the frequency normalized by the overtone order and $C = Z_q/(2f_o^2)$ is the mass sensitivity constant where $f_o$ is the fundamental frequency.
and $Z_0$ is the acoustic wave impedance of AT-cut quartz equal to $8.8 \times 10^5$ g/(cm²s).

For a 5-MHz crystal, $C = 17.7$ ng/(cm²Hz). $F_{\text{Faraday}} = \Delta f/n$ is calculated using the same

Equation 1 relating $\Delta m$ to the intercalation charge obtained by integration of the CV
curves (using the Faraday law).

The coincidence of the experimental values of $\Delta f/n$ with $F_{\text{Faraday}}$ (Figures 3B and 3C)
implies that the mass-per-charge ratios of the intercalated Li and Na ions are 7 and
23 $\mu$g/cm² per pmol/cm² of inserted Li and Na ions, respectively, indicating a simple
intercalation mechanism.

A similar gravimetric limit was also reached with LFP/LiPF$_6$ in EC + DMC and NFP/
NaPF$_6$ in EC + DMC solutions (the CV curves are shown in Figure 3D whereas the
related changes of $\Delta f/n$ and $\Delta D$ are presented in Figures 3E and 3F). The same
mass-per-charge ratios were found for the LFP and NFP electrodes in aprotic solutions.
The conclusion is that once a sufficient amount of the polymer binder reliably
attaches a single layer of intercalation particles to the quartz crystal surface, the only
effect of Li-ion intercalation on the EQCM-D response is the change in the electrode
mass due to Li-ion insertion/extraction. This implies that both LFP and NFP
electrodes operate in the thin-layer mode. Operation in this mode reduces the visco-
elastic contribution to both the frequency and dissipation changes with respect to
the contribution to the measured frequency change caused by the mass of the inserted ions. Once the wavelength of sound (depending on the shear modulus and overtone order, the estimated range implies a length \( \geq 1 \mu m \)) is larger than the electrode thickness (200 nm in this case), the EQCM-D response is reduced to only a frequency change due to the mass of the intercalated ions. When a gravimetric characterization of the intercalation process is the desired goal, the electrodes should be fabricated to work in a thin-layer mode.

The fact that thin LFP and NFP electrodes in both aqueous and non-aqueous solutions behave gravimetrically during ion intercalation, and the experimental frequency change is equal to that calculated for neat (unsolvated) ions, two important conclusions imply that upon intercalation of Li and Na ions into composite LFP and NFP electrodes the only source of gravimetric change is the mass of the inserted unsolvated cations. No additional accumulation/loss of mass occurs during cycling these electrodes in the potential window used herein, implying that there are no side reactions that form surface species and there is no dissolution of active mass during the short experiments thus performed. These important conclusions, derived from EQCM-D experiments with very thin electrodes, should be true for any type of composite LFP and NFP electrodes, because they reflect the intrinsic properties of these systems (the active masses in the relevant solutions). However, since there are obvious mechanical and viscoelastic features of the insertion electrodes that undergo volume changes resulting in active mass-binder interactions, it is clear that too thin electrodes are not suitable for the study of mechanical and viscoelastic properties of composite electrodes comprising LFP and NFP. Hence, thicker (multilayered) composite electrodes must be prepared for EQCM-D studies, aiming at recording intrinsic mechanical and viscoelastic properties of these systems (LFP/NFP, PVdF binder, aqueous and non-aqueous Li/Na salt solutions).

Multilayered (Moderately Thick) Electrodes in Aqueous Solutions
The use of multilayered electrodes allows a reliable determination of the electrodes’ viscoelastic properties because their thickness is a substantial fraction of the wavelength of sound: the related shear displacement profiles become \( n \)-dependent (Figure S1). Since the wavelength of sound is inversely proportional to the overtone order \( n \) (see the sketch in Figure 1 for \( n = 1 \) and 3), the viscoelastic contribution to the total frequency and dissipation changes increases with \( n \). The tested electrodes had loading mass \( \sim 70 \mu g/cm^2 \), i.e., they were twice as thick as the thin-layer electrodes, consisting of bottom and top layers of the active mass particles as illustrated in Figure S1.

