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## Enhancing Electrochemical Cells Performance with Modified Ionic Liquids and Deep Eutectic Solvents using Titanium Dioxide Nanoelectrodes-Graphite

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### Abstract

Ionic liquids (ILs) and deep eutectic solvents (DESSs) have been found to be highly effective as electrolytes in TiO<sub>2</sub> NTAs-graphite cells when combined with additives that enhance conductivity by reducing the viscosity of these liquids. The presence of CaCl<sub>2</sub>.6H<sub>2</sub>O: Acetamide DES with DI water as an additive resulted in a cell voltage of 1.31V and an internal resistance of 19 ohm. This can be attributed to the concentration and quality of the ionic species. The cells exhibited an interesting response to the AlCl<sub>3</sub>-chloroacetamide IL with dichloromethane DCM as an additive, with a cell voltage of 1.81V and an internal resistance of 5.0 ohm. Once again, this is influenced by the quality and concentration of the ionic species. Furthermore, the cells demonstrated thermal stability during the charging and discharging processes. Additionally, the surfaces of the TiO<sub>2</sub> NTAs electrodes were examined, along with the impact of the IL and DES on these electrodes, using SEM and EDXA equipment.

**Keywords:** Ionic liquids, deep eutectic solvents, Aluminum chloride, TiO<sub>2</sub> NTAs, batteries.

### تحسين أداء الخلايا الكهروكيميائية بالسوائل الأيونية والمذيبات عميقة الانصهار المعدلة باستخدام الأقطاب النانوية لثاني أكسيد التيتانيوم-كرافيت

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### الخلاصة

وجد ان للسوائل الأيونية ILs والمذيبات عميقة الانصهار DESSs فعالية مذهلة عند استخدامها في خلايا الأقطاب النانوية نوع ثاني أكسيد التيتانيوم TiO<sub>2</sub> NTAs - كرافيت عند دمجها مع المواد المضافة التي تعزز التوصيلية عن طريق تقليل لزوجة هذه السوائل. حيث أدى وجود CaCl<sub>2</sub>.6H<sub>2</sub>O: Acetamide DES مع ماء منزوع الأيونات كمادة مضافة إلى رفع جهد الخلية إلى 1.31 فولت والمقاومة الداخلية 19 أوم. وأظهرت الخلايا استجابة مثيرة للاهتمام لـ AlCl<sub>3</sub>-chloroacetamide IL مع ثنائي كلوريد الميثان DCM

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كمادة مضافة، بجهد خلية يبلغ 1.81 فولت ومقاومة داخلية تبلغ 5.0 أوم. متأثرًا بجودة وتركيز الاصناف الأيونية. علاوة على ذلك، أظهرت الخلايا ثباتًا حراريًا أثناء عمليتي الشحن والتفريغ. بالإضافة إلى ذلك، تم فحص أسطح أقطاب NTAs  $TiO_2$ ، إضافة إلى تأثير IL وDES على هذه الأقطاب الكهربية، باستخدام تقنية المجهر الإلكتروني الماسح SEM ومطيافية تشتت طاقة الأشعة السينية EDXA.

