

THERMODYNAMICS AND KINETICS OF ELECTRON TRANSFER BETWEEN K_3FeCN_6 ELECTROLYTE AND rGO:PSS MODIFIED ELECTRODE FOR SENSOR APPLICATION

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ABSTRACT

Next-generation devices that are sensitive to stimulus-responsive properties is a highly desired goal in monitoring and diagnostics technology field. Nanomaterial has been extensively used in transducer development for sensor applications. However, sensor devices possess a huge challenge in exhibiting sensitive responses with fast electron transfer. Little studies have been made to understand the thermodynamics and kinetics of electron transfer at the electrode-analyte interface. Therefore in our project, we have utilized the intrinsic property of reduced graphene oxide:polystyrenesulfonate (rGO:PSS) as a transducer of a sensor. Reduced graphene oxide (rGO), poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS), and rGO:PSS were casted onto the active sensing area of glassy carbon electrode (GCE). The developed electrode was electrochemically characterized by cyclic voltammetry (CV) measurement at varying scan rates (75, 100, 150, 200, 250) mV/s. The CV graphs elucidated the thermodynamics and kinetics of electron transfer between potassium ferricyanide (K_3FeCN_6) electrolyte and rGO:PSS modified electrode by analysing the shifts in peak potentials, E_p . The peak potentials of resultant electrodes revealed a shift of 120 mV for rGO modified electrode, which decreased to 90 mV when the electrode was modified with PEDOT:PSS, and further decreased to 30 mV when rGO:PSS was casted onto the GCE. The smaller shift in rGO:PSS electrode suggests that the kinetics or the rate of electron transfer at the electrode-analyte interface was very fast and rapid, indicating a strong electronic coupling between electrode and electrolyte; the electron transfer was reversible. The thermodynamics of the redox process happened easily, which deals with the transformation of energy between the rGO:PSS modified electrode and the ferricyanide electroactive species in the electrolyte. Additionally, the peak potential difference ($\Delta E = E_{pa} - E_{pc}$) was also analysed. The ΔE s were 0.42 V, 0.30 V, and 0.12 V for GCE/rGO, GCE/PEDOT:PSS, and GCE/rGO:PSS, respectively. The lower ΔE for GCE/rGO:PSS implied an improved electrocatalytic ability of the developed electrode. As for the accuracy of the CV analysis, the adsorption from the electrolyte to the electrode was investigated by plotting peak currents against the square root of scan rates. The linear fit for all CV measurements; $R^2 = 0.999, 0.940, 0.930, \text{ and } 0.999$ for GCE, GCE/rGO, GCE/PEDOT:PSS, and GCE/rGO:PSS, respectively, revealed that no adsorption occurred during the redox process. Besides, the lowest scan rate was set as 75 mV/s in order to avoid convection of electroactive species into the diffusion layer. Therefore, the CV analysis was based solely on electron transfer, and not on adsorption and convection, which would otherwise interfere with the CV analysis. As a conclusion, rGO:PSS nanomaterial has a prevalent potential as a transducer and ultimately improve the sensor performance in the monitoring technology field.

Keywords: Thermodynamics, kinetics, cyclic voltammetry, peak potential, rGO:PSS, sensor