The LFP and NFP electrodes were cycled in aqueous solutions of Li2SO4 and Na2SO4 under identical conditions during 70 cycles. The results are conveniently presented in Figure 4. Figures 4A and 4D show the CV curves during 70 cycles (each 10th cycle is indicated) for Li+- and Na+-based electrolytes, respectively, whereas the corresponding \( \Delta f/n \) and \( \Delta D \) changes as functions of time for the entire individual cycle (fifth cycle is shown as an example) appear in Figures 4B and 4E, respectively. Finally, in Figures 4C and 4F, the changes of \( \Delta f/n \) and \( \Delta D \) are presented as a function of the cycle number during the course of the long-term cycling experiments.

From Figure 4A, it is seen that a moderate transformation strain in the composite LFP electrode containing PVdF binder, which is stiff in aqueous Li2SO4 solution, ensures very good electrode cycling performance. The EQCM-D signature of the electrochemical process of Li-ion insertion/extraction is very close to the gravimetric type (Figure 4B). This means that the viscoelastic state of LFP does not appreciably
change during Li-ion intercalation into this low-strained electrode. This is also consistent with the small recorded change in $\Delta D$ (Figure 4B).

The second conclusion that follows from Figure 4C (EQCM-D signature during long-term cycling of the electrode) is that the initial decrease in the baseline of $\Delta f/n$, which then stabilizes as cycling proceeds together with the small increase in $\Delta D$, clearly indicates that Li-ion insertion/extraction into/from these electrodes is accompanied by significant swelling of the composite electrode (i.e., its impregnation with the electrolyte solution resulting in downward shift of the frequency baseline), whereas the electrode softening is only negligible (since the upward shift of the dissipation baseline is very small). This conclusion is consistent with only a small viscoelastic effect in the EQCM-D signature throughout the individual charge/discharge cycles (Figure 4B).

Switching to the case of insertion of large-size foreign Na ions into the FP olivine host that was synthesized as LFP, suitable for transport of much smaller Li ions, we see
After Li\textsubscript{2}SO\textsubscript{4}

Pristine LFP/PVdF

After Na\textsubscript{2}SO\textsubscript{4}

binder

After NaPF\textsubscript{6}
that the intercalation process in NFP, in terms of both cycling performance and the related EQCM-D signature, are drastically different compared with that for LFP. This is seen with each single cycle, and from the large changes in the baselines of $\Delta f/n$ and $\Delta D$ as a function of the number of cycles, which are completely different from that of LFP electrodes (the scale for $\Delta D$ is the same for both electrodes). The difference is naturally assigned to the more than 3-fold larger volume expansion and hence larger transformation strain in NFP compared with that in LFP. NFP electrodes cycled in Na$_2$SO$_4$ solutions progressively lose their reversible capacity (Figure 4D) and the EQCM-D signature is very far from the gravimetric one: all the experimental frequency changes are negative and larger in their absolute values than $F_{\text{Faraday}}$. At the same time, the dissipation factor grows significantly with the overtone order (Figure 4E). The capacity failure of NFP electrodes during cycling is accompanied by a large positive shift in the baselines of $\Delta f/n$ and $\Delta D$ as a function of the cycle number (Figure 4F). Figure S4 shows a gradual increase in the amplitudes of the $\Delta f/n$ and $\Delta D$ responses with cycle number during the initial ten cycles, which become extremely large as the overtone order increases. Indeed the large transformation strains during insertion of Na ions from aqueous Na$_2$SO$_4$ solution into the FP host are accumulated gradually, giving rise to the process “seen” by the EQCM-D as a progressive softening of the composite NFP electrode.

