Iraqi Journal of Science, 2025, Vol. 66, No. 1, pp: 1-13
DOI: 10.24996/ijs.2025.66.1.1

Iraqi Journal of Science

ISSN: 0067-2904

Enhance the Electrical Performance of TiO_2 NTAs Decorated with Cobalt and Compatible with Environmentally Friendly Electrolytes

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Received: 18/6/2023 Accepted: 13/11/2023 Published: 30/1/2025

Abstract

Titanium dioxide nanotube arrays (TiO_2 NTAs) were successfully decorated with nanoclusters of cobalt by an electrochemical deposition method. This Co-TiO_2 NTAs nanostructure exhibited high compatibility with aluminum chloride\ chloroacetamide (an ionic liquid) and calcium chloride dihydrate\ acetamide (a deep eutectic solvent), leading to significant improvements in the electrochemical properties of the system. Significantly, this led to a discernible augmentation in both potential and current values, concomitant with a decrease in internal resistance. The presence of cobalt facilitated a faster transfer of electric charge, enhancing the overall efficiency of the system. Moreover, the incorporation of cobalt exhibited a beneficial effect on the preservation of ideal operational temperatures in the electric cells. The temperature remained below the permissible limit during both the charging and discharging processes. The utilization of scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) provided comprehensive visualization of the Co-TiO_2 NTAs surface.

Keywords: Aluminum chloride, Batteries, Cobalt, Deep eutectic solvents, Ionic liquids, TiO_2 NTAs.

تعزيز الأداء الكهربائي لمركبات TiO_2 NTAs المزينة بالكوبالت والمتوافقة مع الإلكتروليتات الصديقة للبيئة

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الخلاصة

تم تزيين مصفوفات الأنابيب النانوية لثاني أكسيد التيتانيوم (TiO_2 NTAs) بنجاح مع المجاميع النانوية للكوبالت بواسطة طريقة الترسيب الكهروكيميائية، وأظهرت هذه التراكيب النانوية كوبالت-TiO_2 NTAs توافقًا كبيرا مع كل من كلوريد الالمنيوم\كلوريد الاستمايد (السائل الأيوني) وكلوريد الكالسيوم ثنائي الماء\الاستمايد (المذيب عميق الانصهار)، مما أدى إلى تحسينات كبيرة في الخصائص الكهروكيميائية للنظام. فمن الجدير

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بالذكر أن هذا الترسيب ادى إلى زيادة ملحوظة في قيم الجهد والتيار، بالتزامن مع انخفاض في المقاومة الداخلية. حيث سهّل وجود الكوبالت نقلًا أسرع للشحنة الكهربائية، مما عزز الكفاءة الكلية للنظام. علاوة على ذلك، أظهرت إضافة الكوبالت تأثيرًا إيجابيًا في الحفاظ على درجات حرارة التشغيل المثلى في الخلايا الكهربائية. فقد بقيت درجة الحرارة في الحد الأدنى المسموح به أثناء الشحن والتفريغ. ووفر استخدام مسح المجهر الالكتروني (SEM) والتحليل الطيفي للأشعة السينية المشتتة للطاقة (EDX) تصورًا شاملاً لسطح $Co-TiO_2$ NTAs.

1. Introduction

TiO_2 nanotube is considered one of the materials of recent research importance due to its natural abundance and low toxicity, as well as its chemical stability [1-4]. It has entered into various research projects in the field of energy, including batteries, supercapacitors, and photoelectrochemical cells [5-6]. This is due to its electrochemical properties as well as its geometrical shape [7]. When the morphology (nanopillars, nanoparticles, and nano-packages) of titanium dioxide nanoparticles is taken into consideration, the matrix of nanotubes of the titanium dioxide anatase type performs best when used in the electrochemical field. Due to its rule in the transport of electrons through titanium dioxide nanoparticles through charging and discharging, as well as the engineering design that gives the surface area a wide character [8-10], it was used in the field of supercapacitors because of the layers of titanium nanoparticles with back contact with titanium, which is the main substrate [11-12]. Furthermore, its application as an anode electrode in prevalent lithium and sodium batteries has been observed [13]. In order to raise the level of efficiency of nanoscale TiO_2 NTAs, various studies have been conducted that include the deposition of various types of metals, such as cadmium, iron, and manganese, on the surface of TiO_2 NTAs to enhance their electrochemical properties and increase their charge transfer [14-18]. However, it is worth noting that ionic liquids (ILs) and deep eutectic solvents (DESs) exhibit certain similarities with TiO_2 NTAs. This material is also recognized as a participant in green chemistry [19] and possesses properties and characteristics that render it suitable for application in the battery industry [20-22]. Its notable attributes include high conductivity, non-toxicity, and the presence of both positive and negative ions, which contribute to its status as one of the most widely utilized electrolytes. An example is aluminum chloride [23-25], which has a wide electrochemical window and good conductivity, which makes it highly valuable for use in the field of batteries. This work aims to enhance the conductivity of ionic liquids by raising the temperature [26-27] or adding organic or inorganic solvents to help reduce the viscosity of ILs, increasing the conductivity by increasing the freedom of ion movement, and consequently increasing the effectiveness of these liquids as electrolytes within the electrochemical cells [28-30].

