Measuring the Electrochemical Response of a Titanium Dioxide Nanotube Electrode to Various Chemicals as Explosive Components

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Authors' contributions

This work was carried out in collaboration among all authors. Authors SCJ, YXG and SBC designed the study, collected the data, and wrote the initial draft. Authors YXG, JLS and JCO discussed the plan of research and the test protocols. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Sensing and mitigating explosives are critical for homeland security. This paper investigates the electrochemical responses of TiO_2 nanotubes exposed to several chemicals including ammonium nitrate, hydrogen peroxide, methanol, ethanol and ethylene glycol which are used directly as explosives, or as the starting materials for making explosives. Cyclic voltammetry (CV) tests were performed to identify the characteristics of these chemicals at the surface of the TiO_2 nanotube electrode. It is found that the trends for system responses to methanol, ethanol and hydrogen peroxide reveal the oxidation of these chemicals in the low voltage range from 0 V to 0.3 V. For ammonium nitrate, the hysteresis of the CV loops covers a much bigger potential range from 0.1 V to 0.8 V. The ethylene glycol shows the mass transfer controlling response which is due to the high viscosity of the solution.

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1. INTRODUCTION

In the modern era, the threat of explosive use to civilians and standing militaries has become a point of significant international concern. Bombings around the globe have raised the need for detecting the explosive components before they can be made into explosives. Homemade explosives in particular are alarming, as the sales of the components for their production are not as well monitored as more potent explosive materials. Recently, trace explosive detectors have been employed [1-10]. They are able to detect extremely minute amounts of explosive chemicals. Oxides show strong affinity to explosive components and they are considered to be used as sensor materials [11-18]. Using titanium dioxide nanotubes to build sensors is one of such methods that have been employed in the detection of explosives [19,20]. The nanotubes can be bonded with other particles to increase the adsorption of those explosive molecules. Their properties can be modified if it is necessary. Such change in properties can be utilized in determining the presence of chemicals associated with explosives.

2. MATERIALS AND EXPERIMENTAL METHODS

In order to prepare the titanium oxide nanotubes, an electrochemical cell was created using a thin strip of pure titanium as the anode, a small rod of platinum as the cathode, and the solution medium consisted of approximately 1% ammonium fluoride+5% water+94% ethylene glycol. The source of electrical power used for the reaction was a RSR DC power supply (HY5003 No. 35653). The cell was then subjected to increasing voltage for 28 minutes to determine the voltage to form the nanotubes. The specimen was then subjected to the voltage of 50 V for 2 hours for the formation of the TiO_2 nanotubes. After completion of the reaction, the specimens were left exposed to air for another 2 hours. They were then placed into a furnace at 450ºC for 2 hours, then air cooled to homogenize the nanotubes on the titanium strip.

To test the responses of the nanotubes to the explosive components, the experiments utilizing an electrochemical potential scans by the CHI 600E Electrochemical Analyzer (Serial A2801)

were performed. In order to verify the device was functioning properly, calibration of the system was conducted by using a 550 Ohm resistor. It was placed between the positive and negative leads. A linear scan was carried out and checked the output current. Accompanying software with the CHI 600E was used to track corresponding electrical current as the electrical potential varied.

An electrochemical cell consisting of the treated titanium strip as the anode, a platinum rod as the cathode and ground, and a methanol solution was assembled to measure the system response. The anode was made from the titanium dioxide nanotube array setting on the titanium plate substrate with the dimension of 4 mm × 50 mm × 0.127 mm. The dimension of the section immersed into the explosive solution is 4 mm × 20 mm × 0.127 mm. The CHI 600E Electrochemical Analyzer was set to an initial potential of 0V, high of 1V, and low of 0V, scan rate of 0.1 V/s with a sample interval of 0.01V and sensitivity of 1×10^{-5} A/V, with 2 segments. After running the test, a second test was performed, doubling the scan rate and sample interval to get a more accurate response. A third test was run, this time with the original scan rate and sample interval, but with a low potential of -1.0V and 3 segments of electrical potential sweep. This third test would provide a model for using the titanium as the cathode. These sweeps were repeated for ethanol, hydrogen peroxide (with the concentration of 7%, 5% and 3.5% in weight), and ammonium nitrate. For the ethylene glycol, the test was different because the response range of potential is different from other materials. We set 0 to 10 V as the scan range.

3. RESULTS AND DISCUSSION

Fig. 1 (a) presents the anodic oxidation sketch of titanium dioxide nanotube processing. The anodic reaction is the pure titanium dissolution followed by the oxidation to generate nanopores. The nanopores reorganize by themselves and form nanotubes as shown in Fig. 1(b). The average diameter of the nanotube is around 100 nm and the length is more than 50 micron. The inset of Fig. 1(b) represents a higher magnification image to confirm the formation of the titanium dioxide nanotubes.
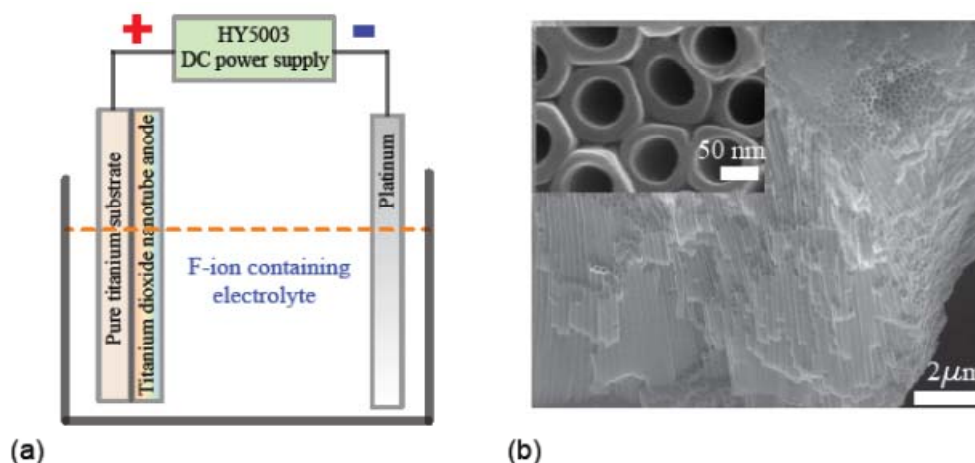
Fig. 1. Schematic of the electrochemical cell for making TiO₂ nanotubes and the image of the nanotube: (a) a sketch of the cell, (b) the image of TiO₂ nanotubes (The inset represents a high magnification image confirming the formation of the nanotubes)