## 1. Introduction

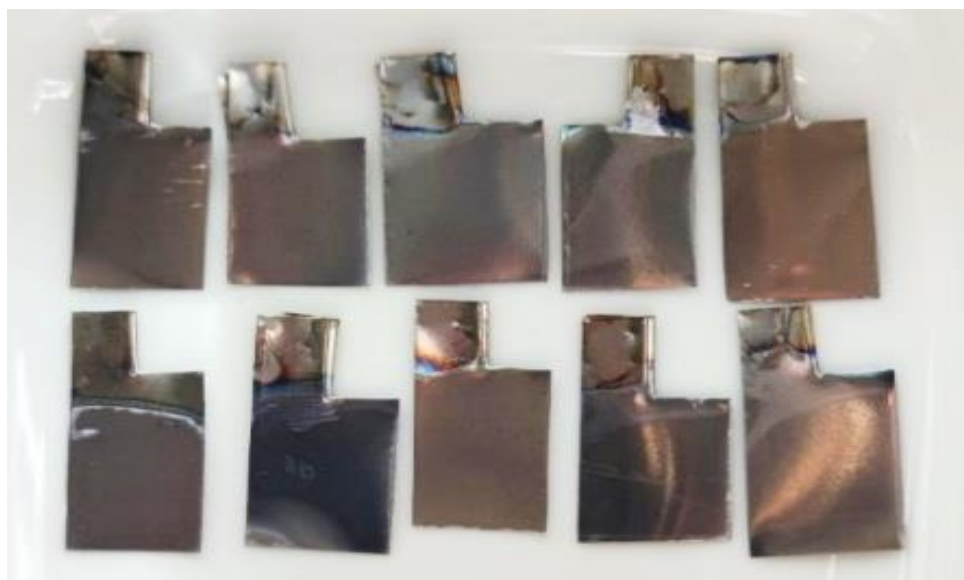
Practical evidence has shown that lead-acid and nickel-cadmium batteries' energy densities are poor and fall short of the demands of the many electronic devices that are becoming more and more common nowadays [1]. Additionally, these batteries performed less well in extremely cold or hot conditions [2]. As a result, the demand for batteries that can provide contemporary machinery, equipment, and devices with a higher energy density arose. In order to get such batteries, an effort has been made to create novel batteries whose negative electrode anodes have a greater potential than lead electrodes or nickel-cadmium electrodes. Batteries made of lithium and graphite LIBs, possessing superior qualities in terms of their long lifetime, high energy, and rechargeability, are presently dominating markets [3]. However, the primary worry of researchers who are seeking batteries that promote perfectionism with all of its traits and features is the issue of flammability and the poisonous nature [4] of some of the materials utilized in the production of these batteries. Aluminium-based batteries (ALBs) [5,6] with graphite electrodes [7,8] are the outcome and were produced as a safer, more accessible, less expensive, and lighter substitute. Furthermore, the electrolytes in these batteries comprised deep eutectic solvents (DESs) and ionic liquids (ILs) [9,10]. Due to their high ionic conductivity, thermal stability, wide electrical window, lack of interaction with the electrodes they are used with, whose surfaces retain their shape and properties despite contact with these liquids, as well as their safety, non-toxicity, and low cost [11,12], these liquids and solvents are safe and non-toxic. Examples of this kind of electrolyte are calcium chloride/acetamide DES [11] and Aluminium chloride anhydrous/urea IL [13]. Where these liquids may be made, together with salts and other ingredients that increase their effectiveness in the creation of different battery kinds [14]. Certain elements may be included and taken care of without adding any further complications. The creation of longitudinal tubes on the outer and inner surfaces of titanium dioxide nanotubes, on the other hand, results in a large surface area, which increases the efficiency of many applications, particularly those requiring surface chemistry [15]. Due to its high resistivity, cheap cost, non-toxicity, and thermodynamic stability, it is regarded as one of the finest semiconductors for electrochemical materials [16-18]. Therefore, this study will be focused on establishing models of battery titanium dioxide nanotube-graphite electrode cells based on electrolytes consisting of  $AlCl_3$ -chloroacetamide ionic liquid enhanced with DCM and  $CaCl_2 \cdot 6H_2O$ - Acetamide DES enhanced with deionized water.

## 2. Materials and Methods

Dichloromethane DCM, deionized water DI water, aluminium chloride  $AlCl_3$ , chloroacetamide CA, calcium chloride dihydrate  $CaCl_2 \cdot 2H_2O$ , acetamide AC, Ethylene glycol, Titanium foil, Nitric acid, Acetone, Isopropanol, and High-density graphite were all used without any purification. The surface morphology of specimens was examined using a high-resolution field emission scanning electron microscope SEMI NSPECT F50, and the X-Flash 6110 Bruker EDX, which were combined to estimate the surface composition of the samples. The resistance was measured using a digital internal resistance tester, Vape YR1030, and the open circuit potential OCP was recorded using a digital multimeter electric tester, INGCO DCM200. Etekcitcity Temp Gun 1080 Infrared Thermometer for Recording Heat Temperature In a glove box filled with argon gas, experiments were carried out, and results were obtained at room temperature.

