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Cyclic Voltammetry and Electrical Impedance Spectroscopy of Electrodes Modified with PEDOT:PSS-Reduced Graphene Oxide Composite

Nurul Izzati Ramli, Nur Alya Batrisya Ismail,
Firdaus Abd-Wahab and
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Additional information is available at the end of the chapter

Abstract

Cyclic voltammetry (CV) and electrical impedance spectroscopy (EIS) are electrochemical techniques to characterize reversibility of electron transfer and impedance at the electrode-solution interface, respectively. Reduced graphene oxide (rGO) and conductive polymer PEDOT:PSS are often used to enhance electron transfer at electrode surface. This chapter provides a step-by-step methodology of CV and EIS conducted on screen-printed carbon electrode (SPCE) modified with rGO-PEDOT:PSS and brief discussion on the CV and EIS results. The CV of rGO-PEDOT:PSS shows a reversible electron transfer in comparison to SPCE modified with PEDOT:PSS. For EIS, rGO-PEDOT:PSS was found to reduce the Warburg impedance, suggesting enhanced electrode conductivity. These results suggest that rGO-PEDOT:PSS is a suitable material for biosensing purpose.

Keywords: PEDOT:PSS, graphene, cyclic voltammetry, electrical impedance spectroscopy, biosensor

1. Introduction

A polymer is made up of repeating subunits of monomers and widely recognized as having good insulating properties. In 1977, three scientists serendipitously discovered that polyacetylene (PA) could become conductive through iodine doping, which consequently

allows electrons at the π-bonds to move along the polymeric chains. This process enables the development of conductive polymers and their exploitation in many applications such as supercapacitors, light-emitting diodes (LEDs), solar cells, field-effect transistors (FETs), and biosensors [1, 2].

One such conductive polymer that is gaining interest is the poly(3,4-ethylenedioxythio phene):poly(styrene sulfonate) or PEDOT:PSS. PEDOT:PSS exhibits high conductivity [3], high stability in liquid media [4], and good mechanical flexibility [5]. These properties make PEDOT:PSS a suitable transducer material in electrochemical biosensors. Furthermore, its ability to intercalate between the layers of reduced graphene oxide (rGO) opens the possibility of combining these two materials as a composite to enhance biosensor performance.

This chapter describes the experimental procedures for the use of PEDOT:PSS and rGO as the transducer composite on a screen-printed carbon electrode (SPCE). Electrochemical analyses are done via cyclic voltammetry (CV) and electrical impedance spectroscopy (EIS) to characterize the electrochemical reversibility of the material, as well as its impedance at the electrode-solution interface.

1.1. Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is used to understand and characterize the redox characteristics, stability, and effective surface area of an electrode for biosensing; such electrodes, modified with materials such as PEDOT:PSS and graphene, function as a transducer to convert ions into measurable electrons. CV typically consists of a three-electrode setup of a working electrode (WE), a reference electrode (RE), and a counter electrode (CE). In CV, a potential applied to the WE is swept back and forth for a defined number of cycles over a given range of voltage and speed of voltage sweep [6]. As the potential is scanned across a specified potential range, the resulting current at the WE is measured. The current generated is then plotted against potential to produce a CV graph that provides insights on the transducer material based on the anodic peak current (I_{pa}) from oxidation process and cathodic peak current (I_{pc}) from reduction process which occur on the WE. The potentials at which the peak currents occur are known as peak potentials (E_p). These peak potentials enable us to analyze the electrochemical reversibility of the reaction at the electrode surface by increasing the scan rates during experiments. Electrochemically reversible reactions often establish fast electron transfer between species and electrode, whereas the electron transfer in irreversible reaction is slower [6, 7].

1.1.1. Experiment

Figure 1 shows the experimental setup for CV using a SPCE connected to a potentiometer and a laptop.