2. Materials and Methods

The following chemicals and materials were used from Sigma Aldrich and Merck without purification: aluminum chloride (98%), dichloromethane (DCM) (99.8%), DI water (100%), chloroacetamide (CA) (99%), calcium chloride dihydrate (98%), acetamide (AC) (98%), ethylene glycol (99.5%), titanium foil (99.7%), nitric acid (65%), acetone (98%), isopropanol (99.5%), $Co(NO_3)_2 \cdot 6H_2O$ (98%), and high-density graphite. The surface morphology was examined using SEM (INSPECT F50 model). To determine the surface composition, the X-Flash 6110 Bruker EDX system was employed. Measurements of the open circuit potential were recorded using a digital multimeter (INGCO DCM200). Furthermore, the VAPCE YR1030 digital internal resistance analyzer was employed to quantify the resistance. The experiments were conducted using an argon gas-filled glove box at ambient temperature. The temperature of the gas was measured using a Temp Gun 1080 infrared thermometer.

2.1. Preparation TiO_2 NTAs

The Ti foil, with a thickness of 0.127 mm and 99.7% purity, was first cut into pieces measuring 1.0 cm by 2.5 cm. These components were degreased by sonicating them with a series of acetone, isopropanol, and DI water in that order. Each solvent was used for 15 minutes. Subsequently, the Ti foil was chemically etched in HNO_3 (6.0 M) for 10 minutes to achieve a clean and smooth surface. The foil was rinsed with deionized water and allowed to dry at room temperature after etching. For the experimental setup, high-density graphite was employed as the cathode electrode, while a clean Ti foil measuring 1.0 cm by 2.0 cm served as the anode. The electrolyte used in the cell consisted of NH_4F (0.5 wt%) and H_2O (5%) mixed with ethylene glycol (EG) (95%), and all anodization parameters were maintained at room temperature with moderate stirring. A gap of 2 cm was maintained between the two electrodes. A DC power source (40 V) was connected to the electrode cell. The samples were promptly washed with DI water and allowed to air-dry following anodization. Subsequently, the films were subjected to a two-hour heat treatment in an air environment using a thermocline furnace with a heating rate of 2 °C/min. The temperature during the heat treatment reached 500 °C [31].

2.2. Preparation of Co/TiO_2 NTAs

To prepare Co/TiO_2 NTAs, cobalt was deposited onto TiO_2 NTAs using an electrodeposition method; this technique includes two electrodes. The prepared specimen of TiO_2 NTAs was used as the cathode, while graphite was used as the anode. Potentials, deposition timeframes, and cobalt salt concentrations were all altered during the deposition procedure. Finally, the prepared Co/TiO_2 NTAs were rinsed with DI water and then dried in the air.

3. Results and Discussion

3.1. Electrodeposition of Co/TiO_2 NTAs

To identify the optimal deposition conditions of Co/TiO_2 NTAs, in each electrochemical deposition, electrochemical cells were assembled with the Co/TiO_2 NTAs electrodes serving as the anode, while graphite electrodes were used as the cathode. The cells were immersed in an electrolyte consisting of IL ($AlCl_3$:CA+DCM) and DES ($CaCl_2$: AC + DI water). The voltage of each cell was recorded as the optimal parameter for the aforementioned set of variables during the deposition process, with the maximum voltage value obtained for each cell serving as the reference point.

3.1.1. Effect of different deposition voltages

The electrodeposition of cobalt onto TiO_2 NTAs was performed using a bath solution consisting of a constant concentration of $Co(NO_3)_2 \cdot 6H_2O$ (0.1 M) as the supporting electrolyte. The deposition process was carried out at various potentials, namely 2.0, 4.0, 6.0, and 8.0 volts, as indicated in Table 1. The applied potential was maintained between the TiO_2 NTAs and graphite electrodes for a fixed duration of 1 minute, and the deposition was conducted at room temperature.