### 2.1. Preparation TiO<sub>2</sub> NTAs

The Ti foil (0.127 mm, 99.7% purity) was first cut into pieces measuring 1.0 cm by 2.5 cm. These pieces were then degreased by sonicating them in acetone, isopropanol, and deionized water for 15 minutes. The DI water used had a resistivity of 18.2 MΩ·cm at 25 degrees centigrade and was obtained from Millipore Corp. After degreasing, the surface of the Ti foil was chemically etched in HNO<sub>3</sub> (6.0 M) for 10 minutes to achieve a clean and smooth finish. The etched foil was then rinsed with DI water again before being dried in the air. In a two-electrode cell setup, the cathode electrode used was high-density graphite, while the anode was a clean Ti foil measuring 1.0 cm by 2.0 cm. The anode was submerged in an electrolyte consisting of NH<sub>4</sub>F (0.5 wt%) and H<sub>2</sub>O (5%), with ethylene glycol (EG) (95%). All the anodization parameters were maintained at room temperature with gentle stirring to prevent localized heating and promote ion diffusion in the viscous electrolyte. The distance between the two electrodes was consistently maintained at a value of 2 centimeters. To provide the required electrical voltage for the anodization process, the electrode cell was connected to a DC power source (Consort Mini, Cleaver Scientific Ltd). After anodization, the samples were immediately rinsed with DI water and then dried in the air. The anodized films underwent heat treatment in an air environment. They were heated at a rate of 2 degrees Celsius per minute for two hours, reaching a temperature of 500 degrees Celsius. The heating process was carried out using a thermocone furnace 21100 (Figure 1) [15].



**Figure 1:** Titania nanotube (TiO<sub>2</sub> NTAs) electrodes after preparation

### 2.2. Preparation of TiO<sub>2</sub> NTAs-graphite cells by the presence of AlCl<sub>3</sub>:CA IL and CaCl<sub>2</sub>.6H<sub>2</sub>O: Ac DES as electrolytes with and without additives [8]

Two different systems of electrolytes were used to create TiO<sub>2</sub> NTAs - graphite cells. In the first system, an ionic liquid, AlCl<sub>3</sub>:CA, was employed without any additives with a mole ratio of 2:1 [19]. The second system utilized a mixture of ionic liquid (IL), and dichloromethane as a solvent. The percentage of dichloromethane included in the ionic liquid varied between 25% and 75% in order to obtain the maximum observed conductivity [20]. The electrolyte in the second system consisted of CaCl<sub>2</sub>.6H<sub>2</sub>O: Ac DES mole ratio of 1:7 [11]. To enhance the movement of ions by reducing the high viscosity of the DES, a helper was introduced by adding water. The water was added to the DES in a ratio of deionized DI water (35%) to DES (65%) [20]. The negative electrode was constructed using TiO<sub>2</sub> NTAs material with dimensions of 0.127 mm thickness, 10 mm width, and 25 mm length. On the other hand, the cathode was made of a graphene electrode with a diameter of 5 mm, and the distance between the electrodes was 1cm (Figure 2).



**Figure 2:** Illustration of a TiO<sub>2</sub> NTAs-graphite electrochemical cells

### 3. Results and discussion

#### 3.1. The self-discharge

After the completion of the battery cell preparation process, involving various systems and additives, all cells underwent a charging phase with a continuous DC voltage of 3 volts for 5 minutes. Subsequently, the cell voltages were regularly measured using a digital multimeter over a period of 7 days. The readings obtained were carefully recorded in Table 1 to assess the extent of energy retention within the respective cells.