This tentative explanation must be supported by the related viscoelastic modeling. Prior to addressing the modeling results, it is instructive to examine the scanning EM images of LFP and NFP electrodes before and after long-term cycling. Figure 5 displays scanning EM images of the pristine LFP electrode, and after cycling in Li$_2$SO$_4$ and Na$_2$SO$_4$ solutions. The images of the PVdF binder are drastically different for the LFP and NFP electrodes. Whereas no essential changes are seen in the image of the LFP electrode before and after cycling, the insertion of Na ions into the FP host are accumulated gradually, giving rise to the process “seen” by the EQCM-D as a progressive softening of the composite NFP electrode.

The source of the stiffness of the entire composite electrode attached to the quartz crystal surface is due to the stiffness of the polymeric binder network. The mechanical destruction of this network resulting in the loss of connectivity between the intercalation particles is formally “seen” by the EQCM-D as a rise in the effective softness of the composite electrode. The higher harmonics, as expected, are more sensitive to the increase in the effective electrode softness.15

The result of fitting of the two-layer viscoelastic model to the experimental shifts of $\Delta f/n$ and $\Delta D$ caused by the insertion of Na ions during the first, fifth, and 50th cycles (the fitting routine was considered in full detail previously$^{22,23}$) is presented in Figure S5. The retrieved viscoelastic parameters are listed in Table S2. From the values of these parameters, we first conclude that destruction of the polymeric network of the top layer during NFP cycling is greater than for the bottom layer: this is seen from the drastic decrease in the storage modulus of the top layer by more than one order of magnitude. Second, the loss modulus of this layer is larger than the storage modulus, indicating that the composite NFP electrode possesses a destroyed polymer binder network such that the separate parts of the electrode

Figure 5. Scanning EM Images of the Pristine and Cycled Composite Olivine Electrodes
(A–H) Pristine LFP/PVdF electrodes (A and E); the electrodes after the 70th cycle in aqueous Li$_2$SO$_4$ solution (B and F), after the 70th cycle in aqueous Na$_2$SO$_4$ solution (C and G), and after the 70th cycle in NaPF$_6$/EC + DMC solution (D and H). The images in the left column relate to the top surface, whereas the right column shows tilted images around the scratch. Scale bars, 1 µm (A–D) and 500 nm (E–H). Note a complete mechanical destruction of the PVdF binder (rigid in aqueous solution), which is unable to accommodate high transformation strain in NFP electrode (C and G), whereas the same high strain is completely accommodated by the binder softened in aprotic solution (D and H). Note the tiny PVdF particles formed by high strain-induced mechanical degradation of the PVdF fibrils clearly seen in (G).
are prone to rearrange their structure or even to creep. This is consistent with the scanning EM image of this electrode after long-term cycling. This statement will be revisited in the next subsection dealing with true viscoelastic effects in NFP/PVdF electrodes in aprotic NaPF6/EC + DMC solutions.

Multilayered Electrodes in Non-aqueous Solutions

The data are presented in Figure 6 in the same format as that for the aqueous solutions (Figure 4). It is clearly seen that both LFP and NFP reveal excellent cycling performance in the aprotic solution, implying that the instability of NFP/PVdF in the aqueous solutions relates indeed to the binder-electrode particle interactions and not to an intrinsic instability of LFP due to the insertion of the large Na ions. The EQCM-D signatures for both Li⁺ and Na⁺ cation insertions are of a purely gravimetric type: $\Delta f/n$ does not depend on $n$ and coincides with $F_{\text{Faraday}}$ whereas the $n$-dependence of $\Delta D$ is either negligibly small for the LFP or only slightly higher for the NFP electrodes (Figures 6B and 6E, respectively). The shift in the baseline for $\Delta f/n$ and $\Delta D$ changes with the cycle number is negligibly small (Figures 6C and 6F, respectively). Comparison between the experimental EQCM-D signature of the NFP electrodes in this non-aqueous electrolyte solution and the calculated one using the fitted viscoelastic parameters is shown in Figure S6, with the related parameters listed in Table S3.

