Electrochemical Characterization and Application of Ni-RuO₂ as a pH Sensor for Determination of Petroleum Oil Acid Number

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Electrochemical characterization and application of nickel ruthenium dioxide (Ni-RuO$_2$) as a pH sensor for the determination of petroleum oil acid number is described. The sensor consists of RuCl$_3$ thermally decomposed onto the upper side of a polycrystalline nickel electrode at 400 °C in an open furnace. The advantages of the sensor are: (i) easy preparation, (ii) fast response in a large pH range, (iii) high physical and chemical stability, and (iv) excellent reproducibility as determined by the reproducible linear variation of charge transfer resistance (R_{ct}) as a function of overpotential (η) obtained by electrochemical impedance spectroscopy (EIS), and the Nernstian slope of the electrode potential in a wide range of pH (1.5-12.5) obtained by potentiometric measurements. The potentiometric selectivity coefficients of the sensor toward some anions and cations were evaluated in aqueous solution. The characterized Ni-RuO$_2$ pH sensor was successfully tested for the determination of petroleum oil acid number.

INTRODUCTION

Glass electrodes have been the most popular pH electrodes for the last seven decades because of their sensitivity, selectivity, stability, and long lifetime [3]. However, glass electrodes have several disadvantages due to the intrinsic nature of the glass membrane. For example, they are easily affected by alkaline or HF solutions, often exhibit a sluggish response, and are difficult to miniaturize and planarize based on current manufacturing technologies [4]. Moreover, these electrodes cannot be used in food or for *in vivo* applications because of their brittle nature. The drawbacks of glass electrodes have led to intensive research for alternative pH electrodes. As a result, various kinds of potentiometric pH sensors have been developed [5-17]. These include coated

[wire pH electrodes 5], polymer modified electrodes [6-8], metal/metal oxide pH electrodes [9], and micro-ISFET electrodes [10]. Among the materials tested as possible pH recognition systems, some metal oxides were most intensively investigated, including Al$_2$O$_3$, RuO$_2$, PtO$_2$, TiO$_2$, IrO$_2$, OsO$_2$, RhO$_2$, TaO$_2$, and SnO$_2$ [9-17]. The results obtained on IrO$_2$ and RuO$_2$ electrodes have indicated that these materials hold the most promise, yielding a near Nernstian response over a wide range of pH.

The acid number (AN) of petroleum oil is an important characteristic that determines the conductivity and corrosion behavior of the oil. Glass electrodes have been used for AN determination, although they suffer from the aforementioned disadvantages. Therefore, it is necessary to seek another type of pH sensor for this application. In this paper, we report a new, all solid-state, pH sensor, using a nickel ruthenium dioxide (Ni-RuO$_2$) electrode. The RuO$_2$ is supported on the

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upper side of a polycrystalline nickel electrode by thermal decomposition of RuCl$_3$. The behavior of the electrode is studied in acidic and alkaline solution by electrochemical methods. The pH-potential response of the sensor is investigated by titration of acidic solutions. The characterized sensor is used successfully for determination of petroleum oil AN.

EXPERIMENTAL

Electrode Preparation

The surface of the Ni electrode was subjected to a pre-treatment consisting of mechanical polishing with emery paper, sonicating in a water bath, and washing thoroughly with H$_2$SO$_4$ solution, acetone, followed by deionized water. Ruthenium dioxide was coated onto the Ni surface (0.314 cm^2) by thermal decomposition of RuCl$_3$. The chloride salt of ruthenium (RuCl$_3$.xH$_2$O, 0.3 M) was dissolved in deionized water. A few drops of hydrochloric acid (1% v/v) were added to prevent the decomposition of the solution. The Ni cylinder was placed into the chloride salt solution in order to apply a layer of this solution on the upper surface of the electrode. A uniform coating was obtained by firing the electrode for 20 s at 200 °C between the applications of each successive layer of RuCl$_3$ solution. A total of twenty layers were applied. At the end of the deposition process, the samples were annealed at 460 °C for 4 h in air. The side walls of the electrodes were coated with epoxy paste and fitted in a heat-shrinkable tube to leave a working surface area of 0.314 cm^2. In this report, the electrodes thus prepared are referred to as Ni-RuO$_2$. The prepared electrodes were conditioned in distilled water for 24 h before use. All chemicals used in this investigation were of analytical reagent grade.

