The 2012 Edward G. Weston Summer Research Fellowship — Summary Report

Stress Evolution and Ion Dynamics in Redox Active Polypyrrole Films

by Sujat Sen

Precise measurement of the stress exerted on conducting polymers (CP) films is important for their long term applications, because this information can be used to minimize stress-induced mechanical instability such as rupture and delamination of CP films, which consequently leads to the failures of the devices based on them. Redox switching of a CP is the basis for a variety of applications including rechargeable batteries,[1] electrochromic devices,[2] sensors,[3] and actuators.[4] Redox switching of CP films is accompanied by a change in the charge density (i.e., oxidation state) of the polymer backbone, which results in ion (and solvent) transport into and out of the film to compensate for excess charge in the polymer, resulting in the swelling and shrinking of CP films.[5]

Measuring this volume change is difficult because the magnitude of the change is typically small.[6] Any volume change in a CP film, however, leads to mechanical tension or compression of an underlying substrate when the film is constrained to a substrate of different mechanical stiffness. As a result, monitoring substrate tension (caused by a decrease in the volume of the CP film) and substrate compression (caused by an increase in the volume of the CP film) enables measurement of the small volume changes in a CP film due to voltage-induced movement of ions into and out of the film. The multi-beam optical tress sensor (MOSS) technique has been used in the past for measuring the stress in thin films of a variety of inorganic materials.[7] Here, it is utilized to monitor stress evolution of a conducting polymer, polypyrrole (pPy) doped with Indigo carmine (IC) in different electrochemical environments to identify optimal cycling conditions. This technique employs an array of parallel laser beams separated by a fixed distance (d) and measures the relative changes in the spacing between them (δd) as shown in Fig. 1. The curvature change measured can then be converted into biaxial stress using the Stoney equation.[8]

Based on the changes in the curvature (tension or compression) of the silicon substrate, we can explain the nature of ion movement occurring as a part of the charge compensation process in pPy, as it swells

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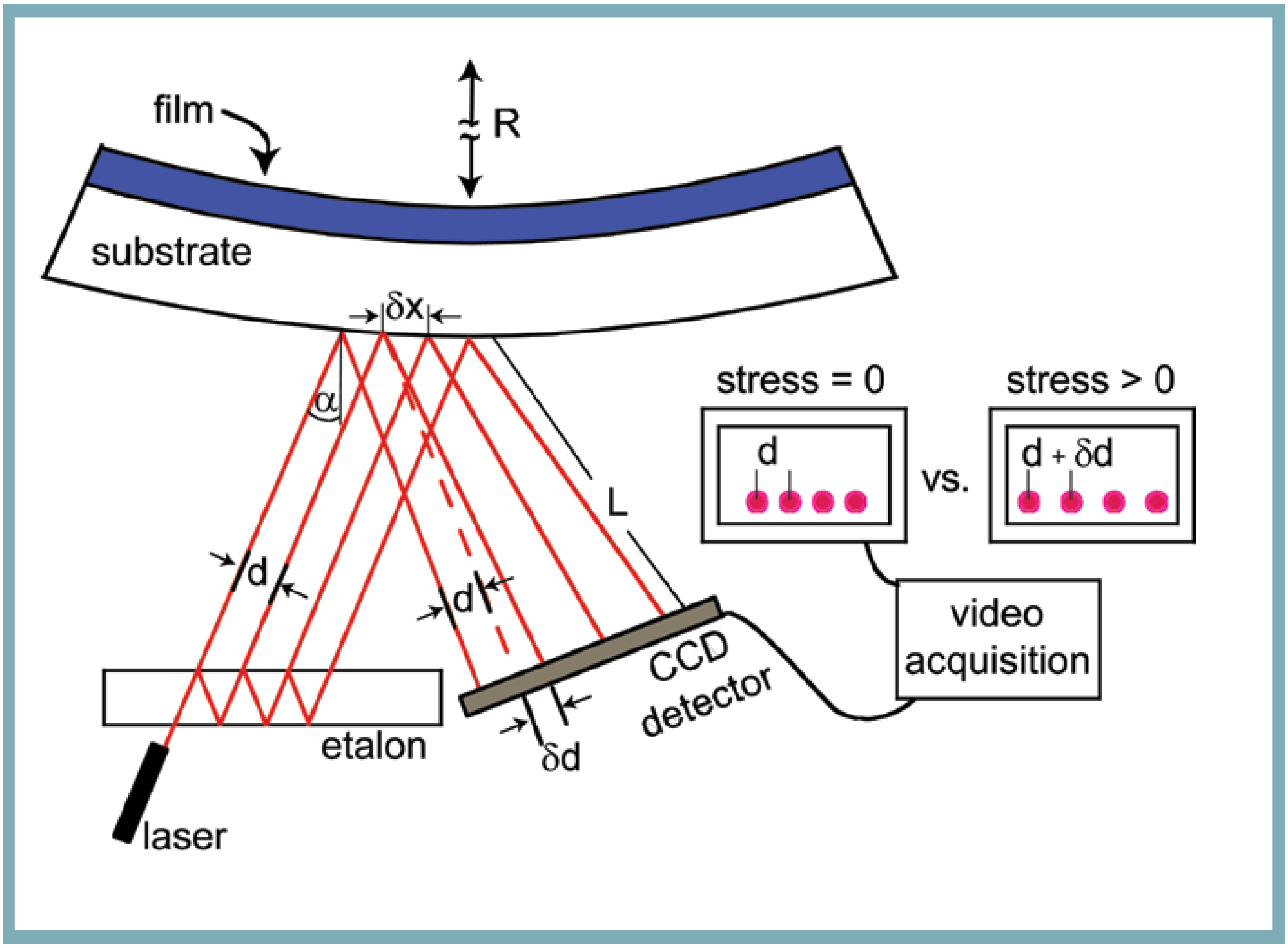

