

Real-time measurement of sodiation induced stress in hard carbon composite electrodes

Supplementary Information

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S1. Stress in electrode due to electrolyte wetting

As mentioned in the main manuscript, composite electrode specimens were soaked in electrolyte for more than 12 h before electrochemical cycling. It was observed that stresses developed in the HC composite electrode during this soaking period due to the interaction of electrolyte with porous electrode. The stress increased gradually when the electrolyte was added and reached at a stable tensile stress ~ 1 MPa after a few hours (Fig. S1).

The tensile stress observed during electrolyte wetting can be attributed to the nature of binder (CMC-SBR or PVdF) used in the samples. Since, CMC and SBR did not absorb the PC based solvent, electrolyte- electrode porosity interaction was dominated by capillary forces and could be the main reason behind the tensile stress development. With time, electrolyte enter into the gaps between particles due to capillary forces. As a result, adhesion force gets induced by electrolyte capillary bridges between particles which is stronger than van der Waals interaction [1]. This could be the main reason behind tensile stress developed in the HC-CMC/SBR electrode during the electrolyte wetting. However, HC with PVdF binder showed slightly different stress behavior during electrolyte wetting (as shown in Fig. S1b). Compressive stress of ~ -0.5 MPa was

developed in HC-PVdF initially followed by tensile stress (of ~ 0.5 MPa). The initial compressive stress evolution can be attributed to the swelling of PVdF (as PVdF absorbs electrolyte). A similar trend was also reported in literature on porous composite electrodes with PVdF binder where compressive stress of the order of ~ -1 MPa was observed after 1 – 2 h of electrolyte wetting [2,3]. Though the swelling of PVdF was dominant deformation initially, capillary interaction between electrolyte and porous electrode becomes dominant after saturation of PVdF, thereby resulting in tensile stress. Overall, a stable tensile stress of 0.5 – 2 MPa was observed in all the HC specimens after several hours of wetting, irrespective of the binder materials used.

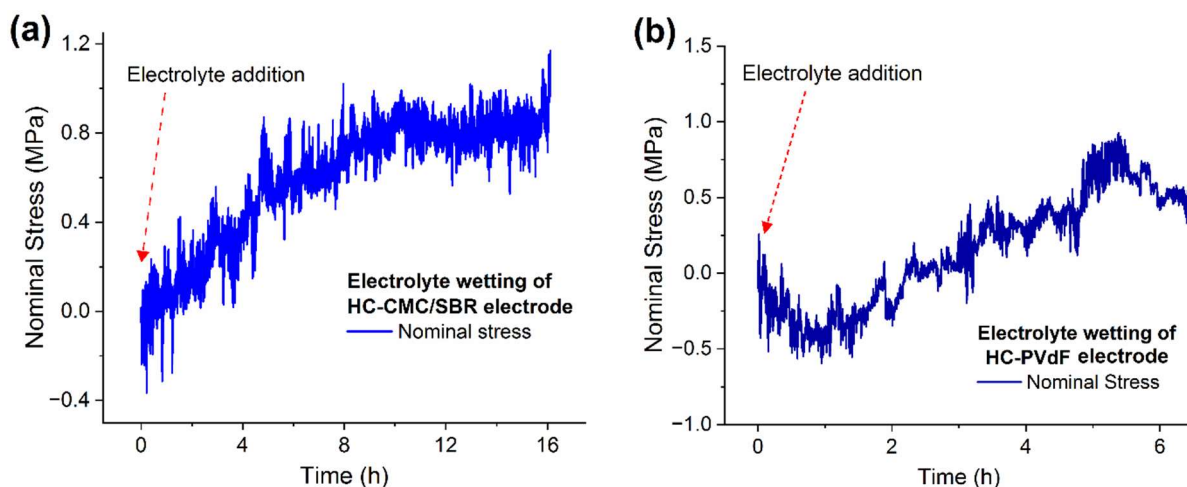


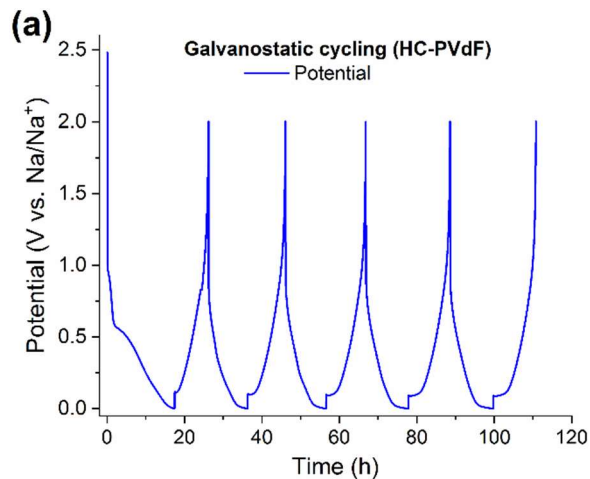
Fig. S1. Stress variation in (a) HC-CMC/SBR and (b) HC-PVdF electrodes due to electrolyte wetting