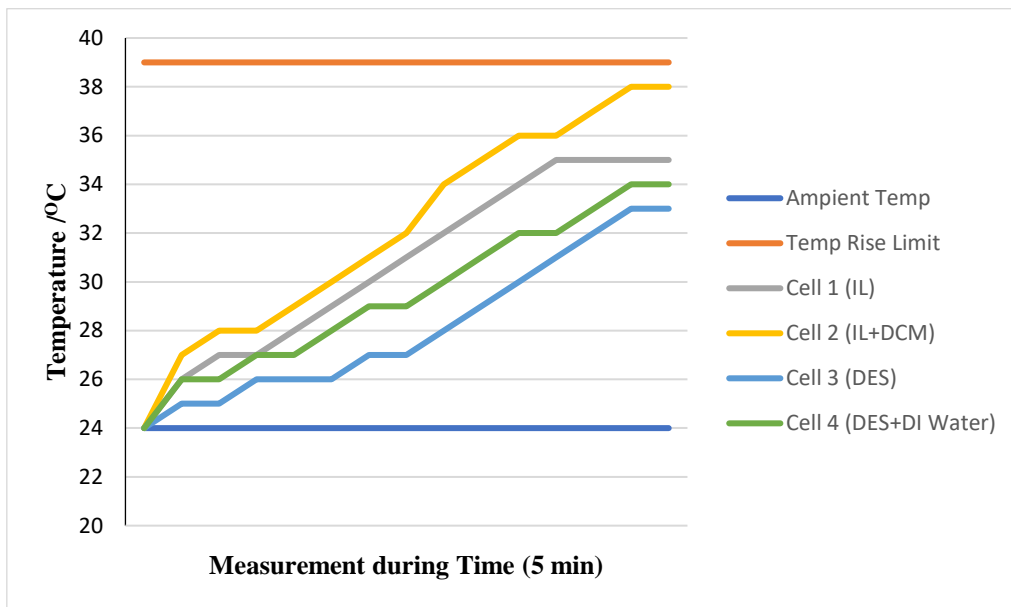
**Table 1:** The voltage measurements of all TiO<sub>2</sub> NTAs -graphite electrochemical cells batteries during one week

TiO <sub>2</sub> 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
<b>IL</b>	1.29	1.25	1.21	1.19	1.17	1.12	1.08	1.06
<b>IL+DCM</b>	1.81	1.79	1.76	1.73	1.69	1.63	1.61	1.58
<b>DES</b>	0.72	0.70	0.67	0.64	0.61	0.57	0.54	0.51
<b>DES+ DI water</b>	1.31	1.29	1.26	1.24	1.20	1.17	1.12	1.09