Electrochemical Measurements

Dynamic measurements were performed in 1 M NaOH and 0.5 M H$_2$SO$_4$ solutions, deaerated with argon gas (99.99%) for 30 min prior to each experiment. All measurements were carried out at room temperature. A 5 mA DC cathodic or anodic constant current, depending on the direction of the experiment, was applied before each experiment for at least 1 h, after which the electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), or polarization curves were recorded. The impedance spectra were recorded at different DC potentials. A 5 mV AC amplitude superimposed on each DC potential was applied and a wide frequency range of 100 kHz to 0.1 Hz was scanned with 10 points/decade using a logarithmic scale. Cyclic voltammograms were recorded in various sweep rates, from 50 to 1100 mV s^{-1} in double-layer potentials between 0.2 and 0.9, and -0.63 and 0.3 V *vs.* Ag/AgCl/KCl (3 M) in 0.5 M H$_2$SO$_4$ and 1 M NaOH, respectively.

The ability of the Ni-RuO$_2$ electrode to determine pH was evaluated by measuring the electrode potential in test solutions *vs.* the reference electrode. The pH of the test solutions was manipulated through acid-base titration and measured simultaneously by a glass-pH electrode. The ionic strength of the solutions was adjusted using 0.2 M KCl.

Instrumentation

A three-electrode conventional cell used for CV, EIS and polarization measurements consisted of the Ni-RuO$_2$ as the working electrode, a large surface area platinum plate (99.99%) as the auxiliary electrode, and Ag/AgCl/KCl (3 M) as the reference electrode. The measurements were carried out using an EG&G potentiostat/galvanostat (P/G) Model 273A, and an EG&G frequency response analyzer (FRA) model 1025, controlled by a personal computer (PCIII 800 MHz) through a GPIB-IEEE NI-488-II card. The EIS and CV data acquisition was performed using EG&G PowerSine® and EG&G M270® software, respectively. The EIS data were approximated using the appropriate equivalent circuit built in EQUIVCRT® 4.55 [18].

Potentiometric measurements were carried out using a Metrohm® model 692 pH/ion meter equipped with a combined LL pH glass electrode, model 6.0222.100, in a two-electrode conventional cell in which the Ni-RuO$_2$ served as a potentiometric-indicator electrode. All measurements were performed at ambient temperature.

RESULTS AND DISCUSSION

Dynamic Studies

Dynamic studies including potential polarization, EIS, and CV measurements were performed to show the stability and reproducibility of the Ni-RuO$_2$ pH-sensor.

Potential polarization. Polarization studies were carried out after holding the working electrode at a constant current density (5 mA) for at least one hour, which resulted in reproducible polarization curves. The slope of the polarization curves obtained on the Ni-RuO$_2$ electrode in a 1 M NaOH solution for the hydrogen evolution reaction (HER) was close to 42 ± 2 mV decade^{-1} in the low overpotential range. This value is close to those previously reported [16,19,20], and has been explained based on the Volmer-Heyrovský reaction mechanism [21-27]. However, we did not continue the HER to very high overpotentials, since it was not the aim of this research. We also studied the oxygen evolution reaction (OER) in 1 M NaOH, and the HER and OER in 0.5 M H$_2$SO$_4$ to ensure the stability of the Ni-RuO$_2$ electrode at low overpotentials (data not shown). The reproducibility of the polarization curves at extreme pHs implies that the Ni-RuO$_2$ electrode has excellent chemical and electrochemical stability at low overpotentials and near the equilibrium.

Electrochemical impedance spectroscopy (EIS). EIS is a powerful, nondestructive and informative method [26] allowing one to trace the electrochemical events at the electrode/solution interface far from, near, or at the equilibrium potentials [27-29]. For example, the effects of grain boundaries [30] and membrane structure [31] on the response of solid-state pH-sensors and potentiometric solid-state membranes have been investigated by EIS. The goal of the EIS studies in this work was to investigate the stability and reproducibility of the Ni-RuO$_2$ electrode in alkaline and acidic conditions. One series of complex plane plots obtained for the HER on the Ni-RuO$_2$ electrode in 0.5 M H$_2$SO$_4$ is presented in Fig. 1. Data for the OER in H$_2$SO$_4$, and for the HER and OER in NaOH solutions are available upon request. Two semicircles were observed on the complex plane plots over the entire range of frequency studied as well as the potential studied (Fig. 1, inset), in both acidic and alkaline solutions. The data were approximated using a two-CPE equivalent electrical circuit model (Fig. 2) [26], from which electrode kinetics as solution resistance (R$_s$), parameter of double layer capacitance (T), dispersion parameter (φ), and R$_{ct}$ were estimated.