S2. Stress and potential response of HC specimens with PVdF binder

Figure 7b and 7d shows the potential and stress evolution in HC electrodes with PVdF binder during galvanostatic cycling. Commercially available hard carbon composite electrodes with PVdF binder was obtained from the same manufacturer (MTI Corporation, USA, HC-CMC/SBR was also purchased from the same manufacturer) and was cycled galvanostatically against sodium at $\sim 80 \mu\text{A cm}^{-2}$. The assembly of electrode-substrate and the beaker cell was carried out as described in the Section 2 of the manuscript.

As shown in the potential profile, the specific capacity and the first cycle coulombic efficiency for the beaker cell (with HC-PVdF) was found to be 239 mAh g^{-1} and 51%, respectively

in comparison to 273 mAh g⁻¹ and 82% for the beaker cell with HC-CMC/SBR. The potential profile showed the signature sloping and plateau region, however, the plateau capacity was smaller compared to that of CMC/SBR binder. As seen in the stress profile, the compressive stress generated during sodiation increased linearly and sharply with time (or capacity) until reaching a value of approximately – 6 MPa and then increased slowly with time to value of – 7.1 MPa at the end of sodiation. During desodiation, the stress increased almost linearly and reached at 1.6 MPa tensile at the end of desodiation. The notable difference between CMC/SBR and PVdF binder could be observed at the plateau region, starting and end of desodiation. The plateau capacity as well as the corresponding compressive stress was comparatively lower in case of PVdF binder. The sudden jump in stress at the starting of desodiation due to elastic unloading was not so profound in the case of PVdF, which was significant in case of CMC/SBR binder system. The tensile stress formed at the end of desodiation during initial cycles was also higher (3 – 5 MPa) in the CMC/SBR system compared to their PVdF (1 – 3 MPa) counterpart. These can be attributed to the higher shear strength and mechanical integrity of CMC/SBR binder bridges compared to PVdF [4]. Except these differences, the pattern of stress evolution (similar stress-potential response) during the sodiation was almost similar in both the specimens irrespective of binder which confirmed the resemblance between sodium ion storage in HC particles and the corresponding volume (or stress) change. Figures S2a, and S2b show that the potential and stress responses of HC-PVdF electrodes for 5 consecutive cycles showed almost similar stress pattern. Specific capacity and coulombic efficiency of the HC-PVdF coin cell are presented in Fig. 5.



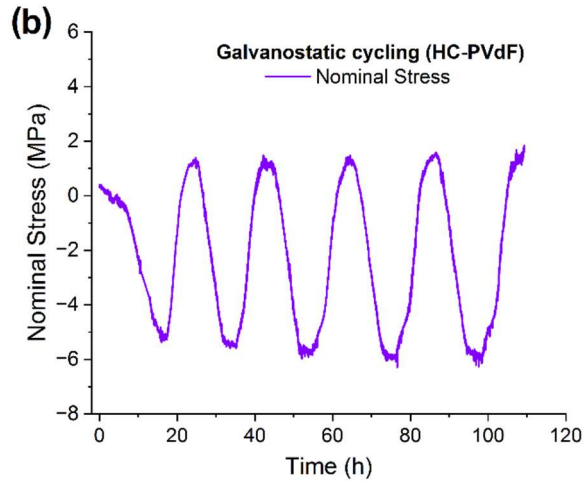
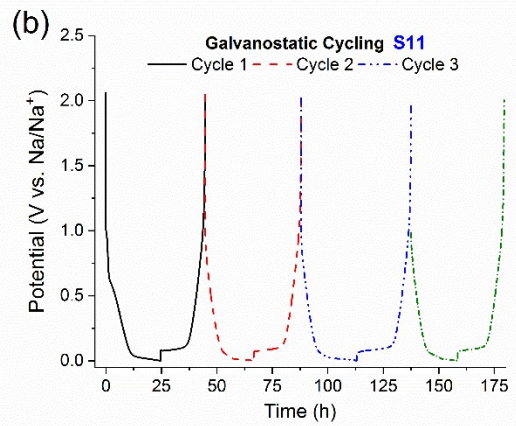
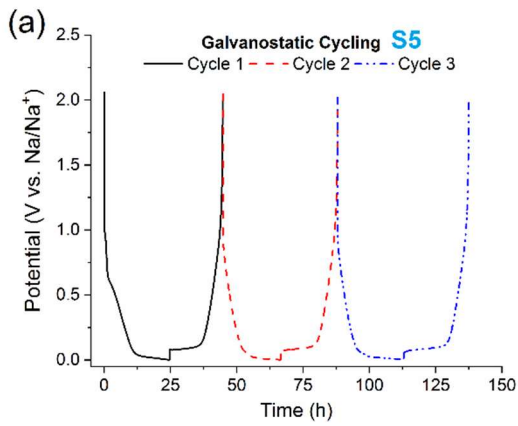