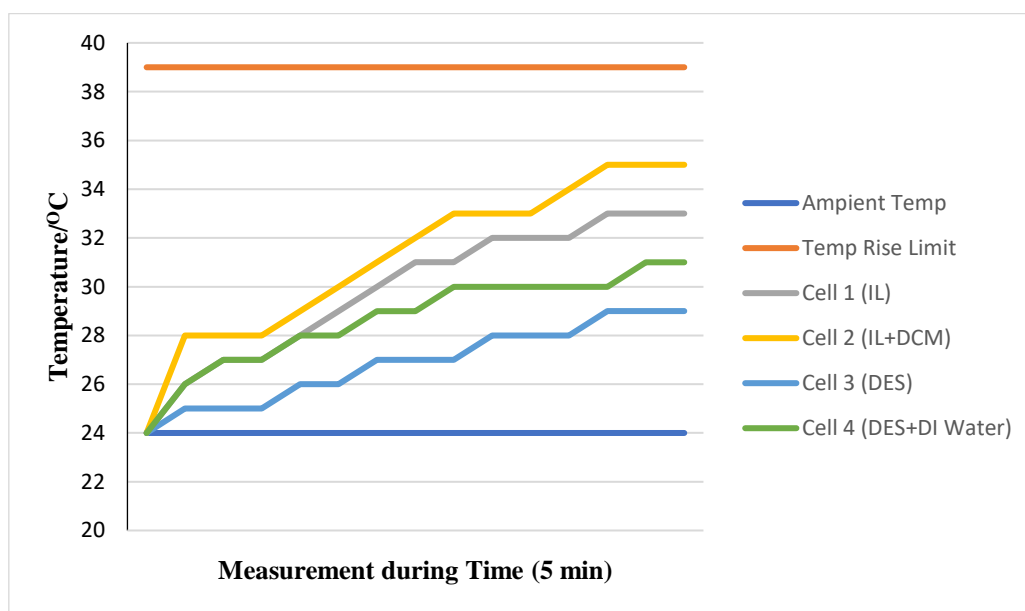
From the data presented in the above table, it is evident that the cells utilizing the IL and DCM electrolytes yield the most favorable results compared to the cells using DES or other systems. Where the additives increase the efficiency of the cell potential by reducing viscosity and enhancing the movement of ions within the electrolytes. The recorded data aim to provide a general understanding of self-discharge, a phenomenon influenced by specific chemical processes occurring within the cells. This self-discharge can be mitigated or minimized through the application of a suitable passivating layer on the electrodes.

### 3.2. Thermal charge-discharge test

To evaluate the charging and discharging processes of each cell, temperature measurements were taken for all four graphite cells (IL, IL+DCM, DES, and DES+DI water) from both inside the cell and the external ambient temperature. The results of these temperature measurements are represented in the accompanying figures.



**Figure 3:** Thermal charge test for TiO<sub>2</sub> NTAs-graphite cells with different electrolytes.



**Figure 4:** Thermal discharge test for TiO<sub>2</sub> NTAs -graphite cells with different electrolytes

During the charging and discharging processes of the batteries, it was observed that the temperature remained below the permitted threshold of 15 degrees Celsius, as specified in the approved guidelines for battery charging and discharging [21]. The cells were fully charged for 5 minutes at a voltage of 3 volts DC, and the temperature was measured during this period. Subsequently, the cells were discharged for 5 minutes at a current of 0.5 amperes, and the temperature was measured concurrently with the elapsed time.

### 3.3. Internal resistant test

Internal resistance, which measures the amount of resistance to current flow inside batteries, provides a general understanding of the viability of battery cells and their capacity to produce energy. The digital internal resistance tester was used to measure the internal resistance of the four TiO<sub>2</sub> NTAs-graphite cells. This gave important information about how well they worked and how much energy they could produce. In order to determine the current flowing through each cell in the absence of an external load, Ohm's law was applied as described in equation 1.

$$R = \frac{V}{I} \quad (1)$$

Where  $R$  resistance is in Ohm,  $V$  is volte,  $I$  current in amperes.

According to the recorded data in Table 2, the quality, concentration, and distance between the electrodes, among other factors, have an impact on the internal resistance. It is worth mentioning that the efficiency of the cell increases with decreasing levels of internal resistance [22].

