



ISSN: 0067-2904

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

Bassam Baqer Hasan^{1*}, Taghried Ali Salman¹, Asmaa Kadim Ayal²

¹Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

²Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad, Iraq

Received: 15/6/2023 Accepted: 1/9/2023 Published: xx

Abstract

Ionic liquids (ILs) and deep eutectic solvents (DESs) have been found to be highly effective as electrolytes in TiO₂ NTAs-graphite cells when combined with additives that enhance conductivity by reducing the viscosity of these liquids. The presence of CaCl₂.6H₂O: 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 AlCl₃-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 TiO₂ 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, TiO₂ NTAs, batteries.

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

بسام باقر حسن^{1*}، تغريد علي سلمان¹، أسماء كاظم عيال²

¹ قسم الكيمياء، كلية العلوم، جامعة النهرين، بغداد، العراق

² قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق

الخلاصة

وجد ان للسوائل الأيونية ILs والمذيبات عميقة الانصهار DESs فعالية مذهلة عند استخدامها في خلايا الأقطاب النانوية نوع ثاني أكسيد التيتانيوم TiO₂ NTAs - كرافيت عند دمجها مع المواد المضافة التي تعزز التوصيلية عن طريق تقليل لزوجة هذه السوائل. حيث أدى وجود CaCl₂.6H₂O: Acetamide DES مع ماء منزوع الايونات كمادة مضافة إلى رفع جهد الخلية إلى 1.31 فولت والمقاومة الداخلية 19 أوم. وأظهرت الخلايا

* Email: bassam78bh@gmail.com

استجابة مثيرة للاهتمام لـ AlCl_3 -chloroacetamide IL مع ثنائي كلوريد الميثان DCM 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 TiO_2 NTAs، إضافة إلى تأثير IL وDES على هذه الأقطاب الكهربائية، 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 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ - 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 $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 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, INSCO 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_2 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 $M\Omega\cdot cm$ at 25 degrees centigrade and was obtained from Millipore Corp. After degreasing, the surface of the Ti foil was chemically etched in HNO_3 (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_4F (0.5 wt%) and H_2O (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 thermocline furnace 21100 (Figure 1) [15].

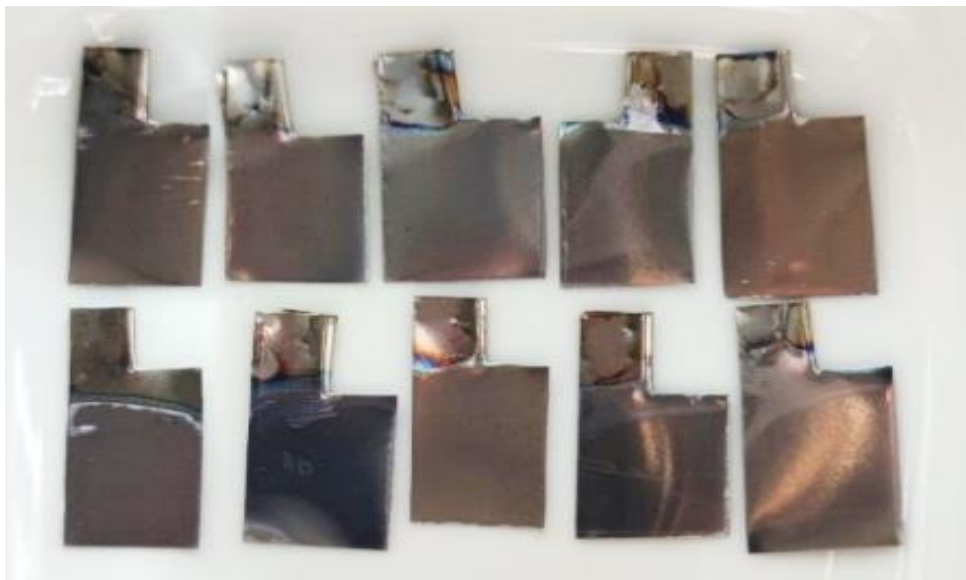


Figure 1: Titania nanotube (TiO_2 NTAs) electrodes after preparation

2.2. Preparation of TiO_2 NTAs-graphite cells by the presence of $AlCl_3:CA$ IL and $CaCl_2\cdot 6H_2O:Ac$ DES as electrolytes with and without additives [8]