The φ parameter was virtually potential independent, with values of 0.7 and 0.9 in 0.5 M H$_2$SO$_4$, and 0.85 and 0.87 in 1 M NaOH for the HER and OER, respectively. Variation of

log(1/R$_{ct}$) as a function of overpotential (η) was linear (data
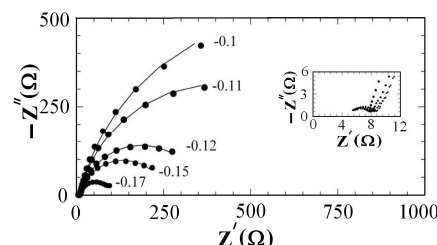
Fig. 1. Complex plane plots obtained on Ni-RuO$_2$ electrode for the HER in 0.5 M H$_2$SO$_4$ at 25 °C. The numbers indicate DC potentials in volts *vs*. Ag/AgCl/KCl (3 M). Dots show the experimental data and lines show fitted data approximated using a two-CPE model and complex nonlinear least squares (CNLS) method. The inset shows high frequency semicircles (see the text).
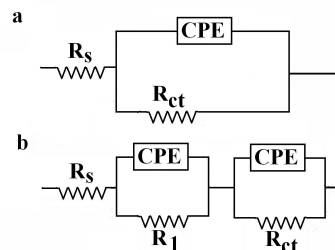
Fig. 2. Equivalent circuits used for impedance data approximation: (a) modified Randles' model in which the double layer capacitance is replaced by CPE, without Warburg element for charge transfer control process only, and (b) two-CPE model. The R$_s$, R$_{ct}$, and C$_{dl}$ represent the solution resistance, charge transfer resistance, and double-layer capacitance [29].

not shown) with slopes of -18 ± 1 and 17 ± 1 mV decade^{-1} in 0.5 M H$_2$SO$_4$, and -22 ± 1 and 15 ± 1 mV decade^{-1} in 1 M NaOH for HER and OER, respectively. These results allowed us to estimate the C$_{dl}$ values as 0.1 F cm^{-2} for both the HER and OER in 0.5 M H$_2$SO$_4$, and 0.06 and 0.09 F cm^{-2} in 1 M NaOH for the HER and OER, respectively. The values were almost potential independent, and close to the previously

reported values [15,16,25], which briefly means that the mechanism and kinetics of the reaction at the electrode/ solution interface did not change over time. The stability and reproducibility of the results obtained using the EIS studies, especially C_{dl} and slopes of $\log(1/R_{ct})$ *vs.* η, confirm the stability behavior observed for the Ni-RuO$_2$ modified electrode obtained by potential polarization.

Cyclic voltammetry. C_{dl} of the Ni-RuO$_2$ electrode was also evaluated in 0.5 M H$_2$SO$_4$ using the equation j = ν C$_{dl}$ and the average of the capacitive current densities, j, [average of j *i.e.*, (|j$_c$| + |j$_a$|)/2] in the double-layer region at E = +0.5 V as a function of scan rate, *v*, (Fig. 3). The same tendency was observed for 1 M NaOH at -0.15 V (data not shown). The values found for C_{dl} are 0.097 and 0.067 F cm^{-2} in 0.5 M H$_2$SO$_4$ and 1 M NaOH, respectively, which are also in good agreement with those obtained by potential polarization and EIS measurements for dynamic behavior of Ni-RuO$_2$ electrode.

The dynamic studies including potential polarization, EIS, and CV measurements show that the equilibrium potential of the Ni-RuO$_2$ electrode is re-established after removing an applied potential, i.e., the electrode pH-potential response is practically reversible. Therefore, the electrode can abide the dynamic electrochemical signals, and return to its equilibrium potential in given conditions, when the applied electrical signal is removed. This is an interesting behavior for a pH-indicator electrode.