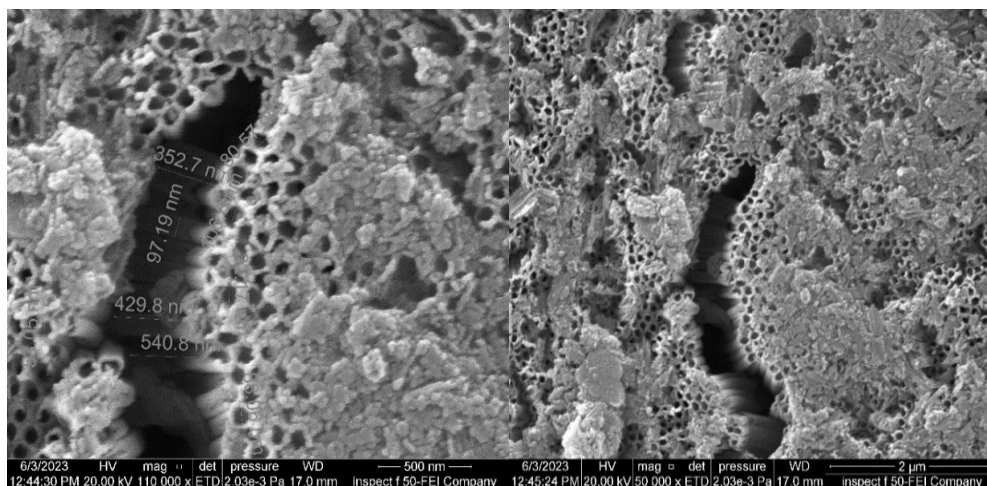
**Table 2:** Voltage, internal resistance, and current measurements for TiO<sub>2</sub> NTAs-graphite cells with different electrolytes

TiO <sub>2</sub> NTAs -Graphite cells with:	Volte (V)	Internal Resistance (Ohm)	Current (A)
<b>IL</b>	1.29	12	0.108
<b>IL+DCM</b>	1.81	5	0.362
<b>DES</b>	0.72	29	0.025
<b>DES+ DI water</b>	1.31	19	0.069

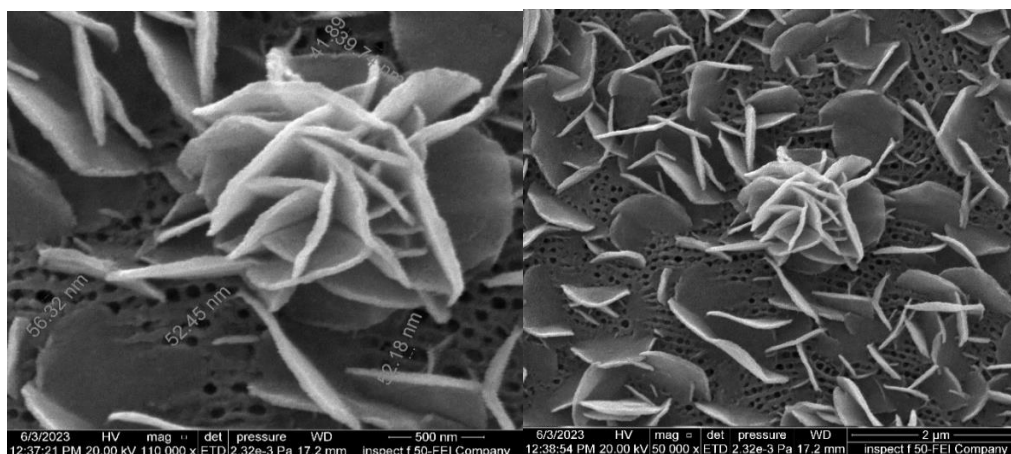
### 3.4. Scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDXA): Examination Results

The diameter of the nanotubes has the most effect on how well the electrode works in TiO<sub>2</sub> NTAs-graphite cells. A scanning electron microscope image reveals a smooth and coherent surface with well-arranged nanotubes of similar diameters; these pores are estimated to be approximately 60-90 nm and the wall thickness is 8 nm, clearly separated in a regular manner, indicating the efficacy of the nanoelectrode preparation process. Therefore, TiO<sub>2</sub> NTAs structure densely and uniformly grows on the Ti substrate, which is staggered and supported by each other according to former studies [23,24]. It is noteworthy to note that when the ionic liquids were used as electrolytes in TiO<sub>2</sub> NTAs-graphite cells, nanoforms formed on the surface of TiO<sub>2</sub> NTAs nanotubes. These liquids play a crucial role in rearranging and shaping the nanosurface, potentially deviating from the conventional tubular nanosurface. They achieve this by removing a thin layer of oxide and subsequently reshaping it into different forms, as depicted in Figure 5. Furthermore, when employing deep eutectic solvents (DES) in electrochemical cells containing TiO<sub>2</sub> NTAs nanotubes, hierarchical, flower-like TiO<sub>2</sub> nanostructures are formed. These nanostructures are considered highly favorable for TiO<sub>2</sub> NTAs due to their excellent conductivity and charge distribution capabilities [25]. Moreover, they provide protection for the underlying nanotubes, leading to a significantly prolonged cell lifespan and enhanced efficiency. The aforementioned statement highlights the significance of ionic liquids in promoting the development of TiO<sub>2</sub> nanotube array (NTAs) layers. On the other hand, the oxide mixes with the ionic liquid, forming layers that may be similar to the intrusion host due to the high ionicity of the ionic liquid, as well as the shape of the tubes that will be like towers for the ions of the ionic liquid to enter into them by increasing the contact surface area exposed to the ion exchange process and the measured electron flow, as shown in the Figure 6, where its noticed the ionic liquid layer mixed with some oxide displaced from