Fig. S2. (a) Potential and (b) stress response of Na-HC (PVdF) during 5 consecutive cycles of galvanostatic cycling

S3. Potential and stress evolution in different HC-CMC/SBR specimens



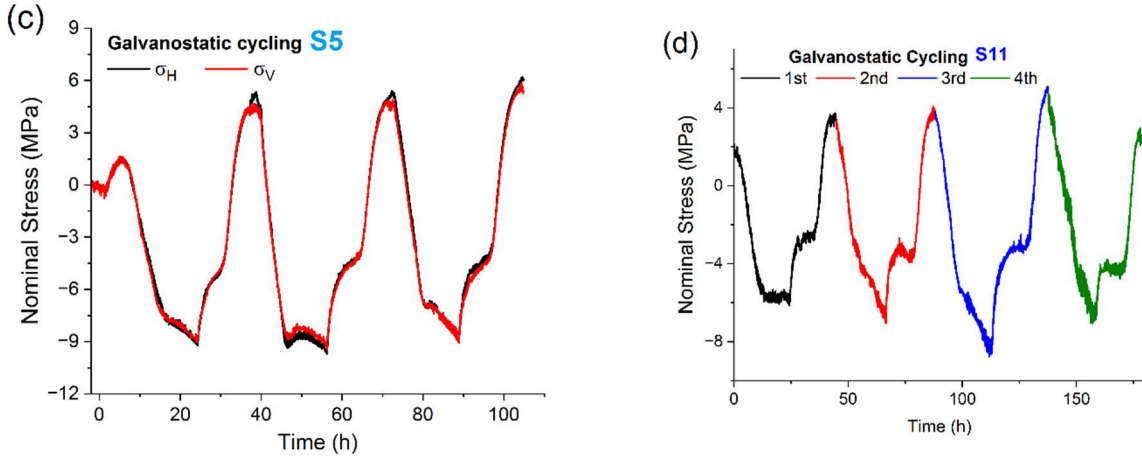


Fig. S3. Potential and stress evolution in HC-CMC/SBR electrodes (different specimens) during galvanostatic cycling against sodium

Fig. S3 shows the potential and stress response of HC-CMC/SBR electrodes during galvanostatic cycling against sodium. Both the potential and stress pattern were found to be almost similar in different specimens tested for this study. However, a few variations in the stress pattern were observed in consecutive cycles. For example, stress during 3rd cycle (see Fig. S3d) was found to be higher (-8.6 MPa) compared to that of 2nd (-7 MPa) and 4th (-6.9 MPa) cycle. This could be correlated with the increased capacity in that cycle. The plateau capacity in the 2nd, 3rd, and 4th cycles were $\sim 150 \text{ mAh g}^{-1}$, $\sim 190 \text{ mAh g}^{-1}$, and $\sim 145 \text{ mAh g}^{-1}$ respectively. The additional stress increment can be attributed to increased volumetric expansion due to insertion of more number of Na^+ . The overall trend in the stress and potential data was found to be almost similar in consecutive cycles of different specimens.

S4. Stress evolution in two different orthogonal directions

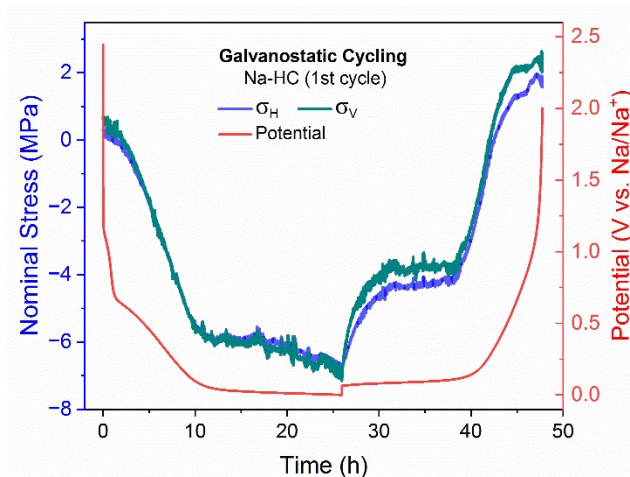


Fig. S4. Representative stress evolution in HC-CMC/SBR electrode for two different orthogonal directions during 1st cycle of galvanostatic cycling (σ_H and σ_V are the in-plane stresses in two different orthogonal directions).

References

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