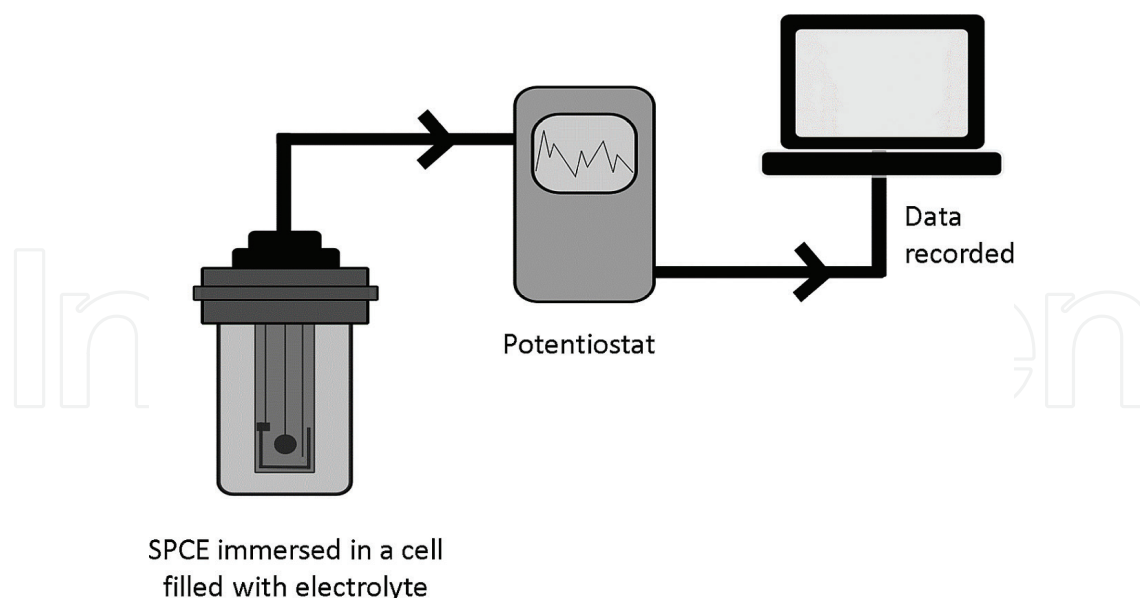CV experiments were conducted on SPCEs modified with PEDOT:PSS and rGO-PEDOT:PSS composite.

Figure 1. Experimental setup for CV. The SPCE is immersed in a cell filled with electrolyte. The cell is connected to a potentiometer and a laptop.

1.1.2. Materials and equipment

1.1.2.1. Consumable items and equipment

- Magnetic stirrer

- Sonicator

- Pipette and pipette tips

- Potentiometer (IVIUM Technologies, Eindhoven, Netherlands)

- Screen-printed carbon electrode (SPCE with 2 mm diameter, Pine Instruments, Grove City, Pennsylvania, USA)

1.1.2.2. Chemicals and reagents

- PEDOT:PSS solution (1.3 wt% dispersion in H_2O, high-conductivity grade, Sigma-Aldrich, St. Louis, MO, USA)

- Ultrahighly concentrated GO (UHC GO) solution (6.2 mg/ml, Graphene Supermarket, USA)

- M potassium ferricyanide $K_3Fe(CN)_6$ (R&M Chemicals, Selangor, Malaysia)

- M PBS, pH 5 (Sigma-Aldrich, St. Louis, MO, USA)

- Deionized (DI) water

1.1.3. Method

1.1.3.1. Fabrication of PEDOT:PSS/SPCE

1. Drop cast 3 µl PEDOT:PSS onto the WE of a SPCE.

2. Dry for 24 h in ambient conditions.

1.1.3.2. Fabrication of rGO-PEDOT:PSS/SPCE

1. Mix 500 µl PEDOT:PSS with 500 µl ultrahighly concentrated GO solution.

2. Stir the solution using a magnetic stirrer, and sonicate at 30°C for 10 min in order to form a well-mixed GO and PEDOT:PSS solution.

3. Drop cast 3 µl solution onto the WE of a SPCE, and dry in ambient conditions.

4. Reduce the electrode using a portable potentiostat via repetitive cyclic voltammetry (CV) with potential range from 0 to −1.5 V at 0.1 V/s in 0.01 M PBS, pH 5, for 15 cycles. Make sure that all electrodes (WE, RE, and CE) are fully dipped in the PBS during the reduction process. The reduced electrode is denoted as rGO-PEDOT:PSS/SPCE.