Following the preparation of the nanotubes, the electrochemical response measurement was performed using the Electrochemical Workstation as schematically shown in Fig. 2. Also illustrated in this figure is the electrochemical response measurement configuration. The electrode was made from the titanium dioxide nanotube array setting on the titanium plate substrate with the dimension of 4 mm × 50 mm × 0.127 mm. The dimension of the section immersed into the explosive solution is 4 mm × 20 mm × 0.127 mm. In the forward potential scanning segment, the titanium dioxide serves as the anode. Electron ejection to external circuit is the major event under the positive potential pushing. At the same time the hole goes into the solution, which triggers the decomposition of explosive components such as the organic compounds and the ammonium salt as mentioned in the previous section of the paper.

In view of the explosive detection and decomposition mechanisms, we may classify them as two categories. The first category is the organic compounds including the ethanol, methanol, and ethylene glycol. Using R represents the carbon containing groups, the following reaction as shown in Eq. (1) happened under the driving force of the forward bias voltage.
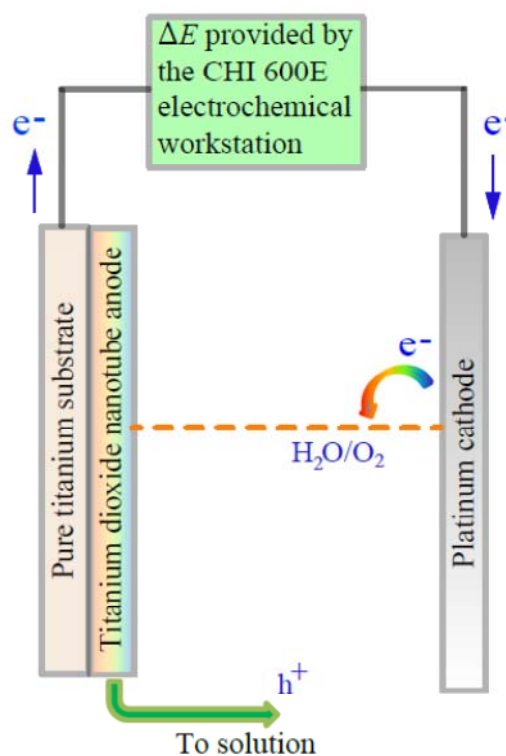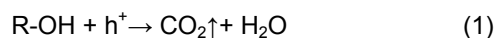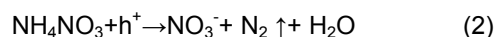
$$R\text{-}OH + h^+ \rightarrow CO_2\uparrow + H_2O \qquad (1)$$

Fig. 2. Illustration of the electrochemical response measurement configuration (The electron flow in a forward potential scanning is shown.)

The second category is the ammonium nitrate compound and the hydrogen peroxide. The proposed mechanisms include Eq. (2) and (3), respectively.

$$NH_4NO_3 + h^+ \rightarrow NO_3^- + N_2 \uparrow + H_2O \tag{2}$$

$$H_2O_2 + h^+ \rightarrow O_2 \uparrow + H_2O \tag{3}$$

In the reverse scan segment, the oxide nanotube electrode becomes a cathode. Hydrogen formation will be the main reaction at the titanium dioxide nanotube surface.

From Figs. 3 to 8, we will systematically present the electrochemical responses of the titanium dioxide nanotubes to different explosive components. The concentration effect of the hydrogen peroxide at the TiO_2 nanotube surface is also studied. Fig. 3 shows the response of the oxide nanotube electrode in a 95% ethylene glycol solution. Since the high viscosity of ethylene glycol slows down the mass transport process in the electrochemical reaction, only a low current was observed at the low potential range. In order to examine the electrochemical behavior of the cell in a wider potential range, we set the potential variation from 0.0 V to 10.0 V. It is interesting to see that, at the higher potential range from 3.5 V to 10.0 V, the current increased a lot. This behavior is due to the high polarity of ethylene glycol. The electrical field induced mass transfer accelerated the electrochemical reaction. That is why the electrical current increases significantly.

Figs. 4(a), 5(a), 6(a), and 7(a) illustrate the electrochemical responses of other chemicals at the titanium dioxide nanotube surface. As can be seen from these figures shown below, most of the electrical response curves had similar trends.

However, the peak values of the plots during anodizing scans had significant changes. With the increasing in the scan cycles, the hysteresis loops of the current-potential are observed for all the solutions containing such explosive components. Obviously, this is due to the decomposition of the explosives. In Fig. 4(a), the current for the methanol solution varies within -11~5µA. In Fig. 5(a), the ethanol causes variation from -125 to + 63µA, which means that the ethanol decomposes faster than methanol does. The 7% hydrogen peroxide shows the equal electrochemical kinetics as methanol, as shown by the current changes from -5 to + 14µA in Fig. 6(a). Surprisingly, the ammonium nitrate causes current changes from - 14000 to + 6000µA as shown by Fig. 7(a). This indicates that the nitrate explosive decomposes thousand times faster than the others.