Table 1: Potentials values at varied voltages with constant time and concentration

Potentials of cells V		Voltage (Volt)	Time (minutes)	Concentration (M)
IL	DES			
1.7	1.4	2	1	0.1
1.9	1.5	4	1	0.1
1.8	1.4	6	1	0.1
1.7	1.3	8	1	0.1

From Table 1 and Figure 1, it can be observed that the highest voltage value obtained in the deposition of cobalt on TiO_2 NTAs is 4.0 volts, which corresponds to a deposition potential of 4.0 volts. This electrochemical cell exhibited the highest voltage among the tested potentials. Based on these results, a deposition potential of 4.0 volts will be adopted for the subsequent steps of the experiment.

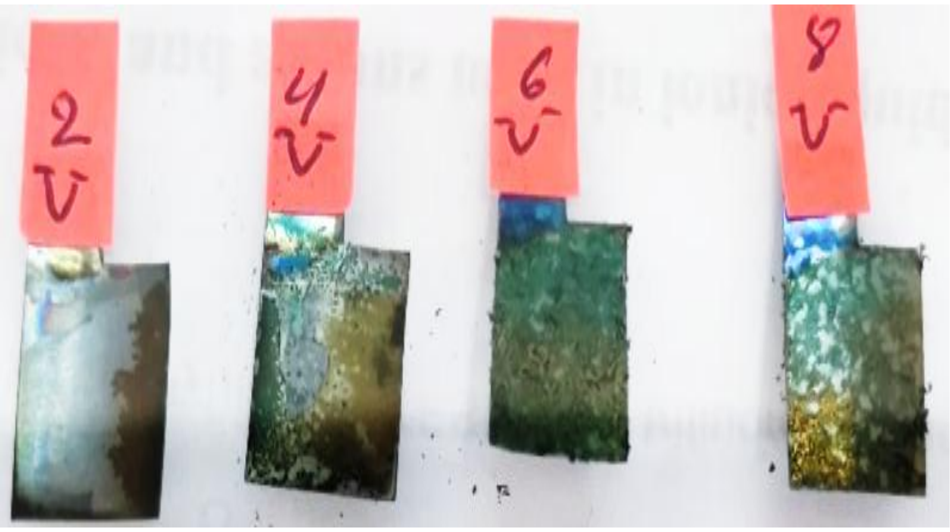


Figure 1: Cobalt-TiO_2 NTAs electrodes with different deposition potentials

3.1.2. *Effect of deposition times*

The cobalt electrodes were put on TiO_2 NTAs in a bath solution that had an electrolyte based on cobalt salt and a constant concentration of 0.1 M $Co(NO_3)_2 \cdot 6H_2O$. The deposition process was conducted using different time intervals, as shown in Table 2. The intervals tested were 0.5, 1, 1.5, 2, 2.5, and 3 minutes. The deposition time was applied between the TiO_2NTAs and graphite electrodes at room temperature while maintaining a constant potential of 4.0 volts. From Table 2, it can be observed that the highest voltage value obtained during the cobalt electrodeposition on TiO_2 NTAs was 2.1 volts, which was achieved with a deposition time of 1.5 minutes. As shown in Figure 2, this indicates that a deposition time of 1.5 minutes produced the highest voltage among the intervals tested. Therefore, a deposition time of 1.5 minutes will be utilized in the subsequent steps of the experiment, with a constant potential of 4.0 volts.

Table 2 : Potentials values at varied times with constant voltage and concentration

Potentials of cells V		Voltage (Volt)	Time (minutes)	Concentration (M)
IL	DES			
1.7	1.4	4	0.5	0.1
1.9	1.5	4	1.0	0.1
2.1	1.7	4	1.5	0.1
1.9	1.6	4	2	0.1
1.8	1.5	4	2.5	0.1
1.7	1.4	4	3	0.1

