Lithium-Ion Batteries

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Non-Invasive In Situ Dynamic Monitoring of Elastic Properties of Composite Battery Electrodes by EQCM-D**

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Abstract: *Reversible Li-ion intercalation into composite Li-ion battery (LIB) electrodes is often accompanied by significant dimensional electrode changes (deformation) resulting in significant deterioration of the cycling performance. Viscoelastic properties of polymeric binders affected by intercalation-induced deformation of composite LIB electrodes have never been probed in situ on operating electrochemical cells. Here, we introduce a newly developed noninvasive method, namely electrochemical quartz-crystal microbalance with dissipation monitoring (EQCM-D), for in situ monitoring of elastic properties of polymeric binders during charging of LIB electrodes. As such, we find EQCM-D as a uniquely suitable tool to track the binder's structural rigidity/softness in composite Li insertion electrodes in real-time by the characteristic increase/decrease of the dissipation factor during the charging–discharging process. The binders partially swollen in aprotic solutions demonstrate intermediate viscoelastic charge-rate-dependent behavior, revealing rigid/soft behavior at high/low charging rates, respectively. The method can be adjusted for continuous monitoring of elastic properties of the polymeric binders over the entire LIB electrodes cycling life.*

Lithium-ion batteries (LIB) offer a very broad spectrum of applications, from portable devices to larger scale all-electric vehicles.[1] For large-scale applications, porous composite LIBs electrodes are usually used, containing at least three components: electrode particles (e.g., $LiFePO_4$), a binder (commonly, polyvinylidene fluoride, PVdF, and sodium carboxymethylcellulose, NaCMC),[2] and conductive additives such as carbon black, graphene, or carbon nanotubes. The processes of ions extraction/insertion occurring in LIBs electrodes during their charge/discharge result in periodic potential-dependent changes of the electrodes' volume (i.e., their deformation), bringing about a variety of undesirable mechanical effects, such as high-enough stresses, fatigue, fracture, and delamination from current collector.[3] Current techniques for in situ monitoring of electrodes strains include atomic force microscopy (AFM)[4] and electrochemical dilatometry.[5] A common drawback of these techniques is that they do not provide direct information on the potential-induced changes of the electrode porosity, which is an important factor of stress relaxation in LIB electrodes.

It has been recently shown that electrochemical quartz-crystal microbalance (EQCM) has a tremendous benefit of direct in situ gravimetric probing of ionic fluxes into composite nanoporous carbon electrodes during charging and discharging.[6] Later we have developed a self-consistent in situ methodology for tracking dimensional changes of this electrode based on EQCM with dissipation monitoring (EQCM-D) and we demonstrated this method's potential for two systems: $LiFePO_4$ olivine as a typical composite intercalation-type LIB cathode's material[7] and $Ti_3C_2M_x$ MXene as a composite material with properties intermediate between battery and supercapacitor electrodes materials.[8] A unique feature of this approach is the simultaneous recording of changes of two experimental EQCM-D parameters, namely frequency $\Delta F(E)$ and resonance width shifts $\Delta W(E)$ as a function of the applied electrode potential (see also the Supporting Information, SI). However, this approach is only compatible with rigid binders, which is a severe limitation when addressing complex situations of realistic electrochemical energy storage systems. In fact, actually often overlooking the importance of binders beyond the scope of electrochemical stability, their role cannot be ignored when attempting to understand long-term behavior and mechanical properties of composite electrodes.

Motivated by the usefulness of QCM-based methods and the need to advance our understanding of the role of the binders in composite electrodes, we demonstrate for the first time in this study the vast potential of our newly developed EQCM-D-based methodology for monitoring viscoelastic properties of polymeric binders (PVdF or NaCMC) in composite $LiFePO_4$ electrodes which are affected by the intercalation-induced deformation of the electrodes particles.

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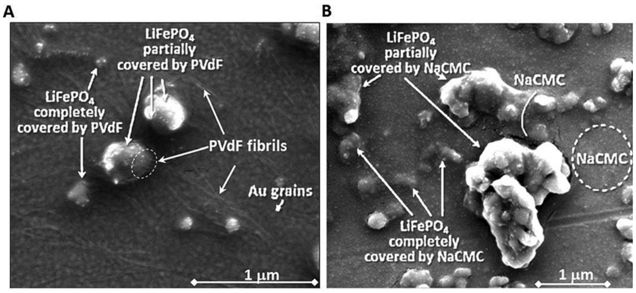

Figure 1. SEM images of thin composite $LiFePO_4$ electrode coating on quartz-crystal-containing PVdF and NaCMC binders (A and B, respectively). Grains of Au current collector, electrode particles (completely or partially covered by the polymeric binder) are indicated.