5. Rinse the rGO-PEDOT:PSS/SPCE with DI water, and dry at room temperature for 24 h.

1.1.3.3. CV measurement

1. To perform CV on the rGO-PEDOT:PSS/SPCE, insert the modified SPCE into a cell filled with 0.1 M $K_3Fe(CN)_6$ solution. Make sure all electrodes (WE, RE, and CE) are immersed in the solution.

2. Run a CV scan from initial potential of −0.5 to 1 V and back to −0.5 V at a scan rate of 25 mV/s. Repeat the scans at 50, 100, 150, and 200 mV/s.

1.1.4. Results

1.1.4.1. Discussion of results

Figures 2 and **3** show CV plots for PEDOT:PSS and rGO-PEDOT:PSS in 0.1 M $K_3Fe(CN)_6$ with increasing scan rates of 25, 50, 100, 150, and 200 mV/s. The peak current (I_p) produced at 200 mV/s is higher than the I_p at 25 mV/s for both PEDOT:PSS/SPCE and rGO-PEDOT:PSS/SPCE. However, the peak potentials (E_p) of the rGO-PEDOT:PSS transducer are shifted to more extreme values with increased scan rate than PEDOT:PSS transducer. The shift in the E_p as observed in the PEDOT:PSS/SPCE suggests that the electron transfer takes place heterogeneously—the redox species adsorbs onto the electrode surface prior to electron transfer. The addition of rGO to the composite could help reduce the adsorption of the redox species and enable the electron to be electrochemically reversible [6, 7]. This also suggests that
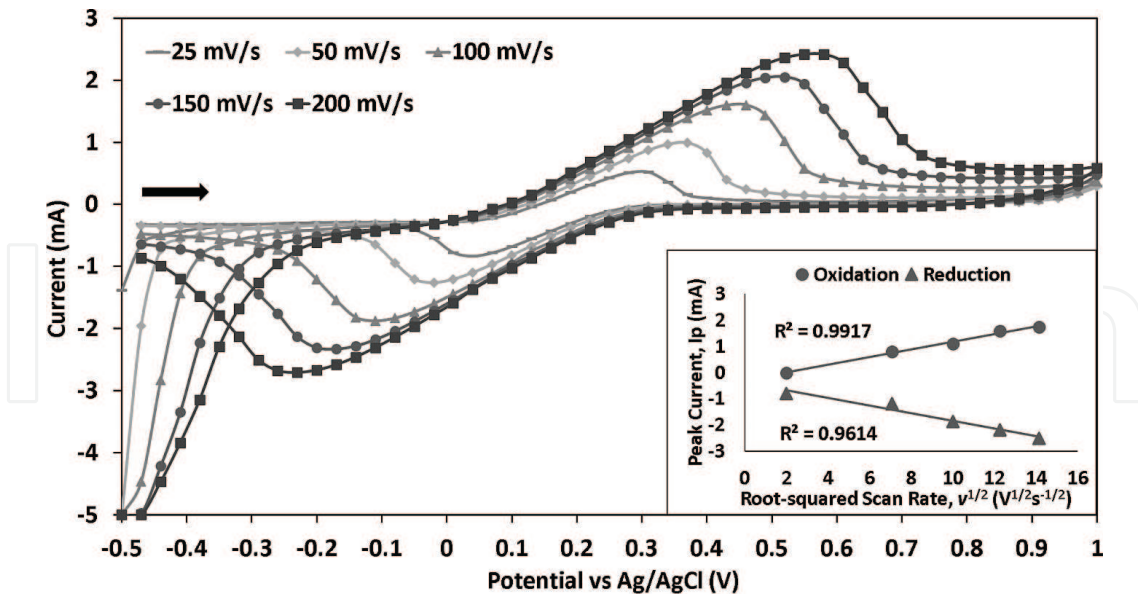
Figure 2. Cyclic voltammetry at different scan rates for PEDOT:PSS transducer. The electrolyte used in this experiment is 0.1 M $K_3Fe(CN)_6$ solution. Voltage was swept at potentials from −0.5 to 1 V and back. The arrow shows the direction of the initial voltage sweep. Inset shows the Cottrell plot for the CV.