Equilibrium Response

pH-potential. The pH response of the Ni-RuO$_2$ electrode was investigated by the titration of 0.05 M H$_3$PO$_4$ (30 ml) with 0.10 M NaOH. Titration curves were obtained using the combined LL pH glass electrode and Ni-RuO$_2$ indicator electrode. The pH-potential curve was obtained by varying the Ni-RuO$_2$ indicator electrode potential as a function of pH measured using the combined glass-pH electrode (Fig. 4).

A linear response was obtained in the pH range of 1.5-12.5, with a slope of -52 ± 2 mV/pH, an interpolated potential of 595 ± 10 mV at pH = 0 (i.e., E^0), and a correlation coefficient of r^2 = 0.999. Since the slope is less than 59.02, a sub-Nernstian behavior is indicated [32]. The acids used in the various parts of this study included weak (acetic), strong (nitric), multiproton (phosphoric) acids, and a mixture of

phosphoric and acetic acids to measure the pH response of the electrodes. The linear pH-potential responses obtained from the mixtures were in good agreement with those obtained from the abovementioned simple solutions.
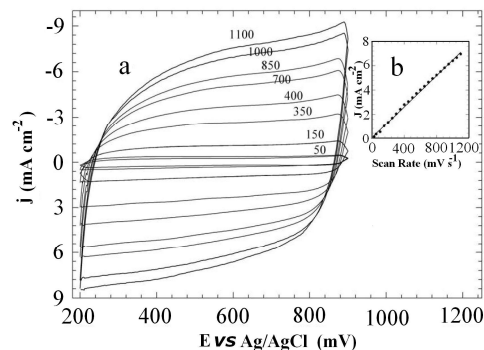
Fig. 3. (a) Cyclic voltammograms obtained on the Ni-RuO$_2$ electrode at different potential scan rates (*v*), from 50 mV s^{-1} to 1100 mV s^{-1}. The numbers show the scan rates. For clarity, only some of the CVs are shown here. (b) Variation of j as a function of scan rate at E = +0.5 V in 0.5 M H$_2$SO$_4$, j/(mA cm^{-2}) = 0.0064 + 0.097 *v* mV s^{-1}, r^2 = 997.
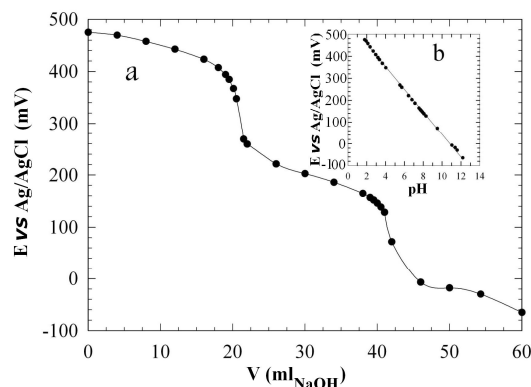

Fig. 4. Titration curves obtained using combined the LL pH glass electrode and Ni-RuO$_2$ indicator electrode, (a) pH response for titration of 0.05 M H$_3$PO$_4$ (30 ml) with 0.10 M NaOH, and (b) pH-potential curve obtained by varying the Ni-RuO$_2$ indicator electrode potential as a function of pH measured using the combined glass-pH electrode.

Long-term stability of slope and E°′. To test the long-term stability or shelf-life of the electrode, two separate runs were performed using the same Ni-RuO$_2$ electrode. One run was performed when the electrode had been newly prepared. The second run was performed on the same electrode after it had been stored in distilled water for over 50 days. In each run, the pH was adjusted through the titration of phosphoric acid with sodium hydroxide.

The long-term stability or shelf-life of the Ni-RuO$_2$ electrode over 50 days is shown in Fig. 5. The calibration curves showed a good linear pH-potential response, and were stable over a long test period. The average variations of the $E^{0′}$ and slope were less than 10 mV and 1 mV/pH with RSD less than 2.2% and 1.2% at CL = 95%, respectively, for six tests during the 50-day test period, with no specific direction of potential variations. Temperature variations due to day-to-day room temperature changes may explain the $E^{0′}$ changes over this period. However, there was no change in pH-potential sensitivity of the Ni-RuO$_2$ electrode from either long-term storage in distilled water (tested directly) as shown in Figure 5, or long-term storage in air followed by conditioning in distilled water for a few minutes before testing (results not shown). The slope remained approximately -52 ± 2 mV/pH. The results showed that Ni-RuO$_2$ electrode was highly stable for long-term applications in pH measurements.