Two different systems of electrolytes were used to create TiO_2 NTAs - graphite cells. In the first system, an ionic liquid, $AlCl_3:CA$, 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 $CaCl_2\cdot 6H_2O:Ac$ 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_2 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 TiO₂ 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 TiO₂ NTAs -graphite electrochemical cells batteries during one week

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	1.29	1.25	1.21	1.19	1.17	1.12	1.08	1.06
IL+DCM	1.81	1.79	1.76	1.73	1.69	1.63	1.61	1.58
DES	0.72	0.70	0.67	0.64	0.61	0.57	0.54	0.51
DES+ DI water	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.

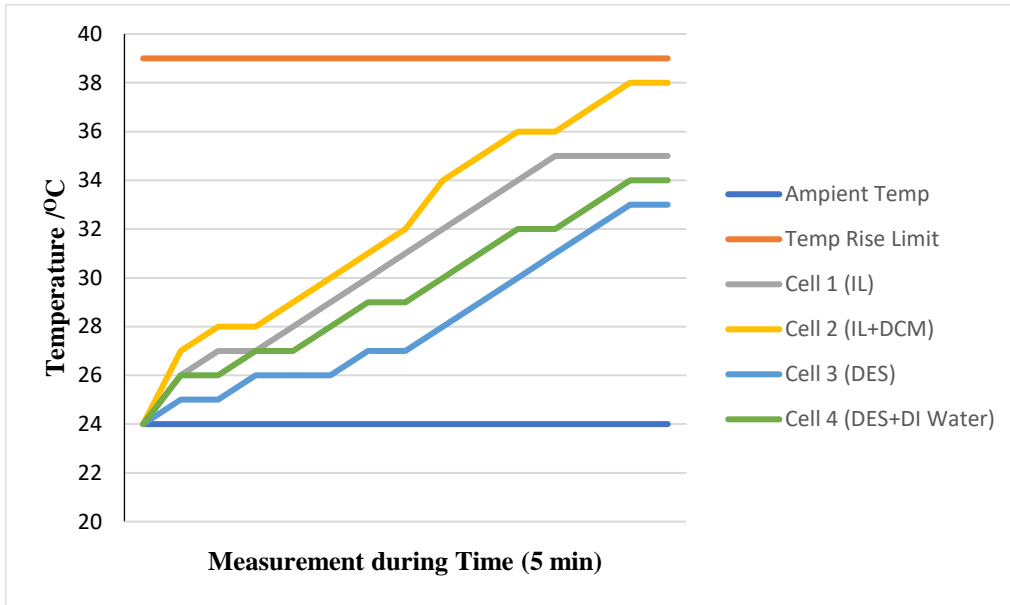


Figure 3: Thermal charge test for TiO₂ NTAs-graphite cells with different electrolytes.