Additionally, cathodic scan results are shown in Figs. 4(b), 5(b), 6(b), and 7(b). The response of these solutions at the titanium dioxide nanotube surface was hydrogen reduction as more negative potential was imposed. It is also found that when the CHI 600E workstation reverses the flow of electricity through the cell, the irreversible response was seen. But the changes in the trends are depending on the different solution used. When reversing the flow in the methanol and hydrogen peroxide cells, somewhat linear responses were displayed as illustrated by Figs. 4(b) and Fig. 6(b).
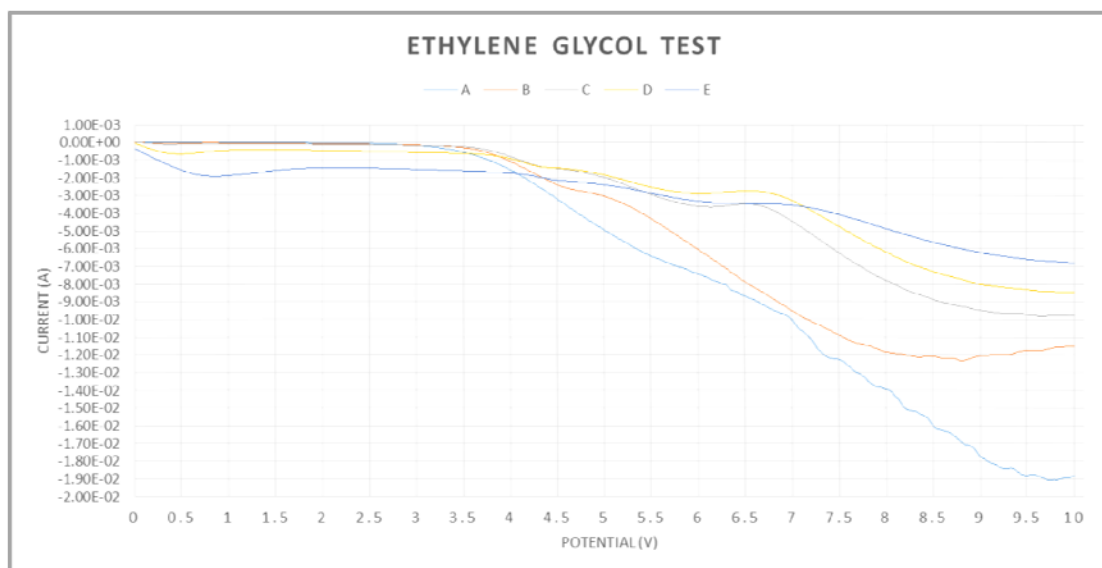

Fig. 3. Electrochemical response of ethylene glycol at the TiO_2 nanotube electrode (A-sweep 1, B-sweep 2, C-sweep 3, D-sweep 4, E-sweep 5)

Nevertheless, the ethanol and ammonium nitrate cells revealed the non-linear curves as can be seen from the results illustrated in Fig. 5(b) and Fig. 7(b). The ammonium nitrate in particular had an interesting response. When the potential was swept towards 1.0 V, there was a noticeable spike in the current of the system. This could be used as an indicator for the detection of said material. It is also implies that the nitrate explosive can be decomposed very quickly by the electrochemical method.

Lastly, we investigated the effect of explosive component concentration on the electrochemical response behavior at the titanium oxide nanotubes taking hydrogen peroxide as the