Stability of equilibrium potential. Potential drift in a continuous test will introduce error into pH measurements. The drift behavior of the Ni-RuO$_2$ electrode was evaluated in a pH 6.6 buffer solution stirred under air at room temperature. The equilibrium potential was measured continuously as a function of time for 28 measurements over a period of 30 min. The response time of the electrode could not be established from the present test. Therefore, the Ni-RuO$_2$ electrode was first exposed to a pH 2.2 solution and then NaOH was added to increase the pH to 6.6.

The drift behavior of the Ni-RuO$_2$ electrode showed a constant value of 212 ± 2 mV (RSD less than 1% at CL = 95%) for 28 measurements over a period of 30 min. Part of this small deviation is most likely from the fluctuation in potentials of the Ni-RuO$_2$ and Ag/AgCl/KCl (3 M) reference electrodes at room temperature. The response time for the Ni-RuO$_2$ electrode is shown in Fig. 6 (vertical part). The electrode quickly responded to the pH change (initially
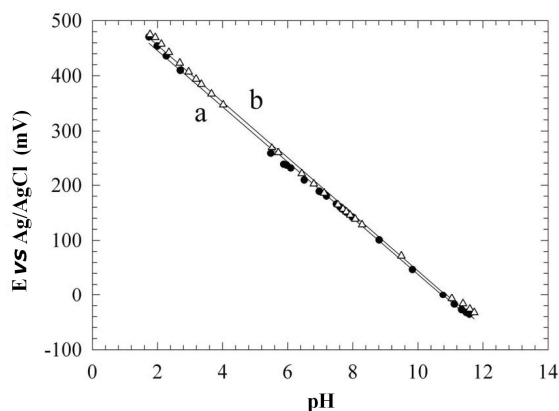
Fig. 5. pH-Potential response obtained using: (a) newly prepared Ni-RuO$_2$ electrode (●), and (b) Ni-RuO$_2$ electrode stored for 50 days in distilled water (Δ).
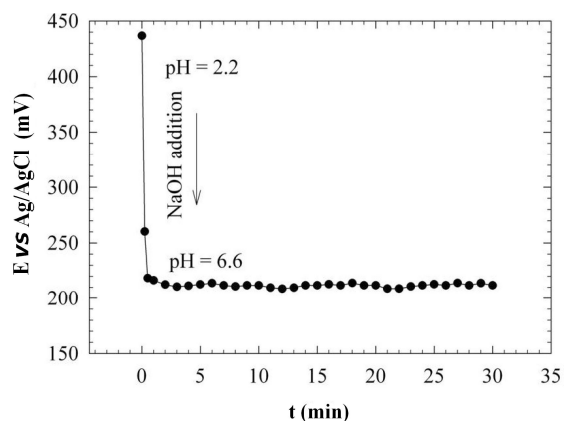
Fig. 6. Potential stability of the Ni-RuO$_2$ electrode in a pH 6.6 buffer solution after a pH change from 2.2 to 6.6 by NaOH addition at room temperature.

pH 2.2 and then rapidly increased to 6.6) and established a new equilibrium potential. The quick response of Ni-RuO$_2$ electrode, besides its high physical, chemical, and electrochemical stability, makes it suitable for continuous determination of pH without the need for frequent calibration. Obviously, the Ni-RuO$_2$ electrode is durable and exceedingly robust, the electrode preparation is not time or labor intensive, and, unlike a glass electrode, does not require special care. The only deterioration that may occur is due to scratching of the electrode by hard equipment, such as the sharp edges of

tools.

Electrode selectivity. The interference from many cations and anions on the response of Ni-RuO$_2$ electrode was carried out at different pHs using a mixed solution method (MSM) and separate solution method (SSM) [33-35].

Good agreement was observed between the results obtained by the MSM and SSM methods. Only small interferences were imposed at low pH by moncharged cations with the given $\log(K_{i,j}^{pot})$ in the following order: NH$_4^+$ (-1.51) > Li$^+$ (-1.88) and anions CN$^-$ (-1.15) > SCN$^-$ (-1.39) > NO$_2^-$ (-1.39) > NO$_3$.