Fig. 1. *A schematic of the MOSS system, illustrating the relationship between stress-induced substrate curvature and the deflection of an array of parallel beams of light. Dimensions are exaggerated for clarity.*

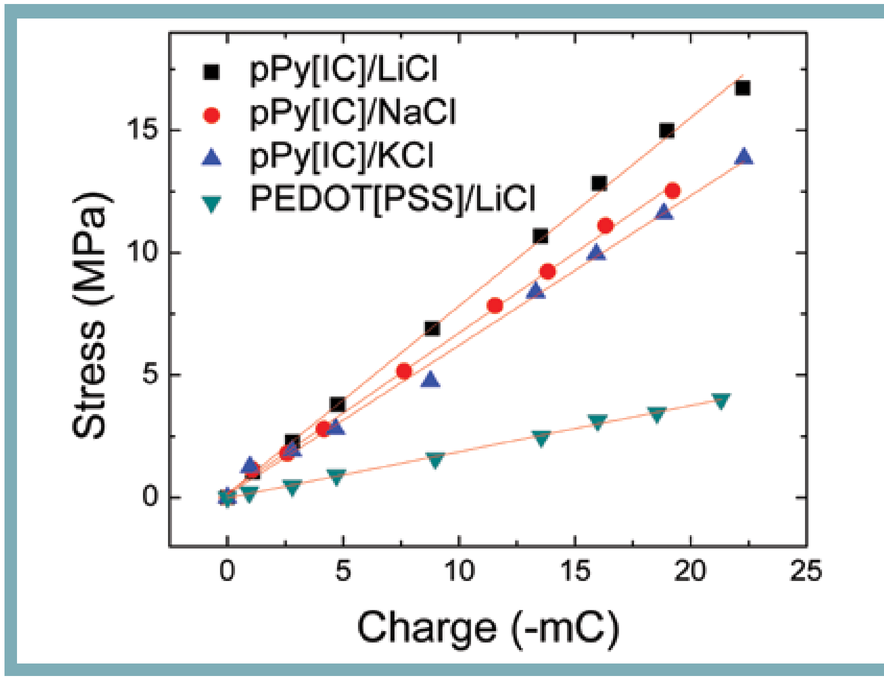

Fig. 2. *Plot of stress as a function of charge during potential cycing from 0.25V to -0.25V (vs.SCE) for pPy[IC] and PEDOT[PSS] in 0.2M aqueous electrolyte.*

or contracts. By integrating the current over time in CV sweep, we obtained the charge which is then plotted as a function of the stress during the potential sweep from +0.25V to -0.25V (vs.SCE) in different electrolytes, shown in Fig. 2. The magnitude of the induced stress within pPy[IC] at neutral pH correlated with the radius[9] of the hydrated mobile ion in the order $Li^+ > Na^+ > K^+$, as indicated by the stress to charge ratio (i.e. slope of the graph). Additionally, the stress to charge plot of PEDOT[PSS] is included for comparison indicating the significantly lower stress response. A higher stress to charge ratio would be suitable for CP applications such as actuators where maximum strain is desirable. Alternatively, a lower stress response would be suitable for energy storage applications where minimal strain would extend device lifetime. Future studies will examine voltage-induced stress in other combinations of CP/dopant/electrolyte as well as effects of the redox activity of the dopant on the stress profile.

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