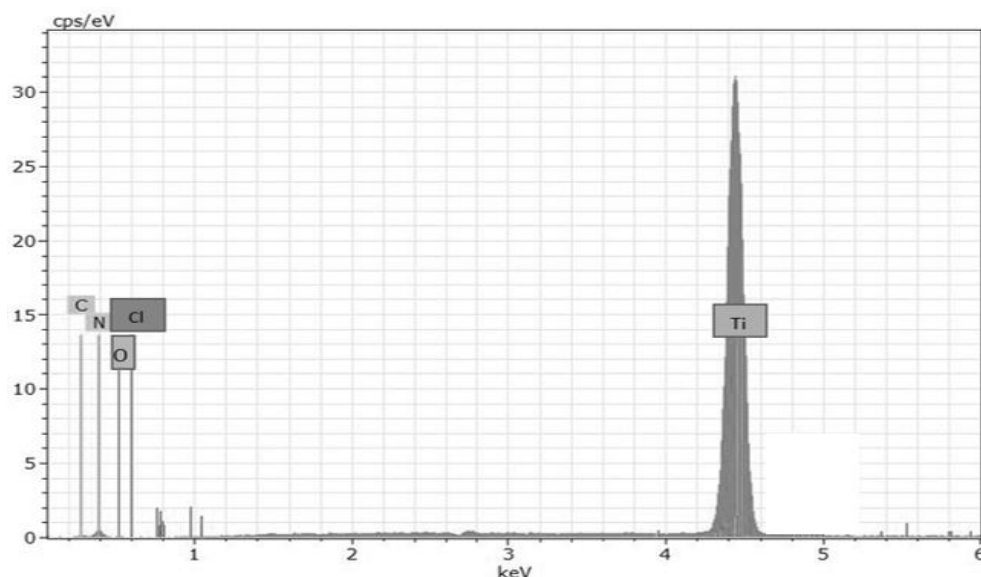
the upper layers of the oxide, which is formed during the process of charging and discharging when using electrochemical cells, and this is also due to the formation of some aluminum oxides on the surface and opening of the nanotube when charging and discharging for long periods. Additionally, in the measurements of EDX, the mechanism of its work depends on analyzing the surface of the electrode to find the constituent elements above it, where it is noticed that the electrode retains its main and highest component, which is titanium, as well as the presence of oxygen and the appearance of the chloride element in Figure 7, which are considered to be among the components of DES. Figure 8 shows the elements aluminium, nitrogen, carbon, and chloride in the ionic liquid. Throughout the testing period, all cells exhibited consistent energy levels in terms of voltage, ampere, and internal resistance without any noticeable changes. Furthermore, the electrodes' surfaces remained free from corrosion or interactions with the electrolytes, indicating their durability and stability. Additionally, it was observed that the ionic liquid, or DES, used in the electrochemical cells, which contained TiO<sub>2</sub> NTAs electrodes and graphene, maintained its purity. This indicates that the ionic liquid did not degrade or become contaminated over time. Moreover, the electrolytes exhibited persistent strength and effectiveness, even after six months of repeated charging and discharging cycles. These findings highlight the excellent performance and long-term stability of the electrochemical cells, demonstrating that the chosen materials and electrolytes could sustain their integrity and functionality over an extended period of use.