Figure 3. Cyclic voltammetry at different scan rates for an electrode modified with reduced graphene oxide and PEDOT:PSS as the transducer. The electrolyte used in this experiment is 0.1 M $K_3Fe(CN)_6$. Voltage was swept at potentials from −0.5 to 1 V and back. The arrow shows the direction of the initial voltage sweep. Inset shows the Cottrell plot for the CV.
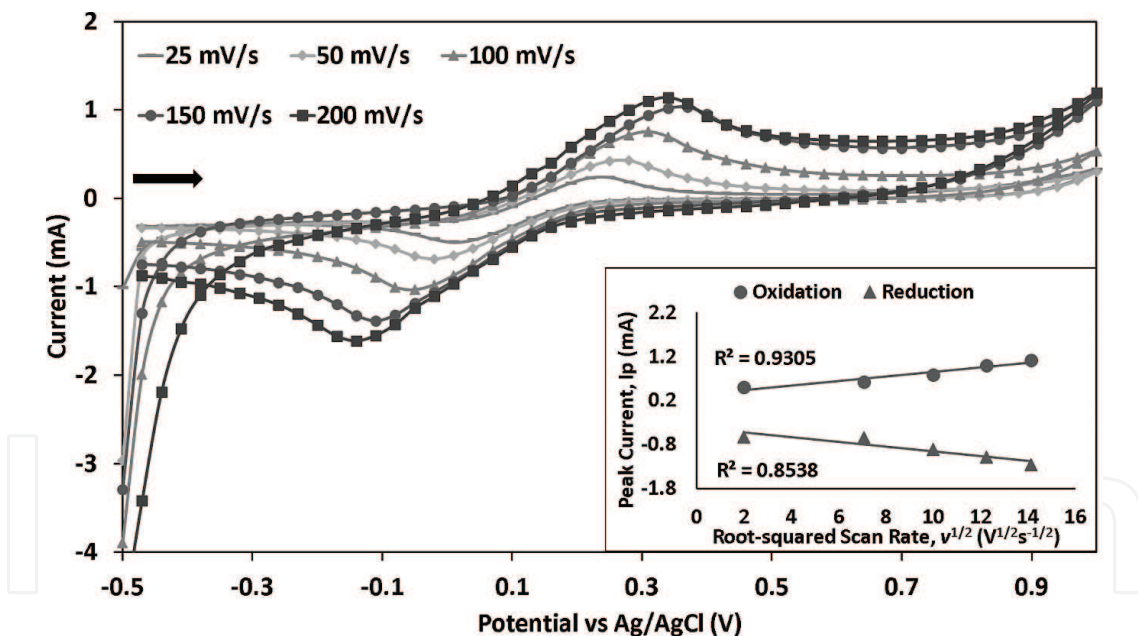
PEDOT:PSS with rGO can potentially increase the electron transfer rate at the electrodes, further improving the performance of the biosensor in terms of sensitivity to changes in analyte concentration.

1.2. Electrical impedance spectroscopy (EIS)

EIS is an analytical tool to study the interfacial behavior occurring on the surface of an electrode. The impedance of an electrode at the electrode-solution interface is determined by applying a small alternating (AC) sinusoidal voltage (~10 mV peak-to-peak) perturbation and tracking the current output. Since an AC is applied across the surface of the electrode, the voltage–current output will also be observed in a range of frequencies [8]. The experimental data can be represented in two ways, i.e., the Nyquist plot (where the real vs. imaginary impedance components are plotted) and the Bode plot (where the impedance and phase angle were plotted against frequency). The data obtained from experimental studies can be analyzed and evaluated using an equivalent circuit comprising a series of resistances and capacitances in parallel (Randles equivalent circuit) [9]. Note that the Nyquist plot will be preferred in this study because of the extensive information that can be obtained to understand the impedance at the electrode-solution interface, charge transfer resistance, and Warburg impedance.