It is important to explain why the large transformation strain developed in the NFP electrodes is completely accommodated during electrode cycling in the aprotic solutions.

Figure 6. CV and EQCM-D Characterization of Moderately Thick Composite Olivine Electrodes

(A–F) Long-term cyclic voltammetry responses for 1M LiPF₆ (A) and NaPF₆ (D) (both dissolved in EC:DMC). $\Delta f/n$ and $\Delta D$ signals recorded during one insertion/extraction cycle of Li⁺ (B) and Na⁺ (E), and during prolonged cycling in LiPF₆ (C) and NaPF₆ (F). The panel order and symbol designations are the same as in Figure 4.
solution but results in total mechanical destruction of the polymeric binder during cycling in the aqueous solution. A straightforward explanation is that the PVdF binder is softened in the aprotic solution and for this reason allows the intercalation particles to freely expand, thereby accommodating the large transformation strain. The electrochemical process of Na- and Li-ion insertions into FP look like a nearly pure gravimetric processes because the formally determined viscoelastic parameters are not significantly different for both intercalated and deintercalated states of the electrode (Table S3), and, in addition, the viscoelastic correction is much smaller than the mass effect due to inserted Li ions (see the EQCM-D signatures for intercalated and deintercalated states in Figure S6).

To reach a better understanding of the origin of the excellent cyclability of NFP in the aprotic solution, it is insufficient to guess or study the viscoelastic properties of composite electrodes at the rate of electrode charging (i.e., at low frequencies), as in this way only elastic modulus rather than loss modulus is assessed. In contrast, probing the viscoelastic properties of the electrodes by EQCM-D in the MHz frequency range of crystal oscillations provides assessment of changes in both shear elastic and loss moduli caused by the high transformation strain in the intercalation particles. The frequency dependence of the shear modulus allows us to analyze the viscoelastic dispersion in the polymeric binder network of the composite electrodes.

From Table S3, it follows that the shear moduli of the top layer of the composite NFP electrodes are similar in both the intercalated and deintercalated states, implying a complete and fast relaxation of the stress exerted by the high strain of the electrode particles. From Table S3 it is also evident that the frequency dependence of the storage and loss moduli of the top layer (i.e., viscoelastic dispersion) is close to each other for both the intercalated and deintercalated electrodes. This is seen from the fact that the fitted exponent of the storage modulus is high (1.6; the limiting value is 2.0), implying that the electrodes become progressively stiffer as the frequency (in the MHz frequency range) increases. Hence observation of the relaxation in the polymer network of the composite electrodes in the MHz frequency range did not reveal any specificity for the intercalated versus deintercalated states of the NFP electrode. This is consistent with the complete accommodation of the high transformation strain in the NFP intercalation particles.