Non-uniform distribution of polymeric binders in electrode coatings. Figure 1 A and Figure 1 B show scanning electron microscopy (SEM) images of spray-coated composite $LiFePO_4$ electrodes with PVdF and NaCMC binders, respectively.[6b,7] A single/few layer(s) of intercalation particles are partially or entirely covered by binder fibrils or filaments, which attach them to the gold electrode deposited on the quartz-crystal surface (QCS). Non-uniform binder distribution in such composite electrode coatings is due to the intrinsic asymmetry of the electrode particles, different electrode's thickness, and the nature of the substrate surface. Small $LiFePO_4$ particles are completely covered by binder whereas larger particles are non-uniformly covered. Elongated larger polymer fibrils and semispherical PVdF particles (ca. 200 nm in diameter) consisting of shorter polymer fibrils, which in turn are built by spherical particles with ca. 7 nm diameter, are seen in SEM and AFM images of neat PVdF coating (Figures 2 A and B, S2). Figure 2 B relates to AFM image of PVdF coating obtained from very diluted solution: spherical particles with a diameter of 40–50 nm are grains of Au electrode film deposited onto the QCS whereas the bright small spherical particles of average diameter ca. 7 nm are the primary PVdF particles, which due to a small concentration and electrode surface roughness do not form polymeric fibrils, in contrast to the case of more concentrated solutions (Figures S2 and 2 A). An important property of PVdF is that it does not swell in water as evidenced by the fact that very similar AFM images of PVdF coatings are obtained in air and in water (Figure S2).

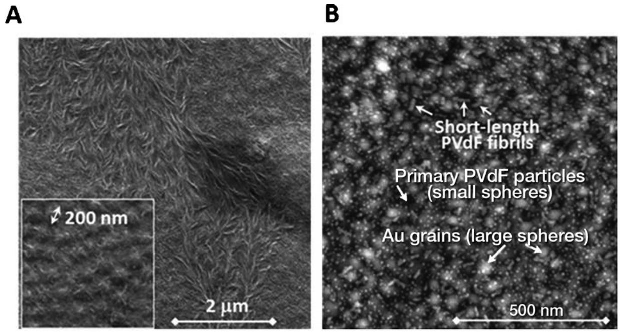

Figure 2. SEM (A) and AFM (B) images of neat PVdF coating on a quartz crystal obtained from concentrated and diluted solutions, respectively, revealing the multiscale character of the polymer film morphology.

Neat NaCMC films have a completely different morphology: The AFM image (Figure S3B) shows a filamentous network whose meshes form polygons with a characteristic size 150–200 nm. The SEM image at a higher resolution (inset in Figure S3A) implies that thick NaCMC filaments consist of networks of nanoscopic primary filaments which are also seen in the AFM image of the film prepared from very diluted solution (Figure S3B). In contrast to PVdF, NaCMC films strongly swell in water revealing an increase in mesh size up to 15–25 nm (Figure S3C). The filamentous network morphology of NaCMC films is consistent with the formation of gel of this polymer in the presence of water[9] (the softness of this polymer as compared to rigidity of PVdF in aqueous solutions were confirmed by QCM-D, see Figure S4). For this reason they are excellent model systems for probing their mechanical properties in composite electrodes by EQCM-D. Most importantly, when the same binders are brought in contact with typical Li-battery organic electrolyte solutions, the PVdF binder becomes softer than NaCMC[2] providing an excellent case study to validate our EQCM-D methodology.

Deformations of composite electrodes tracked by electrochemical quartz-crystal admittance technique. QCM-based methods are widely used in analytical chemistry, especially in electroanalysis, because they provide both gravimetric and nongravimetric (viscoelastic) sensing of the coatings rigidly attached to QCS operated in liquid environments.[10] Less known is that any QCM instrument recording both shifts in resonance frequency (F) and resonance width (W, or dissipation factor $D = W/F$) can be employed as a sensitive probe of the potential-induced deformations of composite electrode coatings.[7,8,11] The electrode particles deformations (i.e., a change in their shape and size) modify their hydrodynamic interactions with the contacting liquid, thereby directly affecting experimentally measured values of shifts in F and W.[7,8,11]