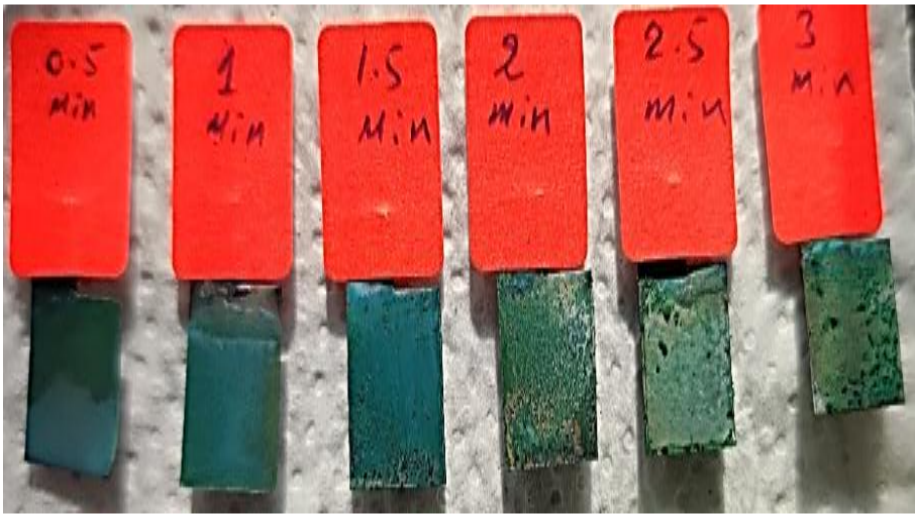


Figure 2 : Cobalt-TiO_2 NTAs electrodes with different deposition times

3.1.3. Effect of deposition concentrations

The results showed that the cobalt was electrodeposited onto TiO_2 NTAs at room temperature using a bath that had different concentrations of cobalt salt ($Co(NO_3)_2.6H_2O$). The deposition process was conducted with a fixed time of 1.5 minutes and a potential of 4 volts, as indicated in Table 3, which presents the results of the electrodeposition experiment, showing the effect of different concentrations of $Co(NO_3)_2.6H_2O$ on the cobalt deposition process. It likely includes information such as the resulting cobalt deposition efficiency, coating thickness, or any other relevant parameters for each concentration of the supporting electrolyte.

Table 3 : Potentials values at varied concentrations with constant voltage and time

Potentials of cells V		Voltage (Volt)	Time (minutes)	Concentration (M)
IL	DES			
1.7	1.4	4	1.5	0.05
2.1	1.7	4	1.5	0.1
2.0	1.6	4	1.5	0.15
1.9	1.6	4	1.5	0.2
1.8	1.5	4	1.5	0.25
1.7	1.4	4	1.5	0.3

As this electrode was used in the electrochemical cell that produced the highest voltage, Table 3 demonstrates that 0.1 M is the best concentration value for the cobalt to be placed on TiO_2 NTAs (Figure 3).

Figure 3 : Cobalt-TiO_2 NTAs electrodes with different deposition concentrations

Based on the information provided, it can be concluded that the optimal parameters for achieving a useful and effective deposition of cobalt on TiO_2 NTAs are as follows: 4 volts, 1.5 minutes, and cobalt salt ($Co(NO_3)_2.6\ H_2O$) (0.1 M). These parameters were adopted in the preparation of electrochemical cells, where the anode electrode consisted of Cobalt-TiO_2 NTAs and the graphite was the cathode electrode, which contained either an IL or DES serving as the electrolyte. The reason for selecting these specific values is that higher values of voltage, time, or concentration may lead to the formation of thick layers that do not deposit appropriately on the surface of TiO_2 NTAs. This excessive thickness can cause the cobalt layers to detach from the TiO_2 NTAs and settle at the bottom of the container containing the electrolyte (Figure 4).

Figure 4 : Pieces of cobalt layers separated from TiO_2 NTAs

3.2. Preparation of cobalt-TiO_2 NTAs-graphite cells by the presence of $AlCl_3$:CA IL and $CaCl_2.6H_2O$:AC DES [32]

To create the cobalt-TiO_2 NTAs-graphite cells, two different electrolyte systems were utilized. The first system employed IL consisting of $AlCl_3$:CA in a mole ratio of 2:1 [33], without the addition of any additives. In the second system, an organic solvent known as DCM illusion was utilized. This solvent was mixed with IL in different proportions ranging from 25 to 75%, with the exact ratio determined by the maximum conductivity value recorded [34]. To enhance the freedom of ion movement and reduce the high viscosity of DES, the second system utilized $CaCl_2.6H_2O$:Ac DES in a mole ratio of 1:7 [19]. Additionally, before and after the addition of water, the DES composition was adjusted to 35% deionized (DI) water and 65% DES, respectively [34]. In the cell configuration, the cathode was a cylindrical graphite column with a diameter of 5 mm. Conversely, the negative electrode was composed of cobalt-TiO_2 NTAs under ideal conditions, which involved a voltage of 4.0 volts, a deposition time of 1.5 minutes, and a cobalt salt concentration of 1.0 M (Figure 5).