candidate. Fig. 8 presents the results. It is found that with the increasing in the hydrogen peroxide concentration, the potential peak shifts leftward from 0.75 V in Fig. 8(a) for the 5% solution to 0.5 V in Fig.8(c) for the 3.5% solution. If one revisited Fig. 6(a), it is easy to see that the potential peak is located at 1.0 V for the 7.5% solution. Therefore, the lower the concentration is, the smaller the value of the potential corresponding to the peak position. In other words, the less energy is needed to decompose the explosive component with a lower concentration. One of the important issues is the detection limit for the analysis of aammonium nitrate, hydrogen peroxide, methanol, ethanol and ethylene glycol. Our future work will emphasize this.
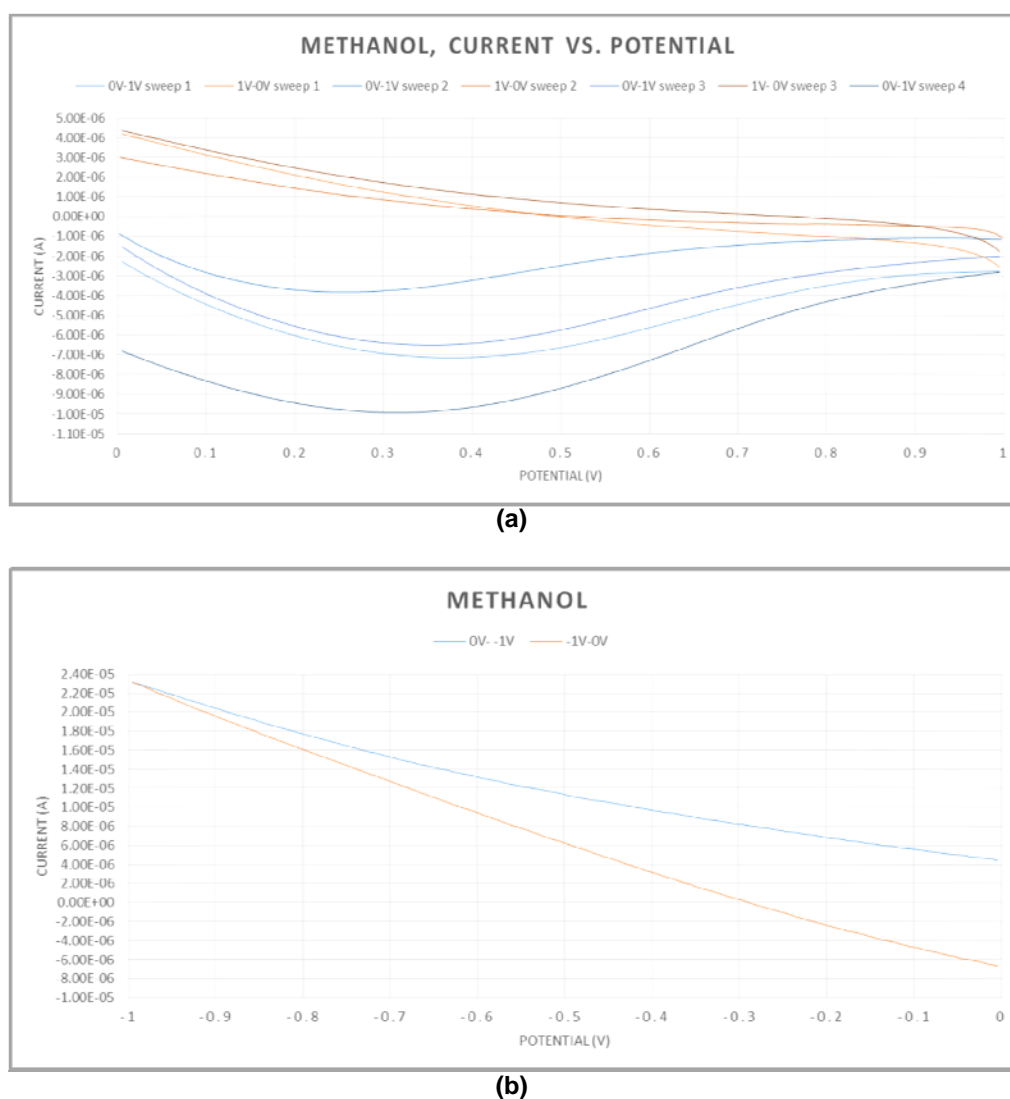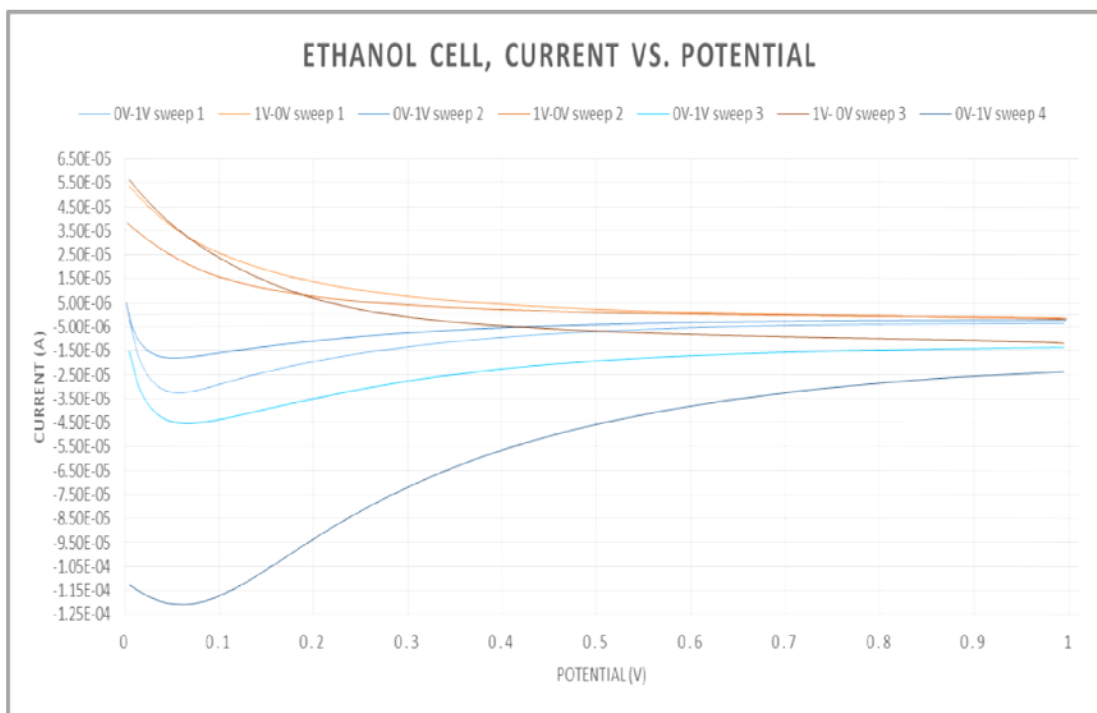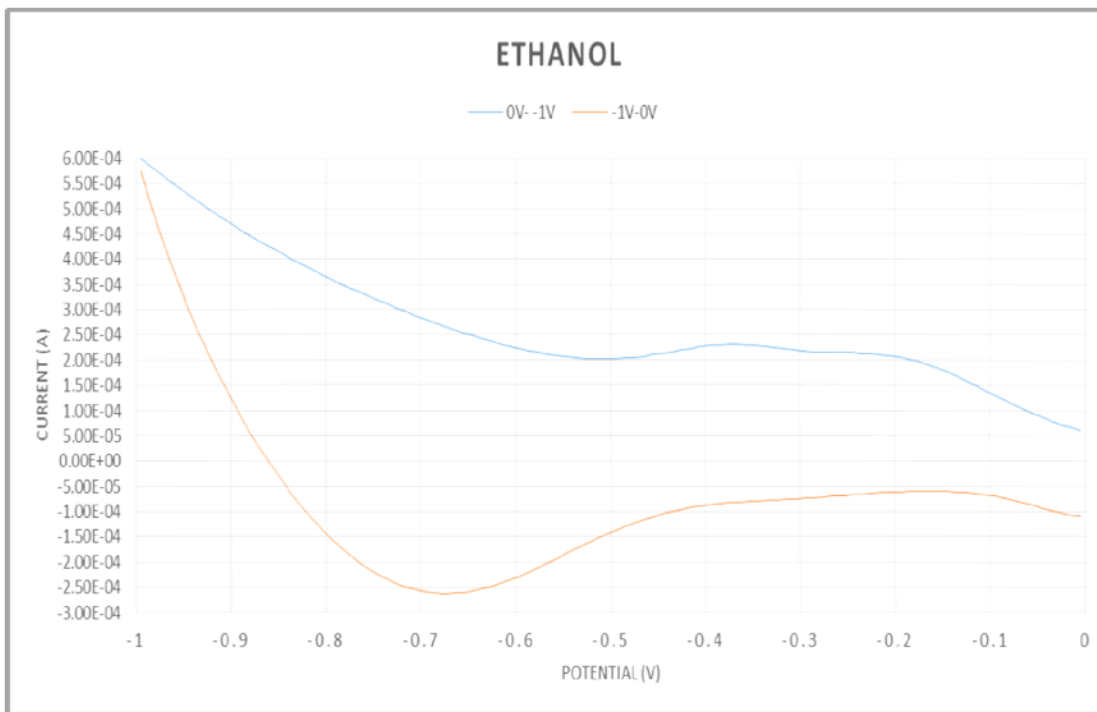