In contrast to conventional mechanical measurements,[12] deformation of the polymeric binders in composite electrodes is caused by contracting/expanding intercalation particles rather than by applied external force. Yet, non-uniform binder distribution at the particle surface affects the character of the particle's deformation. The deformation depends on the polymer and the solution nature (e.g., through the polymer's elastic modulus), and is also a function of the electrodes charging rates since the polymers elastic moduli are time (frequency)-dependent through a variety of relaxation mechanisms.[13] An important feature of our EQCM-D approach is that the deformation of the binder initially caused by the intercalation-induced volume change of the electrode particles affects the deformation of the entire composite electrode coating. For example, if initially in a completely lithiated electrode the binder has a large elastic modulus, the contraction of the intercalation particles during charge, pushes the polymer's stretching above the yield of its stress-strain characteristic. In this way the binder transitions from a rigid to a much softer form, favoring unrestricted (free) intercalation-induced deformation of the electrode particles. Depending on the polymer elastic modulus, the type and extent of particles' deformation (controlled by the electrode's charging rate) is precisely monitored with high sensitivity by EQCM-D recording shifts in values of *F* and *W*.

NaCMC: soft in aqueous but rigid in non-aqueous solution. Figure 3 A compares cyclic voltammograms (CVs) of $LiFePO_4$/NaCMC coatings in 0.1 M aqueous Li_2SO_4 and 1 M $LiPF_6$/EC + DMC solutions. The raw EQCM-D data, that is, ΔF and ΔW, measured simultaneously with the CVs are shown in panels B and C for aqueous and non-aqueous solutions, respectively, as a function of the normalized time (t) of the charge–discharge cycle. The intercalation-induced changes of ΔF are similar for both solutions due to the dominating mass contribution (intercalation charges are similar in both media) whereas the behavior of the resonance peak width, ΔW, is completely different: ΔW decreases and increases when measured in aqueous and non-aqueous solution, respectively. Pristine NaCMC powder is a water-soluble polymer;[14] however, when in contact with water it is prone to form an elastomeric network (evidenced by SEM and AFM images in Figure S3).[14] Gel formation is further enhanced when a thin layer of NaCMC is strongly held by the intercalation particles after complete drying of the electrode at elevated temperature. Swelling of the elastomeric network in aqueous solution facilitates a quasi-uniform deformation of $LiFePO_4$ particles: the effective thickness of the porous electrode's layer decreases because the intercalation particles contract during Li-ions extraction, ensuring a decrease in ΔW due to reduction of solid–liquid hydrodynamic interactions.[7,11] In contrast, NaCMC remains completely rigid in aprotic solutions.[2] Figure 3 C directly confirms this conclusion: the non-uniform deformation of the electrode's active mass (resulting in the increase of the dissipation factor) arises as a consequence of the non-uniform distribution of the rigid polymeric binder. A softer binder (i.e., NaCMC in aqueous solution) causes an opposite change of the dissipation factor (Figure 3 B).

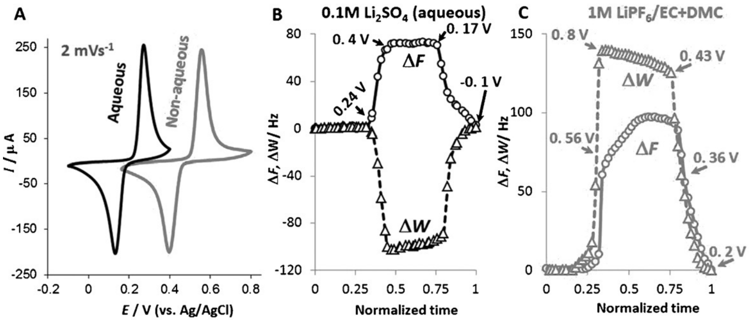

Figure 3. CVs (A) and the related changes in the frequency and resonance width of $LiFePO_4$/NaCMC electrodes in aqueous (B) and non-aqueous (C) electrolyte solutions (the electrode was first tested in aqueous solution, then washed with water and dried before immersion into non-aqueous solution; second cycle is shown). The potential of the electrodes response in the non-aqueous solution was corrected and adjusted to the Ag/AgCl reference electrode in aqueous solution, in order to present both responses on the same potential scale. $t = 0.25$ relates to the beginning of Li deinsertion, whereas normalized $t = 1$ marks the end of a full Li ions deinsertion/insertion cycle (the electrodes are fully relithiated).