Determination of petroleum oil acid number. Acid number (AN) is an important characteristic of petroleum oil quality indicating some properties of oil such as conductive and corrosive effects. The AN is defined as the milligrams of KOH necessary to titrate the acids contained in one gram of oil. This method is time and labor consuming. An alternative method for AN determination without titration has been developed by Tur'yan *et al.* [36,37]. This method is based on the use of the base sodium benzoate in water-isopropanol solvent [36,42,43], using a glass-pH electrode as the indicator. This method was used for the determination of AN in this study, comparing the response of Ni-RuO$_2$ with that of the glass-pH electrode.

To compare the response of Ni-RuO$_2$ with that of the glass-pH electrode in the determination of the AN of oil, 50 ml sodium benzoate [NaBen, 0.05 M in a water-isopropanol solvent (1:1 v/v)] [36,42,43] and 10 grams of the oil test solution were introduced into the potentiometric cell. The mixture was stirred, while being careful not to pull air bubbles into the mixture. The Ni-RuO$_2$ and glass pH-indicator electrodes were introduced into the cell. After 3 min, E$_1$ was read from Ni-RuO$_2$ (175.6 mV) and then pH$_1$ from glass-pH electrode (8.2). Then, 0.2 ml of a 0.05 M HNO$_3$ aqueous standard solution was added while stirring, and E$_2$ (190.3 mV) and pH$_2$ (7.8) were read. The AN was obtained according to the following equation: AN = 56.11{(N$_{st}$ V$_{st}$)/[m (10$^{\Delta X}$-1)]}; where 56.11 is the molecular weight of KOH, N$_{st}$ and V$_{st}$ are the concentration (M) and volume (ml) of the added HNO$_3$ standard solution, respectively, m is mass of the oil sample in grams, and ΔX is absolute value of ΔpH (= pH$_2$ - pH$_1$) or ΔE (= E$_2$ - E$_1$)/59.16.

The resulting AN was 0.0433 and 0.0434 mg$_{KOH}$/g$_{oil}$ with RSD% of 0.46% and 0.50% using glass and Ni-RuO$_2$ indicator electrodes, respectively. The good agreement observed between the results implies that Ni-RuO$_2$ electrode can be used as a substitute for the glass-pH sensor not only for determination of pH in aqueous solution but also for evaluation of crude oil AN.

Comparison with Ni-Zn-P. For comparison, the microporous Ni-Zn-P electrode was prepared as previously published [44], modified with RuO$_2$ [27], and then its pH-potential response was studied. The response of the Ni-Zn-P-RuO$_2$ electrode was so sluggish that a stable and linear signal could not be established even after 30 min on each point. This behavior is probably due to the slow equilibrium between H$^+$ in the solution and RuO$_2$ deposited into the micropores of Ni-Zn-P alloy. However, this electrode has shown a high activity due to the roughness of its surface, and has been recommended for the HER [27]. In contrast, while the pH-potential response of Ni-RuO$_2$ was fast and reversible, its activity towards the HER was low due to the smoothness of its surface, and is therefore not recommended for the HER or OER.

CONCLUSIONS

Kinetic studies of the HER and OER in H$_2$SO$_4$ and NaOH using Ni-RuO$_2$ revealed the physical, chemical, and electrochemical stability of the electrode in both acidic and alkaline solutions. The electrode response is practically reversible. This is an interesting behavior for a pH-indicator electrode. The pH-potential studies of Ni-RuO$_2$ modified electrode showed that electrode has the benefits of speed, linearity, and reproducible response over the entire range of pH in aqueous solutions. These behaviors, in addition to its excellent durability, as well as easy and inexpensive preparation, make the Ni-RuO$_2$ electrode a good substitute for the glass pH electrode for many pH measurements, such as those performed in the oil industry and in environmental analysis. Only small interferences are imposed at low pH by moncharged anions CN$^-$, SCN$^-$, and NO$_2^-$ and cations NH$_4^+$ and Li$^+$. The electrode was successfully tested for the determination of petroleum oil AN.

A comparative study shows that the Ni-Zn-P-RuO$_2$ electrode benefits from a rough surface, and it is

recommended for the HER and OER. On the other hand, its pH-potential response was sluggish and nonlinear, and is not recommended for pH measurements. In contrast, the Ni-RuO$_2$ does not have the advantage of a rough surface, so it is not proposed for the HER or OER. As studied here, the Ni-RuO$_2$ electrode can be proposed as a good pH-sensor.

ACKNOWLEDGMENTS

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