(a)

(b)

Fig. 4. Electrochemical response of methanol at the TiO$_2$ nanotube electrode: (a) with different anodic scanning cycles, (b) response under a cathodic scanning cycle

(a)

(b)

Fig. 5. Electrochemical response of ethanol at the TiO₂ nanotube electrode: (a) with different anodic scanning cycles, (b) response under a cathodic scanning cycle
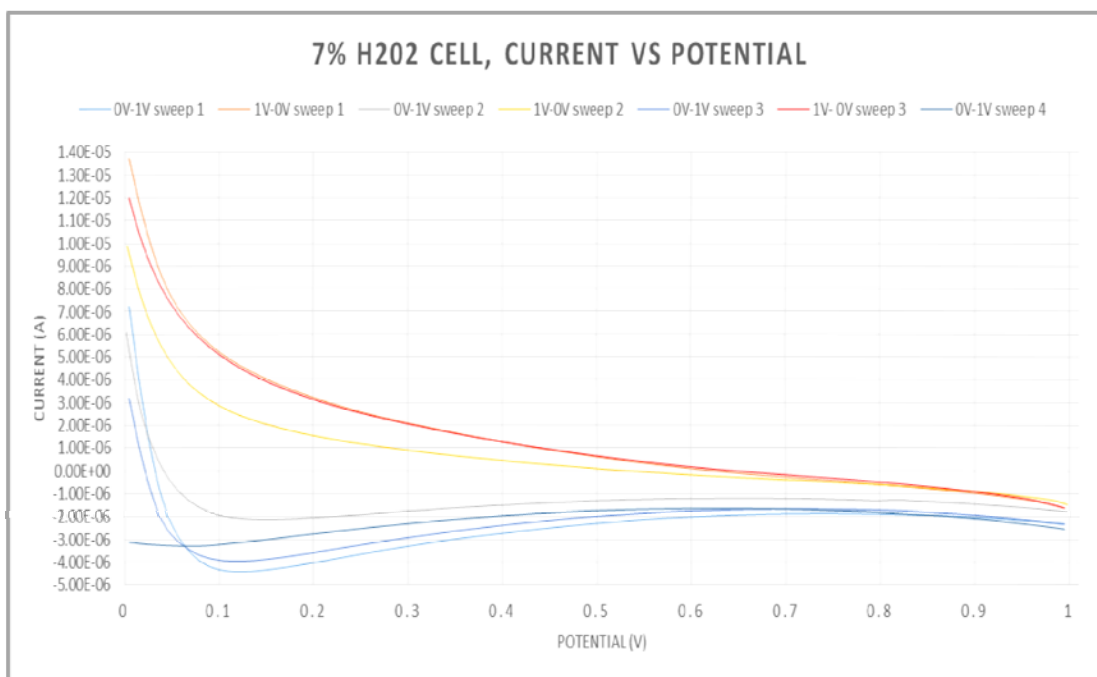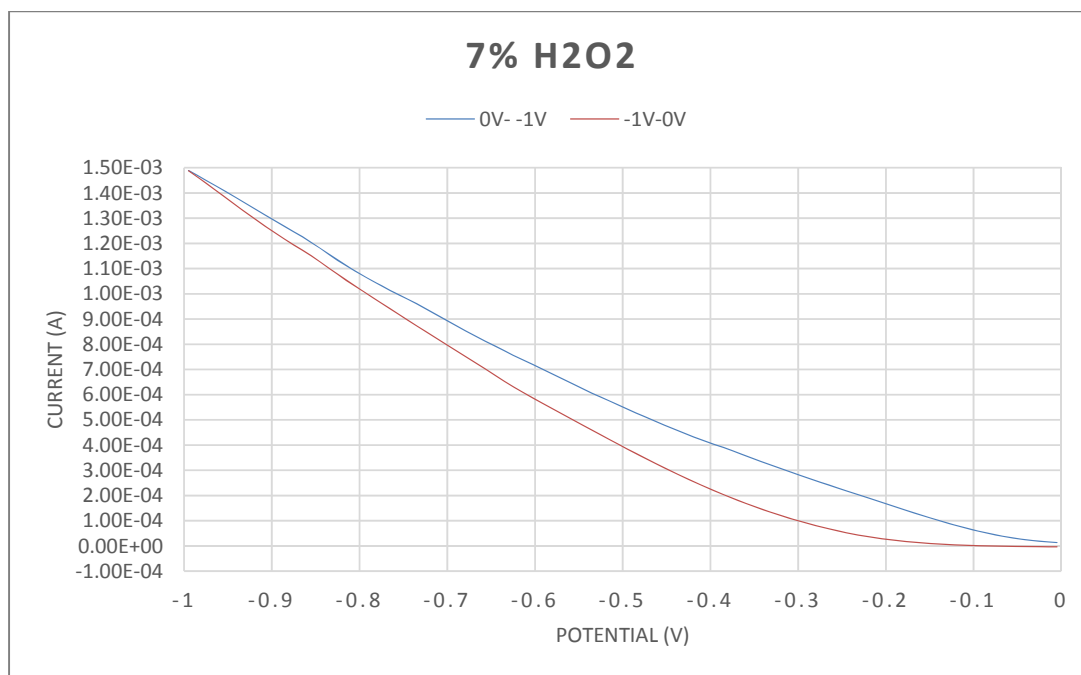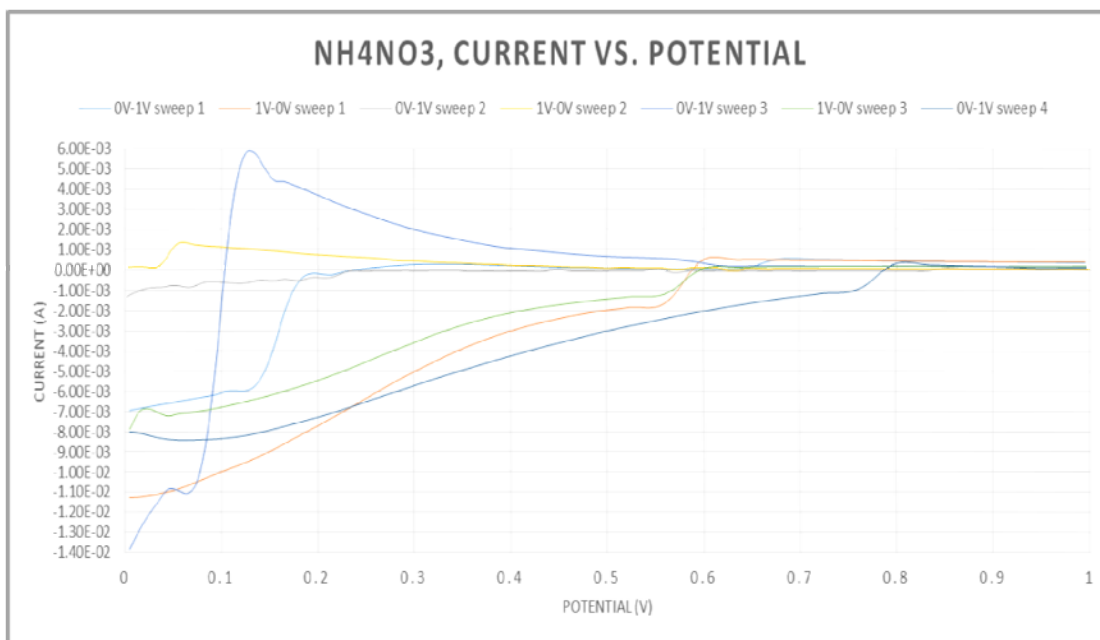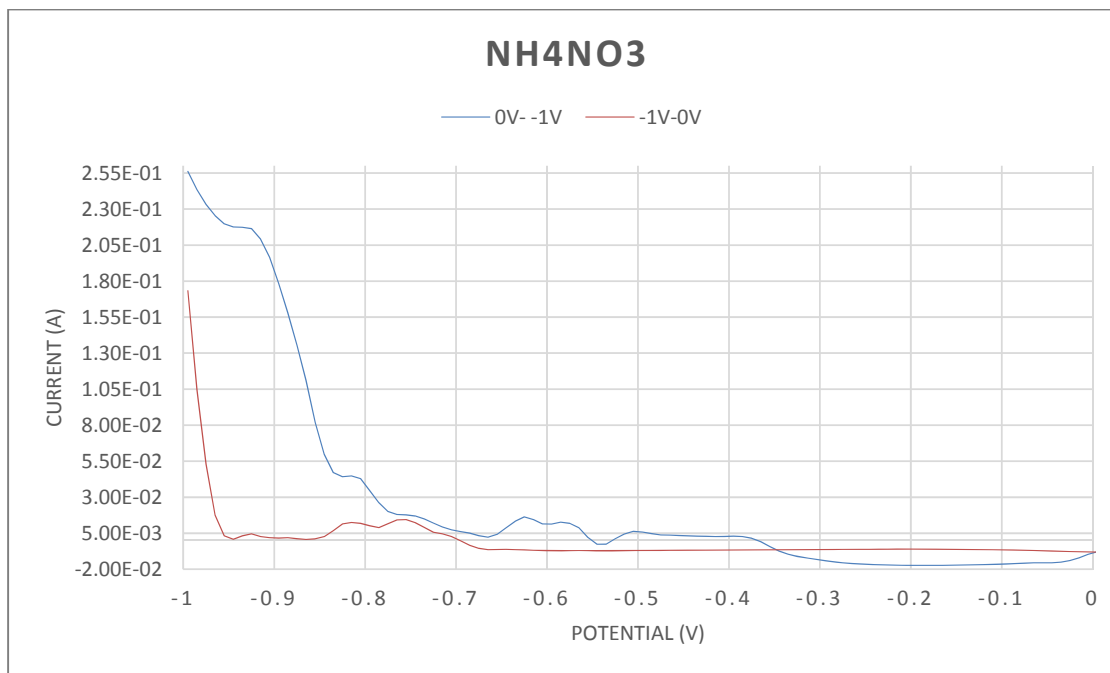
(a)