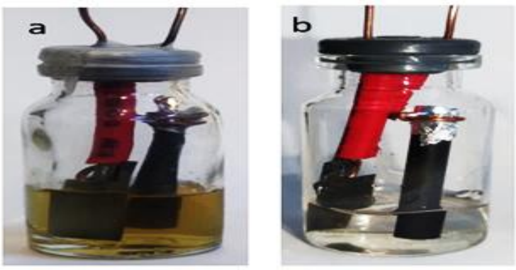


Figure 5: Models of manufactured cells containing Cobalt-TiO_2 NTAs electrodes in the presence of (a) IL+DCM and (b) DES+DI water

3.2.1. Scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDXA) examination for cobalt-TiO$_2$ NTAs electrodes

The examination of the SEM images (Figures 6 and 7) revealed the presence of a well-structured matrix of titanium oxide nanotubes. Asymmetrical configurations and consistent dimensions were observed in these nanotubes. Additionally, cobalt nanoparticles were observed to cluster both on the surface and inside the TiO$_2$ NTAs. The size of these cobalt nanoparticles ranged from 25 to 100 nm, and their distribution was random. The cobalt nanoparticle distribution was a major factor in increasing the electrode's electrical responsiveness and improving the titanium oxide nanoscale's surface efficiency. Furthermore, the influence of IL and DES was evident in the formation of a protective layer over the cobalt-TiO$_2$ NTAs. This layer facilitated smooth and rapid electron charge transfer, resulting in increased electrode surface area and improved electrical efficiency [35]. Regarding the cobalt-TiO$_2$ NTAs electrode, these observations offer additional validation and elucidation. The results obtained from Energy-Dispersive X-ray Analysis (EDXA) support the interpretation. Figures 8 and 9 demonstrate the presence of various elements on the electrode's surface. Titanium was identified as the major element, while other elements, such as cobalt (in the form of a precipitate), aluminum, calcium, chlorine, oxygen, carbon, and nitrogen, were also detected. The concentrations of these elements corresponded to their respective compositions in the IL and DES.