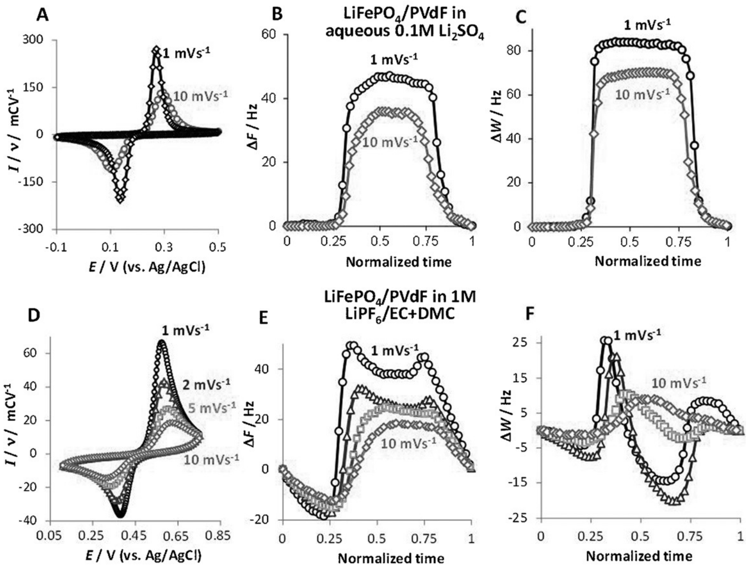

Figure 4. CVs at different scan rates as indicated and the related changes in the experimental frequency, ΔF, and the resonance width, ΔW, of the QC during charging–discharging cycles of $LiFePO_4$/PVdF electrodes in 0.1 M aqueous Li_2SO_4 (A–C) and 1 M $LiPF_6$/EC + DMC (D–F).

PVdF: rigid in aqueous but soft in non-aqueous solutions upon slow charging rates. The concept of uniform and non-uniform deformations was evaluated for similar $LiFePO_4$/PVdF electrodes in contact with both aqueous and non-aqueous solutions (Figure 4 A–C, and D–F, respectively). The CVs normalized by the scan rates for the aqueous electrolyte solution are shown in panel A whereas the related ΔF and ΔW are shown in panels B and C, respectively. Like with NaCMC in aprotic solution, ΔW increases upon Li-ion extraction from these electrodes (due to non-uniform electrode layer deformation), implying that the polymeric binder remains in its rigid state in the entire range of charging rates used.

In contrast, the intercalation-induced resonance width change, ΔW, shows a large difference compared to that obtained for the aqueous solution: 1) In the limit of high scan rates, ΔW shows a maximum for fully deintercalated electrodes (rhomb-marked curve in panel E), implying the rigidity of PVdF. 2) At small scan rates, ΔW increases at the beginning of Li-ions extraction, reaching a maximum at approximately 50 % of Li-ions extraction; on further Li-ions deintercalation, ΔW drastically decreases reaching minimum at full deintercalation. At the beginning of Li-ions insertion, ΔW increases (similar to that for the beginning of Li-ions extraction) passing through a maximum, eventually coming back to the initial value.

The shape of the potential dependencies ΔW for different scan rates can be easily understood assuming that PVdF in contact with aprotic solutions reveals a strain-rate dependence of the elastic moduli which is typical for viscoelastic polymers. The strain-rate increases at higher charging rates, revealing the rigid character of the polymer. In contrast, at lower strain-rates, the relaxation processes are completed making the polymer softer than it was at the high strain-rates. This is a well-known property of viscoelastic polymers[12] which is at the origin of the characteristic scan-rate dependence of $\Delta W(E)$ for $LiFePO_4$/PVdF electrodes in aprotic solutions. According to our model any strain-rate-dependent changes in the binder's elastic modulus affect the geometric parameters of the electrode layer resulting in changes of ΔF and ΔW (Figure 4E and F, respectively). The latter are input parameters for the hydrodynamic admittance model [Eqs. (S1)–(S4)] used to extract the electrode layer thickness (h) and permeability (ξ), respectively, for different scan rates. As seen in Figure S4, the changes in h and ξ are correlated and are qualitatively similar to that of W. For example, when h increases during non-uniform particles deformation with a rigid binder (according to its Poisson ratio: a body being pulled in tension, contracts laterally),[12] and the porosity also increases as it is intrinsically linked to the permeability.

In conclusion, thin composite LIB electrodes coatings onto QCS are attractive model systems for continuous monitoring of the viscoelastic properties of polymeric binders during composite electrodes charge–discharge processes. The method is non-invasive because it is the intercalation-induced electrodes' particles contraction/expansion that deforms the polymeric binder rather than any external forces. The character and extent of the electrode layer deformation during cycling is monitored with high sensitivity by EQCM-D whereas using the suitable hydrodynamic admittance model provides the values of the intercalation-induced changes of the effective composite electrodes thickness and permeability (linked to porosity). This unique method can be extended to the characterization of polymeric binders during long-term cycling and storage of composite electrodes of all kinds of batteries.

Keywords: deformations · Li-ion batteries · polymeric binders · quartz-crystal microbalance · viscoelasticity

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