1.2.1. Experiments

A similar experimental setup as **Figure 1** was used for EIS measurements. The screen-printed carbon electrode (SPCE) was connected to a potentiometer, and the signal obtained was processed for further analysis.

1.2.2. Materials

1.2.2.1. Consumable items and equipment

- Magnetic stirrer

- Sonicator

- Pipette and pipette tips

- Potentiometer (IVIUM Technologies, Eindhoven, Netherlands)

- Screen-printed glassy electrode (SPCE with 2 mm diameter, Pine Instruments, Grove City, Pennsylvania, USA)

1.2.2.2. Chemicals and reagents

- PEDOT:PSS solution (1.3 wt% dispersion in H_2O, high-conductivity grade, Sigma-Aldrich, St. Louis, MO, USA)

- Ultrahighly concentrated GO (UHC GO) solution (6.2 mg/ml, Graphene Supermarket, USA)

- 5 mM potassium ferricyanide/potassium ferrocyanide $K_3Fe(CN)_6$/$K_4Fe(CN)_6$ in 0.01 M PBS, pH 7.4 (R&M Chemicals, Selangor, Malaysia)

- M PBS, pH 5 (Sigma-Aldrich, St. Louis, MO, USA)

- Deionized (DI) water

1.2.3. Methods

1.2.3.1. Fabrication of rGO-PEDOT:PSS electrode

1. Mix 500 µl PEDOT:PSS with 500 µl UHC GO solution (1,1) in a small vial.

2. Stir the solution using a magnetic stirrer, and sonicate at 30°C for 10 min to ensure homogenous mixture of GO-PEDOT:PSS nanocomposite.

3. Drop cast 3 µl GO-PEDOT:PSS mixture onto the WE of a SPCE, and leave to dry at ambient temperature.

4. Reduce the electrode using a potentiostat via repetitive cyclic voltammetry (CV) with potential range from 0 to −1.5 V at 0.1 V/s in 0.01 M PBS, pH 5, for 15 cycles. Ensure that all electrodes (WE, RE, and CE) are fully immersed in the PBS during the reduction process. The reduced electrode is denoted as rGO-PEDOT:PSS/SPCE.

5. Rinse the rGO-PEDOT:PSS/SPCE with DI water, and dry at ambient temperature for 2 h.

1.2.3.2. EIS measurement

1. To perform EIS measurement, dip the rGO-PEDOT:PSS/SPCE into a cell filled with 5 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) in 0.01 M PBS, pH 7.4. Make sure that all electrodes (WE, RE, and CE) are immersed in the solution.

2. Run EIS over a frequency range of 100 kHz–0.1 Hz, amplitude of 20 mV, and applied potential of 0.25 V.

3. Observe and record the real impedance (Z′) vs. imaginary impedance (−Z″) obtained from the EIS measurement. Repeat steps 1–4 with a bare SPCE electrode to show the comparison between SPCE and rGO-PEDOT:PSS/SPCE.