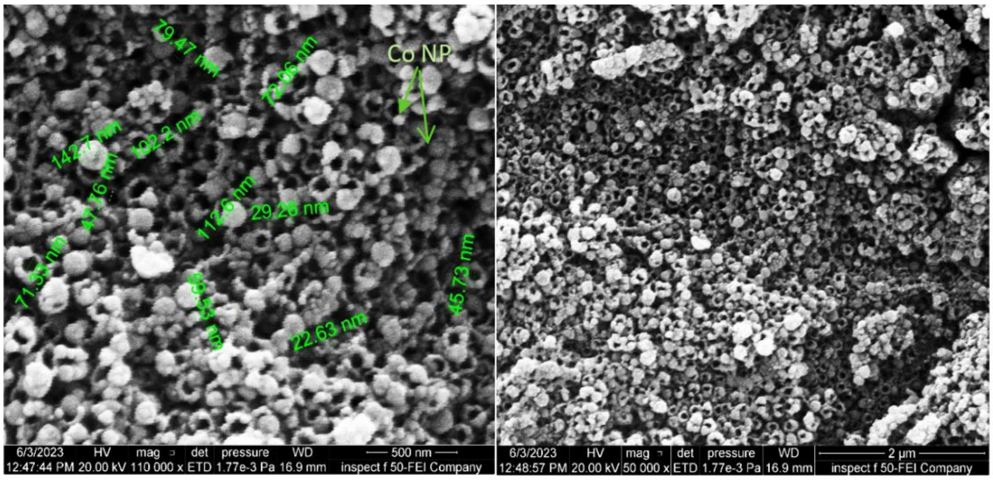


Figure 6: SEM images of Co-TiO$_2$ NTAs electrode in ionic liquid with DCM

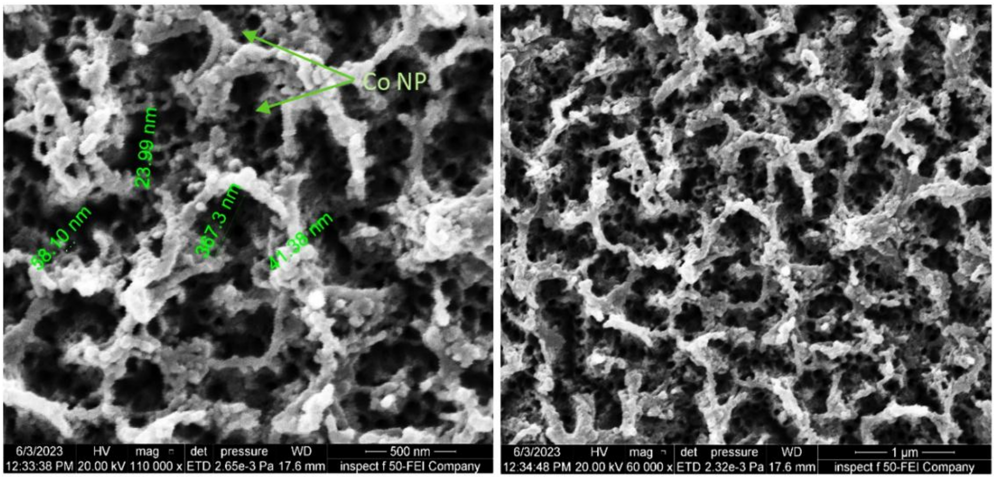
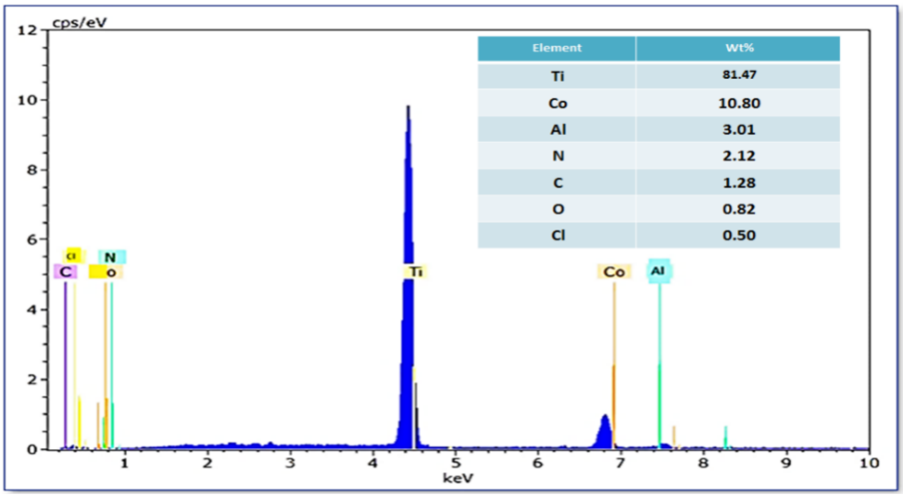
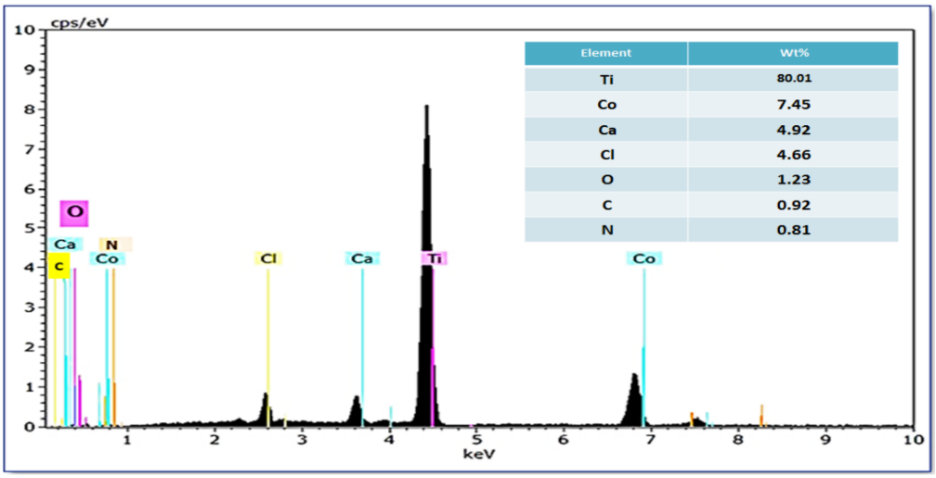


Figure 7 : SEM images of Co-TiO$_2$ NTAs electrode in DES with DI water



Element	Wt%
Ti	81.47
Co	10.80
Al	3.01
N	2.12
C	1.28
O	0.82
Cl	0.50

Figure 8 : EDX image of Co-TiO_2 NTAs electrode in ionic liquid with DCM



Element	Wt%
Ti	80.01
Co	7.45
Ca	4.92
Cl	4.66
O	1.23
C	0.92
N	0.81

Figure 9 : EDX image of Co-TiO_2 NTAs electrode in DES with DI water

3.2.2. Internal resistant test for Co-TiO_2 NTAs-graphite cells

A broad knowledge of the vitality of battery cells and their ability to create energy is provided by internal resistance, which measures the degree of resistance to current flow inside batteries. The internal resistance of the four Co-TiO_2 NTAs-graphite cells was measured using a digital internal resistance tester, and the amount of current flowing through each cell was calculated using Ohm's law (without the need for an external load) (Equation 1).

$$R = \frac{V}{I} \tag{1}$$

Where *R* resistance, *V* volte, *I* current.