DISCUSSION

In the last section, evidence was presented that assessment of the shear storage and loss moduli, and their viscoelastic dispersion in the MHz frequency range by EQCM-D, appears to be very useful in correlating these typically high-frequency mechanical characteristics with the electrode cycling performance occurring at orders of magnitude smaller frequencies (related to the rate of charging/discharging process). The correlation between the high- and low-frequency viscoelasticity could appear as a consequence of the following fundamental facts. The total area on the low-frequency stress-strain relationship up to the breaking point (see Figure S7) is termed the modulus of toughness, defined as the energy required to completely fracture the material.$^{28,29}$ At the same time, EQCM-D measures energy dissipation at high frequency,$^{15}$ and hence linear high-frequency viscoelastic characteristics can be related with energy dissipation due to fracture toughness (low-frequency characteristic). The problem of the link between the low- and high-frequency viscoelasticity for neat bulk polymeric films with a simple thermo-rheology is known as the principle of time-temperature superposition.$^{15,30}$ It is not currently clear whether realistic composite electrodes can be considered as thermo-rheologically simple.
Assuming that the principle of the time-temperature superposition can be applied to composite electrodes containing polymeric binders, at least qualitatively, the high-frequency viscoelastic characteristics measured by EQCM-D for the LFP and NFP electrodes, cycled in aqueous and non-aqueous solutions, can be transformed into the low-frequency domain as schematically shown by the characteristic stress-strain relationships (Figure S7). The LFP/PVdF electrode, having only moderate transformation strains in both aqueous and non-aqueous solutions, corresponds to the elastic and elastic-plastic parts of the stress-strain relationships, respectively. With respect to the location of the breaking point (strain-at-break), the behavior of the NFP/PVdF electrode cycled in aqueous solution resembles that of the hard and tough thermoplastics, whereas in aprotic solution its behavior is similar to the soft and tough thermoplastics. These are the correct terms borrowed from mechanics of polymers to describe the high-frequency EQCM-D signature of the charged high-strain composite electrode/electrolyte solution couples: rather high loss of oscillation energy (high loss modulus) obtained for NFP/PVdF in aprotic solution is evidence of its soft and tough behavior, in contrast to the hard and tough behavior of the same electrode in aqueous solution with its low modulus of resilience, which quantifies the energy that the material can absorb without damage to its structure (up to yield point in Figure S7).

It is extremely interesting to extend the EQCM-D based analysis to the family of new binders for Li-Si anodes with claimed purely elastic properties. Is a viscous contribution to the high-frequency shear modulus of these binders an inevitable necessary condition for the extremely high strain accommodation observed with Li-Si electrodes containing them? We believe that this key question will soon be answered by a breakthrough application of EQCM-D in the energy storage field.

EXPERIMENTAL PROCEDURES
Sample Preparation and Structural Characterization
Electrodes for the EQCM-D study were prepared by coating a slurry containing LFP particles in PVdF dissolved in N-methylpyrrolidone (NMP) (Sigma-Aldrich) on an Au-covered surface of a 5-MHz quartz crystal (14 mm diameter, Biolin Scientific) by the airbrush method. The multi-harmonic EQCM-D measurements were performed with a Q-Sense E1 module (QCM-D from Biolin Scientific) using overtone orders from 3 to 13. The electrodes containing LFP particles (smaller than 500 nm) were prepared in two steps. First, LFP powder (battery-grade powder purchased from Süd-Chemie) was sonicated using a probe type sonicator, then dispersed and settled as sediments in ethanol; after sedimentation, a supernatant with small particles (average particle size ~300 nm) was separated and dried on a hotplate. Second, PVdF (Solef, Solvay) was added to the LFP powder (at a mass ratio of 1:10), and all the components were dispersed in NMP.

Scanning EM images were obtained by a Magellan XHR 400L FE-SEM (FEI Company). Sectioning and cutting off the bottom surface of the electrode coating was performed using a Helios 600 (FEI) FIB instrument with further examination of the multilayered structure of the cut using high-resolution scanning EM.

AFM measurements were performed using a Dimension FastScan Bio instrument (Bruker AXS). All images were obtained using the contact mode with a single FASTSCAN-A silicon probe (force constant of 18 N/m, Bruker). The resonance frequency of this cantilever was approximately 1,400 kHz.
Electrochemical Characterization

A special home-made cell containing a small amount of electrolyte solution (up to 100 µL) was designed and used for electrochemical testing. The distance between the working electrode (a surface of Au-coated quartz crystal covered with composite LFP/PVdF electrode) and counter-electrode (Pt in aqueous solutions and metallic Na in non-aqueous NaPF6/EC + DMC solution) can be precisely varied. An Ag/AgCl/KCl(sat.) reference electrode was hermetically inserted into the cell for measurements in aqueous solutions, which were first bubbled with argon to remove traces of oxygen. CV tests were always performed in aqueous Li2SO4 solution down to −0.6 V to verify the absence of traces of oxygen in the solution. The aqueous electrolyte solutions were composed of Li2SO4 and Na2SO4 (Sigma-Aldrich) in double-distilled H2O at a concentration of 1 or 2 mol/L.