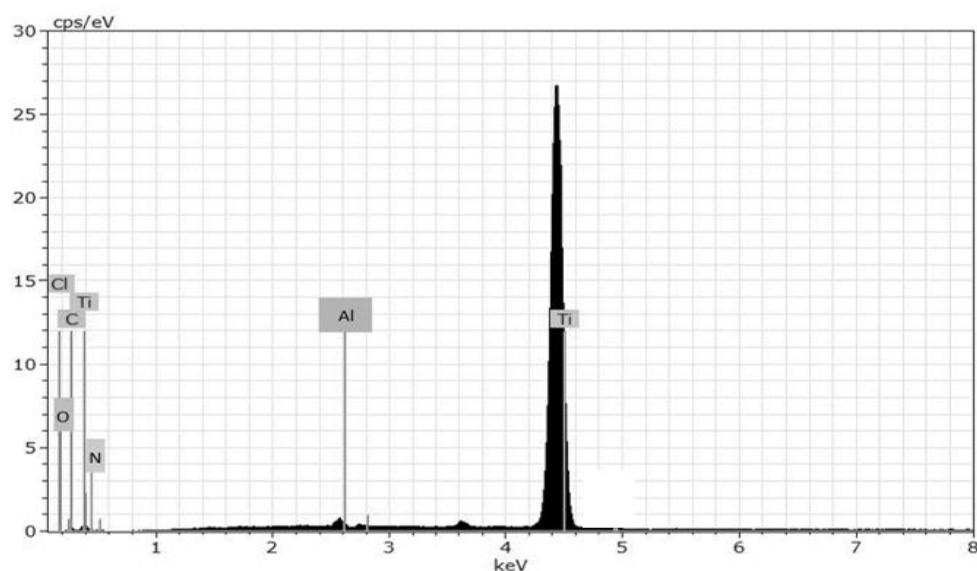
**Figure 5:** SEM images of TiO<sub>2</sub> NTAs -electrode in ionic liquid with DCM



**Figure 6:** SEM images of TiO<sub>2</sub> NTAs -electrode in DES with DI water



**Figure 7:** EDX images of TiO<sub>2</sub> NTAs -electrode in DES with DI water



**Figure 8:** EDX images of TiO<sub>2</sub> NTAs -electrode in ionic liquid with DCM

#### 4. Conclusion

In this study, models of battery cells with TiO<sub>2</sub> NTAs-graphite electrodes using two different electrolytes: AlCl<sub>3</sub>-chloroacetamide ionic liquid enhanced with DCM and CaCl<sub>2</sub>.6H<sub>2</sub>O-Acetamide DES enhanced with deionized water - were established. The cells formed with the ionic liquid electrolyte exhibited an open circuit potential (OCP) of 1.81 volts, an internal resistance of 5.0 ohms, and a current of 0.362 amperes without using an external resistance. In comparison, the cells based on the DES electrolyte had an OCP of 1.31 volts, an internal resistance of 19.0 ohms, and a current of 0.069 amperes without using an external resistance. All the cells demonstrated thermal stability during the charging and discharging processes and exhibited similar behavior in terms of surface oxidation and the role of the ionic species and their concentration in the electrolytes. This was confirmed through measurements and images obtained from a scanning electron microscope (SEM) and energy-dispersive X-ray analysis EDXA. It is important to note that these completed cells serve as experimental prototypes to showcase the feasibility of using ionic liquids and DESs as electrolytes. The aim is to utilize these materials in industrial settings for the development of batteries with high energy and storage capacities that can be deployed at various scales.



### Conflicts of interest

The author declares that they have no conflicts of interest.

### Acknowledgments

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