(b)

Fig. 6. Electrochemical response of hydrogen peroxide at the TiO$_2$ nanotube electrode: (a) with different anodic scanning cycles, (b) response under a cathodic scanning cycle
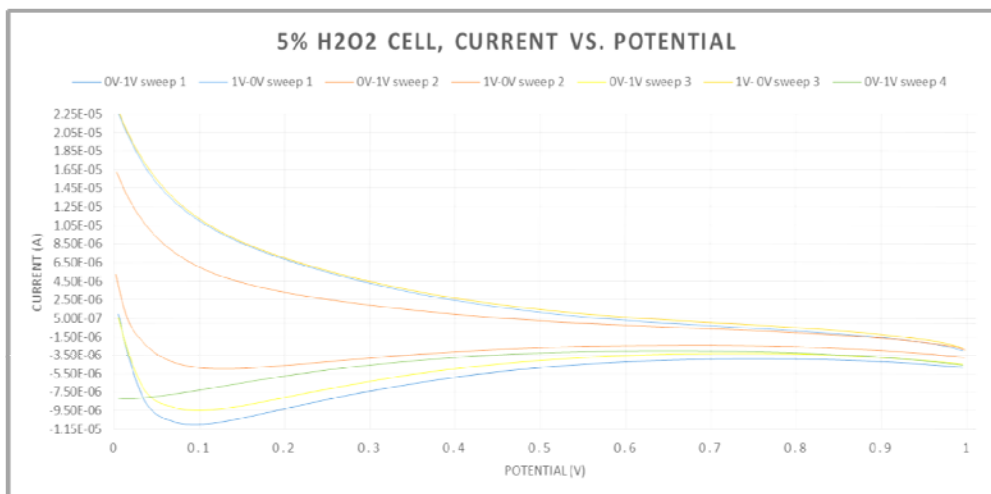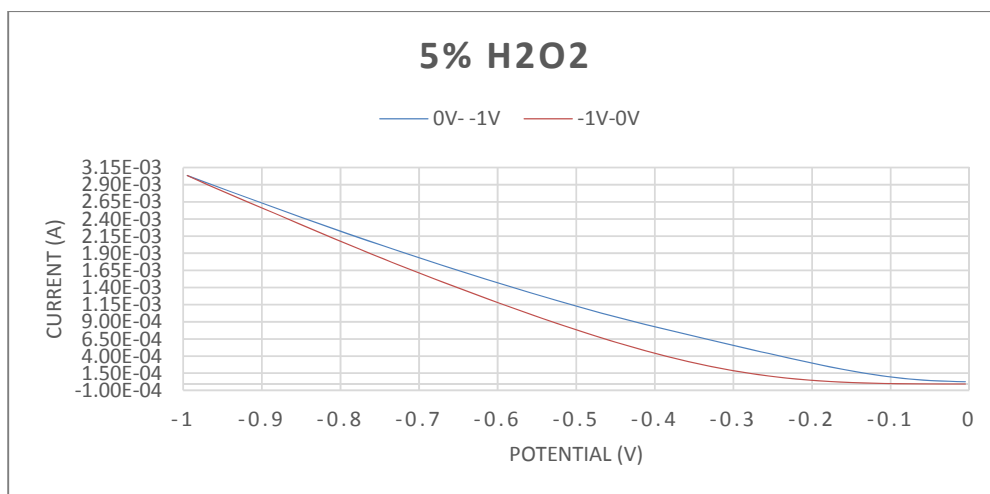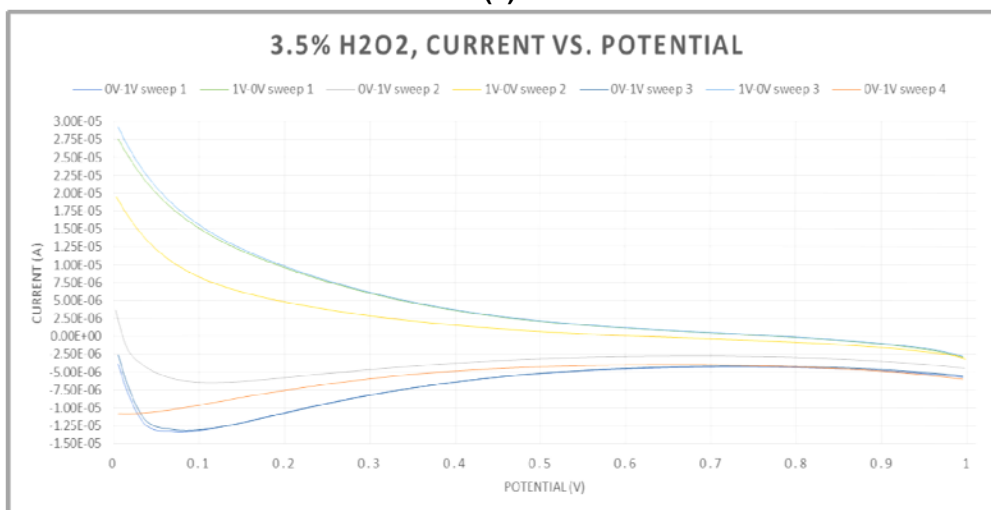
(a)

(b)

Fig. 7. Electrochemical response of ammonium nitrate at the TiO₂ nanotube electrode: (a) with different anodic scanning cycles, (b) response under a cathodic scanning cycle

(a)

(b)

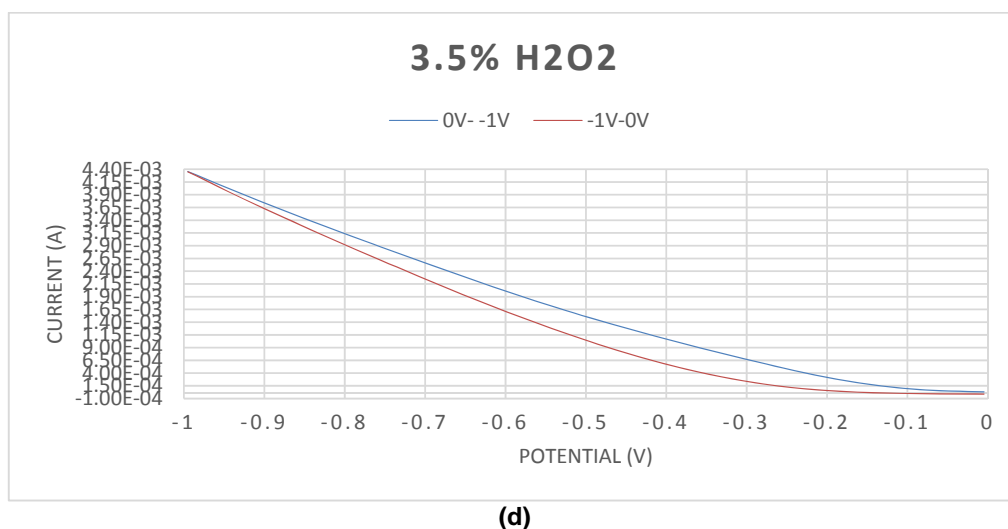**(c)**

3.5% H2O2

(d)

Fig. 8. Effect of concentration on the electrochemical response of hydrogen peroxide at the TiO₂ nanotube electrode: (a) 5% hydrogen peroxide with different anodic scanning cycles, (b) 5% hydrogen peroxide response under a cathodic scanning cycle, (c) 3.5% hydrogen peroxide with different anodic scanning cycles, (d) 3.5% hydrogen peroxide response under a cathodic scanning cycle

4. CONCLUSION

All the explosive components including ethylene glycol, ammonium nitrate, hydrogen peroxide, methanol, and ethanol show the irreversible electrochemical response at the titanium dioxide nanotube electrode. This indicates that all the chemicals can be decomposed through the electrochemical method with an imposed bias potential. The ethanol solution decomposes faster than the methanol at the oxide nanotube anode. Among all the explosive materials studied, the ammonium nitrate decomposes much faster than any of the others. Ethylene glycol shows mass transfer controlled electrochemical reaction kinetics. Such a slow reaction is due to the high viscosity of the solution. Only at very high potential, it is possible to decompose it.