1.2.4. Results

Figure 4 shows a Nyquist plot of real impedance (Z′) vs. imaginary impedance (−Z″) for a SPCE and an rGO-PEDOT:PSS/SPCE. The observed plots are fitted to a Randles equivalent circuit for analysis. A typical Randles circuit includes the solution resistance (R_s), charge transfer resistance (R_{ct}), Warburg impedance (Z_w), and double-layer capacitance (C_{dl}). R_s refers to the resistance between a solution containing ions at a certain concentration and an electrochemical cell, R_{ct} refers to the electron transfer produced by a redox reaction at the electrode interface, Z_w indicates the impedance of electrons due to the diffusion interface between bulk
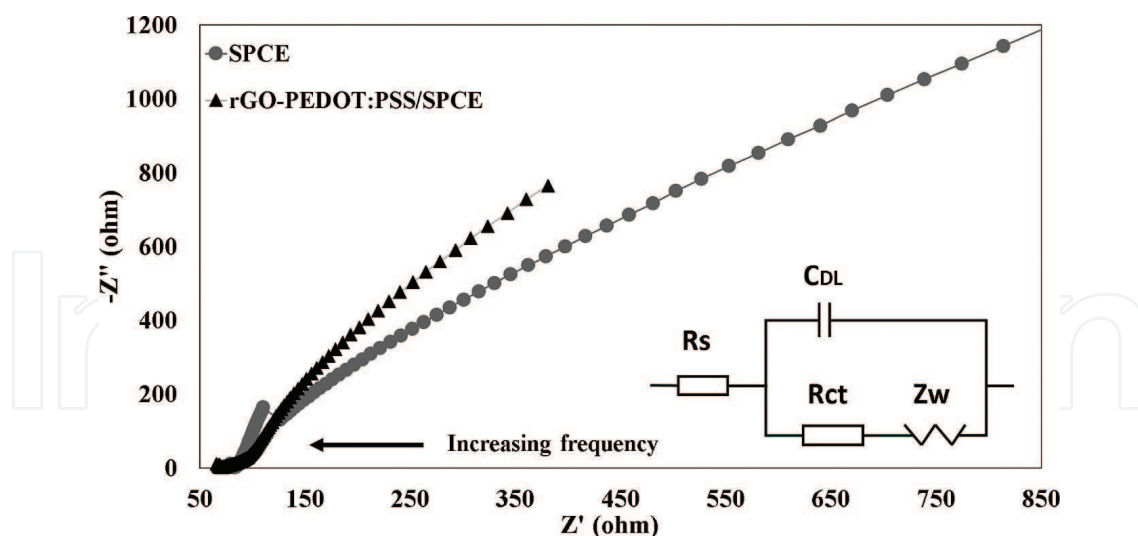
Figure 4. EIS of SPCE and rGO-PEDOT:PSS/SPCE in PBS, pH 7.4, containing 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) over a frequency range of 100 kHz–0.1 Hz, amplitude of 20 mV, and applied potential of 0.25 V. Inset shows Randles equivalent circuit of a typical biological sensor.

solution and the electrode interface, and C_{dl} is the capacitance obtained from stored charge in the double-layer region at the electrode interface [10, 11].

1.2.4.1. Discussion of results

The Nyquist graph in **Figure 4** shows impedance measurements of SPCE and rGO-PEDOT:PSS/ SPCE. Since impedance is a measure of resistance occurring on the electrode interface, the Nyquist plots show that the impedance for rGO-PEDOT:PSS/SPCE increases in comparison to a bare SPCE. In a typical Nyquist plot, a semicircular region is observed in the lower-frequency region, whereas a linear plot is observed in the high-frequency region. For a bare SPCE, the plots are dominated by the linear region, which indicates that the electron transfer occurring on the electrode surface is heavily influenced by a diffusion-limited process [12]. The diffusion-limited process is typically represented by the Warburg impedance (Z_w), which means that the impedance is a result of the diffusion layer between the bulk solution and the electrode surface. For the rGO-PEDOT:PSS/SPCE, the linear region is slightly shorter than that of the bare SPCE, and there is a small half semicircle observed at the low-frequency region, which suggests that the influence of the Warburg impedance is low for the rGO-PEDOT:PSS/ SPCE [8]. The results also suggest that the electrode shows a slightly capacitive behavior, which could be owing to the presence of PEDOT:PSS in the electrode interface [4, 13].

2. Conclusion

Voltammetry characterization of CV and EIS for a conducting rGO-PEDOT:PSS composite is presented. Both CV and EIS are relevant techniques for understanding electron transfer at the electrode-solution interface. The results from CV indicate that the presence of rGO in rGO-PEDOT:PSS/SPCE helps to enable electrochemically reversible electron transfer in

comparison to PEDOT:PSS/SPCE by reducing the shift in the peak potential (E_p). For EIS, the rGO-PEDOT:PSS/SPCE reduces the influence of Warburg impedance in comparison to a bare SPCE. These findings suggest that the rGO-PEDOT:PSS composites in electrochemical devices are very suitable for application in biological sensing.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Abbreviations

CE	counter electrode
CV	cyclic voltammetry
EIS	electrical impedance spectroscopy
PBS	phosphate-buffered saline
PEDOT:PSS	poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)
rGO	reduced graphene oxide
RE	reference electrode
SPCE	screen-printed carbon electrode
WE	working electrode

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