

Investigation of acid deprotonation in electrolyte thin film through protonic field-effect transistor

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The protonic field-effect transistor (H^+ -FET) with electrochemical impedance spectroscopy (EIS) measurement was established to investigate the proton (H^+) transport properties of electrolyte thin film containing a carboxylic acid group. The external gate voltage (V_g) applied to the H^+ -FET device can modulate the flow of the H^+ charge carrier in electrolyte thin film, and then the H^+ transport properties can be extracted.¹⁻³ However, the palladium (Pd) electrode reaction under an H_2 atmosphere with a DC system, which can provide the excess H^+ carrier, was used in the reported H^+ -FETs.^{1,2} Pd electrode reaction and strong contact resistance of a DC system were expected to interrupt the investigation of the thin film properties. In this work, a gold (Au) electrode combined with EIS measurement under air atmosphere was performed. This established method can provide intrinsic information on the H^+ transport properties of electrolyte thin film, including the amount of H^+ charge carrier or carboxylic acid deprotonation behavior without the electrode reaction and contact resistance effects.

Polyacrylic acid (PAA) thin film (45 nm) was studied using our H^+ -FET, which consists of comb-shaped Au electrodes deposited on a Si/SiO₂ substrate. V_g from -5 V to $+5$ V was applied, and the V_g dependence of in-plane H^+ conductivity (σ) was observed (Fig. 1a). The H^+ transport mobility (μ_{H^+}) of $8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was successfully estimated. The mobile H^+ concentration (n'_{H^+}) was calculated from μ_{H^+} , showing the dependence on V_g . The change of H^+ carrier concentration depending on V_g might refer to the difference in carboxylic acid deprotonation behavior. Therefore, the effective pK_a (pK_a') was then estimated and displayed in Fig. 1b. Furthermore, the influence of V_g on the electrolyte thin film Debye length (κ^{-1}) would be discussed.

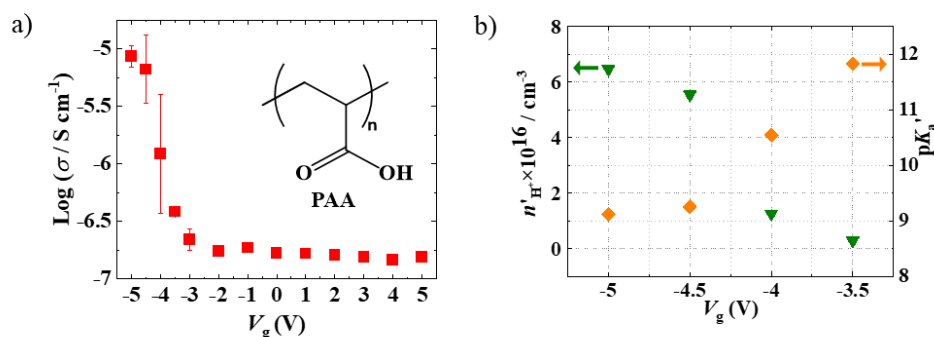


Figure 1 The V_g dependence of PAA thin film's a) σ , and b) n'_{H^+} and pK_a' .

References; 1) C. Zhong *et al.*, *Nat. Commun.* **2011**, 2, 476. 2) H. Zhong *et al.*, *Adv. Mater.* **2020**, 32, 2000730.

3) S. Mondal *et al.*, *Small* **2020**, 16, 2005526.