According to the recorded data in Table 4, the quality, concentration, and distance between the electrodes, among other factors, have an impact on the internal resistance. It is noteworthy to mention that as internal resistance decreases, the efficacy of the cell increases [36].

Table 4 : Voltage, internal resistance and current measurements for Co-TiO_2 NTAs-graphite cells with different electrolytes

Co-TiO_2 NTAs-graphite cells with:	Volte (V unit)	Internal Resistance (Ohm unit)	Current (A unit)
IL	1.82	10	0.182
IL+DCM	2.18	4	0.545
DES	0.97	24	0.040
DES+ DI water	1.77	11	0.161

3.2.3. The self-discharge of Co-TiO_2 NTAs-graphite cells

After the completion of the battery cell preparation with different systems and additives, all the cells were charged with a constant DC voltage of 3 volts for 5 minutes. Over the course of seven days, the voltage of each cell was assessed by employing a digital multimeter subsequent to the charging procedure. The recorded voltage values were analyzed to determine the level of energy retained by the respective cells during this time. The specific voltage measurements and corresponding data can be found in Table 5.

Table 5 : The voltage measurements of all Co-TiO_2 NTAs-graphite cells battery during one week.

Co-TiO_2 NTAs-graphite cells with	Self-voltage discharge per unit time							
	First Voltage	Voltage after 1 day	Voltage after 2 days	Voltage after 3 days	Voltage after 4 days	Voltage after 5 days	Voltage after 6 days	Voltage after 7 days
IL	1.82	1.78	1.74	1.72	1.67	1.61	1.57	1.52
IL+DCM	2.18	2.16	2.13	2.11	2.08	2.05	2.03	2.01
DES	0.97	0.91	0.85	0.79	0.72	0.66	0.61	0.56
DES+ DI water	1.77	1.72	1.65	1.58	1.53	1.48	1.44	1.39

The data presented in the table demonstrates that the IL and DCM cells outperformed the DES and other cells. These results highlight the superior performance of the IL and DCM electrolytes in the electrochemical cells. The data also shows that the additives used in the IL and DCM electrolytes help to lower viscosity and improve the mobility of ions, which ultimately raises the voltage of the cells. The purpose of collecting this data is to provide a comprehensive understanding of the concept of "self-discharge" in batteries. Self-discharge refers to the phenomenon where batteries undergo certain chemical reactions internally, resulting in a loss of charge over time. To mitigate or minimize self-discharge, it is crucial to apply an appropriate passivation layer to the electrodes.

3.2.4. Thermal charge-discharge test of Co-TiO_2 NTAs-graphite cells

To assess the charging and discharging of each cell, the temperatures of all four Co-TiO_2 NTAs-graphite cells (IL, IL+DCM, DES, and DES+DI Water) were monitored from within the cell and the external ambient temperature. The results are represented in the following figures:

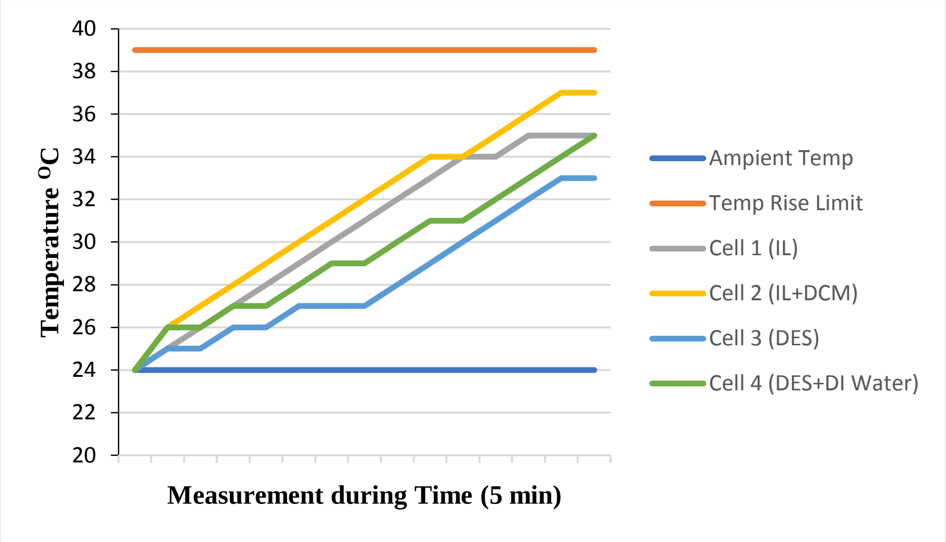


Figure 10 : Thermal charge test for TiO_2 NTAs-graphite cells with different electrolytes