The study of the concentration effect indicates that the lower the concentration of hydrogen peroxide is, the smaller the value of the potential corresponding to the peak position. In other words, the less energy is needed to decompose the explosive component with a lower concentration.

Ammonium nitrate has a special response at the oxide nanotube anode surface under the cyclic potential scan. When the potential is close to 1.0 V, there exists a noticeable spike in the current of the system. This characteristic could be used for the detection of the explosive. It is also implies that the nitrate explosive can be decomposed very quickly by the electrochemical method.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Sekhar PK, Brosha EL, Mukundan R, Linker KL, Brusseau C, Garzon FH. Trace detection and discrimination of explosives using electrochemical potentiometric gas sensors. Journal of Hazardous Materials. 2011;190:125-132.

2. Miao C, Li D, Zhang Y, Yu J, Xu R. AIEluminogen functionalized mesoporous silica nanoparticles as efficient fluorescent sensor for explosives detection in water. Microporous and Mesoporous Materials. 2014;196:46-50.

3. Montmeat P, Veignal F, Methivier C, Pradier CM, Hairault L. Study of calixarenes thin films as chemical sensors for the detection of explosives. Applied Surface Science. 2014;292:137-141.

4. Blue R, Vobecka Z, Skabara PJ, Uttamchandani D. The development of sensors for volatile nitro-containing compounds as models for explosives detection. Sensors and Actuators B: Chemical. 2013;176:534-542.

5. Patil SJ, Duragkar N, Rao VR. An ultra-sensitive piezoresistive polymer nano-composite microcantilever sensor electronic nose platform for explosive vapor detection. Sensors and Actuators B: Chemical. 2014;192:444-451.

6. Singh S. Sensors—an effective approach for the detection of explosives. Journal of Hazardous Materials. 2007;144:15-28.

7. Chu F, Tsiminis G, Spooner NA, Monro TM. Explosives detection by fluorescence quenching of conjugated polymers in suspended core optical fibers. Sensors and Actuators B: Chemical. 2014;199:22-26.

8. Dudhe RS, Sinha J, Sutar DS, Kumar A, Rao VR. Poly(3-hexylthiophene) and hexafluoro-2-propanol-substituted polysiloxane based OFETs as a sensor for explosive vapor detection. Sensors and Actuators A: Physical. 2011;171:12-18.

9. Long Y, Chen H, Wang H, Peng Z, Yang Y, Zhang G, Li N, Liu F, Pei J. Highly sensitive detection of nitroaromatic explosives using an electrospun nanofibrous sensor based on a novel fluorescent conjugated polymer. Analytica Chimica Acta. 2012;744:82-91.

10. Tournebize A, Chung PW, Thérias S, Bussière PO, Rivaton A, Caron T, Serein-Spirau F, Lère-Porte JP, Montméat P, Gardette JL. Why do chemical sensors for explosives detection lose their fluorescence under UV–visible exposure? Polymer Degradation and Stability. 2012;97:1355-1365.

11. Brudzewski K, Osowski S, Pawlowski W. Metal oxide sensor arrays for detection of explosives at sub-parts-per million concentration levels by the differential electronic nose. Sensors and Actuators B: Chemical. 2012;161:528-533.

12. Ray RS, Sarma B, Mohanty S, Misra M. Theoretical and experimental study of sensing triacetone triperoxide (TATP) explosive through nanostructured TiO_2 substrate. Talanta. 2014;118:304-311.

13. Liu Y, Wang HH, Indacochea JE, Wang ML. A colorimetric sensor based on anodized aluminum oxide (AAO) substrate for the detection of nitroaromatics. Sensors and Actuators B: Chemical. 2011;160:1149-1158.

14. Chu Y, Mallin D, Amani M, Platek MJ, Gregory OJ. Detection of peroxides using Pd/SnO_2 nanocomposite catalysts. Sensors and Actuators B: Chemical. 2014;197:376-384.

15. Kilinc N, Cakmak O, Kosemen A, Ermek E, Ozturk S, Yerli Y, Ozturk ZZ, Urey H. Fabrication of 1D ZnO nanostructures on MEMS cantilever for VOC sensor application. Sensors and Actuators B: Chemical. 2014;202:357-364.

16. Francioso L. Chapter 5 - chemiresistor gas sensors using semiconductor metal oxides in nanosensors for chemical and biological applications. Woodhead Publishing Limited. 2014;101-124.

17. Fonollosa J, Fernández L, Huerta R, Gutiérrez-Gálvez A, Marco S. Temperature optimization of metal oxide sensor arrays using Mutual Information. Sensors and Actuators B: Chemical. 2013;187:331-339.

18. Lee SP. Chapter 3 - electrode materials and electrode-oxide interfaces in semiconductor gas sensors, in Semiconductor Gas Sensors. Woodhead Publishing Limited. 2013;64-113.

19. Gan YX, Yazawa RH, Smith JL, Oxley JC, Zhang G, Canino J, Ying J, Kagan G, Zhang L. Nitroaromatic explosive sorption and sensing using electrochemically processed polyaniline-titanium dioxide hybrid nanocomposite. Materials Chemistry and Physics. 2014;143:1431-1439.

20. Boehme M, Voelklein F, Ensinger W. Low cost chemical sensor device for supersensitive pentaerythritol tetranitrate (PETN) explosives detection based on titanium dioxide nanotubes. Sensors and Actuators B: Chemical. 2011;158:286-291.

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