Commercial 1 M LiPF6 in EC + DMC (1:1) and 1 M NaPF6 in EC + DMC (1:1) were used as the electrolyte solutions to study Li-ion and Na-ion intercalation into FePO4. Both CE and RE were fabricated from metallic Li and Na, respectively. The cell was assembled in a glovebox (humidity and oxygen contents less than 1 and 10 ppm, respectively), closed hermetically, and measured electrochemically outside the glovebox.

Viscoelastic Modeling

Viscoelastic modeling for the contact of electrodes with air and with liquids was performed following our previously published papers and literature data.22,23 The relevant necessary equations were implemented in the commercial software Qtools (3.1.25.604 from Biolin Scientific, Sweden) supplied together with an EQCM-D instrument. By fitting the viscoelastic models to the experimental ΔD and Δf/n changes, one can evaluate the solid-layer density d_s, the thickness h_s, the elastic shear storage modulus G’ (sometimes designated as μ, especially for a quartz plate), and the shear loss modulus G”, which is linked to the solid shear viscosity, η_s = G”/2πnf_s. Through a built-in menu, the user chooses to fit (model) with one or two viscoelastic layers in sequence, in contact with either air or liquid. If the top viscoelastic layer is in contact with a Newtonian liquid (electrolyte solution), the menu allows the addition of a liquid layer characterized by the density of the liquid d_L and its viscosity, η_L.

Statistical Reproducibility of EQCM-D Measurements

Error bars on the plots of the experimentally measured frequency changes versus overtone order, both for the acoustic measurements in air and after immersion in the electrolyte solution under open circuit voltage, are shown in Figures S8A and S8B, respectively. For both types of measurements, the reference state was the neat Au-coated quartz crystal in air. We provide below details of the error estimation of the acoustic measurements of electrode coatings of complex geometry in air and electrolyte solution. They are different since the viscosity and density of gas and liquid phases are very different.

The standard precision of the QCM-D instrument is very high, ±0.1 Hz.15 The precision of the electrode coating fabrication is limited by the airbrush spraying technique, which was manually controlled. After some training, we achieved a frequency change in the air for the coated crystals with a precision of ±15 Hz. However, one should realize that the complex frequency measurement is performed in the EQCM-D separately, first for the neat (uncovered) crystal and then for the
electrode-coated crystal. Hence this measurement in air requires reassembling of the cell since the electrodes’ coatings are fabricated separately on a hot plate out of the cell. When complex frequency changes are monitored without reassembling the cell, then indeed the precision can be as high as ±0.1 Hz.

We have found a random (statistical) error in the frequency measurements of even a neat (uncoated) crystal after each reassembling of the cell: ±15 Hz. The source of the statistical error is due to static stress on the crystal from the o-ring used to keep the cell hermetically closed. The fact that the coated crystals are measured with the same precision means that uniform (compared with the wavelength of sound \( \lambda = 330 \text{ m} \) for the fundamental frequency 5 MHz) and almost identical distribution of the electrodes mass on the quartz crystal surface.

However, during measurements in liquid phases, the rough/porous structure, which was uniform on the scale of \( \lambda \) during complex frequency measurements in air, can be irreproducible during the measurements in solution whereby the size of heterogeneity should be compared with the much smaller penetration depth \( \delta \) (250 nm for the fundamental frequency of 5-MHz crystal). From the independent measurements of three physically different electrode coatings in solution, we have reached a precision of the frequency change in the solution of ±20 Hz. Hence all the electrodes explored herein possess the same structure when measured in air and in solutions.

SUPPLEMENTAL INFORMATION
Supplemental Information includes eight figures and three tables and can be found with this article online at https://doi.org/10.1016/j.joule.2018.02.014.

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AUTHOR CONTRIBUTIONS

DECLARATION OF INTERESTS
The authors declare no competing interests.
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