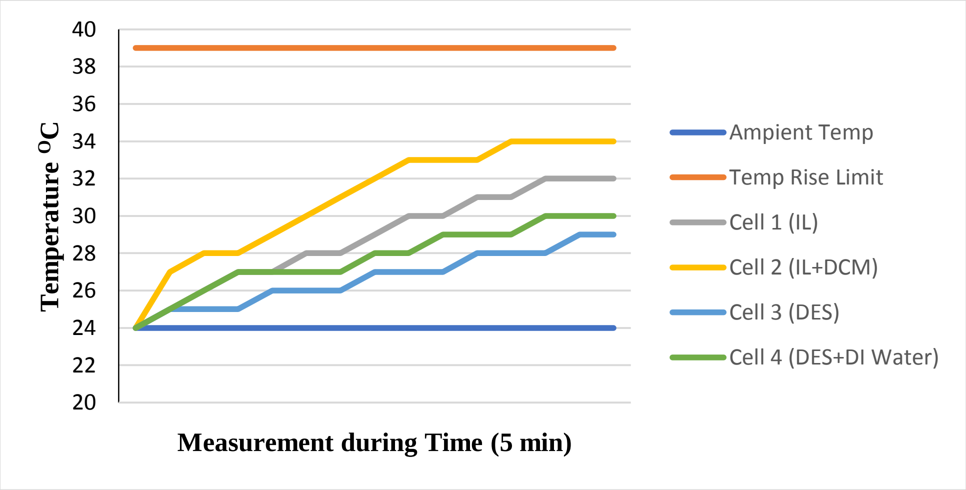


Figure 11 : Thermal discharge test for TiO_2 NTAs-graphite cells with different electrolytes

After subjecting the electrochemical cells to a charging process of 5 minutes at 3 volts, it was observed that the temperature did not exceed the permissible limit of 15 degrees, which is within the approved range for battery charging and discharging [37]. Following a 5-minute discharge of the batteries at a current of 0.5 amperes, the temperature was subsequently reassessed. Throughout these charging and discharging cycles, it was noted that the cells maintained the integrity of their electrode surfaces without any signs of corrosion when in contact with the electrolytes. Furthermore, the cells retained their original energy characteristics in terms of voltage, current, and internal resistance. It was also found that the quality and effectiveness of the IL or DES electrolytes did not change in the Co-TiO_2 NTAs-graphite-based electrochemical cells after six months of continuous charging and discharging. The IL or DES remained pure and retained their strength and efficacy. To summarize, the electrochemical cells demonstrated stable performance with respect to temperature, electrode surface condition, and the integrity of the IL or DES electrolytes throughout the charging and discharging processes. These findings highlight the durability and reliability of the Co-TiO_2 NTAs- graphite-based cells.

4. Conclusion

The surface of titanium dioxide nanoparticles is coated with cobalt to enhance the charge transfer capabilities of electrochemical cells. Through a series of experiments, a technique for electrochemical deposition was identified, and the coating process variables were optimized. The optimal parameters included a voltage of 4 volts, a concentration of cobalt salt in the electrolyte of 0.1 M, and a deposition time of 1.5 minutes. The SEM and EDX confirm the randomly dispersed clusters of cobalt nanoparticles on the surface of titanium oxide as well as characterize their components. In addition, cobalt nanoclusters have covered a wide area of TiO_2 NTAs; moreover, cobalt nanoclusters were deposited inside the nanotube. To assess the electrical sensitivity of the electrochemical cells, Co-TiO_2 NTAs electrodes and graphite electrodes were created. These electrodes were immersed in IL and DES electrolytes to a depth of 1 cm. The IL+DCM cells demonstrated an OCP of 2.18 volts, an internal resistance of 4.0 ohm, and a current of 0.545 ampere. On the other hand, the DES cells exhibited an OCP of 1.77 volts, an internal resistance of 11.0 ohm, and a current of 0.161 ampere. All cells displayed thermal stability during the charging and discharging processes, with regards to surface oxidation, the behavior of ionic species, and the concentration of these species in the electrolytes.

Conflicts of interest

The author declares that they have no conflicts of interest.

Acknowledgments

The authors would like to express their deepest gratitude to the Department of Chemistry and Physics, College of Science, Al-Nahrain University, and the Department of Chemistry, College of Science for Women, University of Baghdad.

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