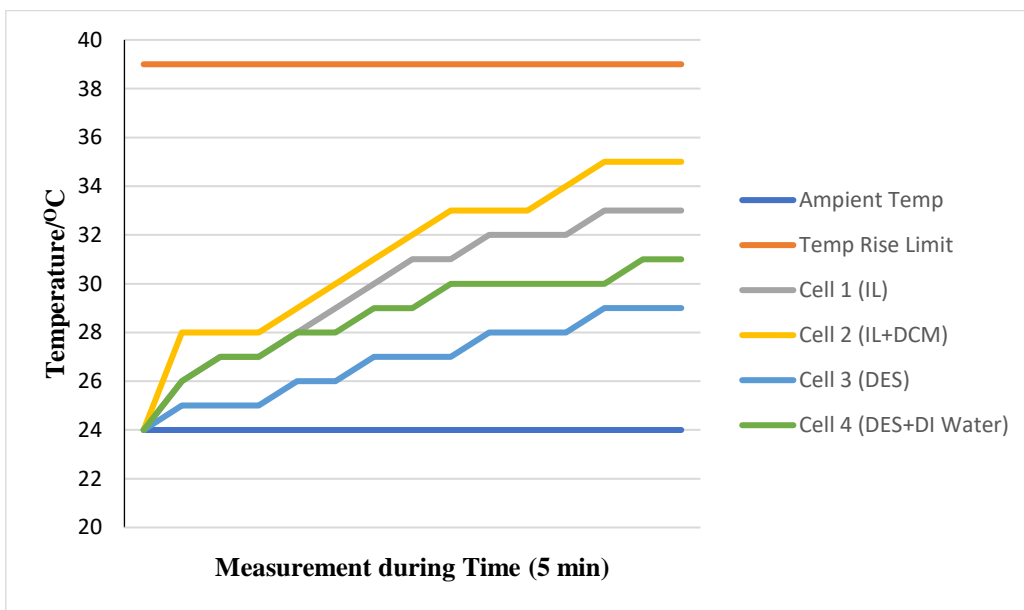


Figure 4: Thermal discharge test for TiO₂ NTAs -graphite cells with different electrolytes

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 TiO₂ 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 TiO₂ NTAs-graphite cells with different electrolytes

TiO ₂ NTAs -Graphite cells with:	Volte (V)	Internal Resistance (Ohm)	Current (A)
IL	1.29	12	0.108
IL+DCM	1.81	5	0.362
DES	0.72	29	0.025
DES+ DI water	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 TiO₂ 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, TiO₂ 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 TiO₂ NTAs-graphite cells, nanoforms formed on the surface of TiO₂ 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 TiO₂ NTAs nanotubes, hierarchical, flower-like TiO₂ nanostructures are formed. These nanostructures are considered highly favorable for TiO₂ 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 TiO₂ 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 TiO₂ 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.

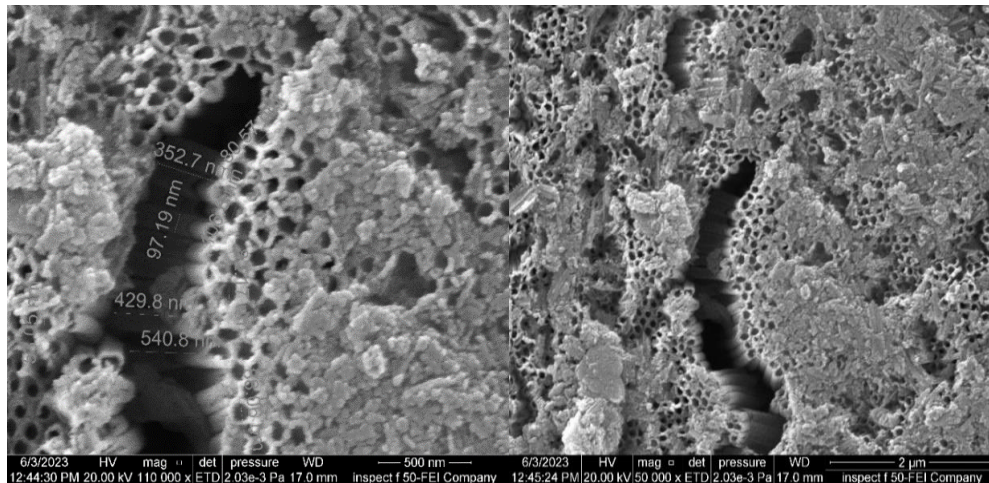


Figure 5: SEM images of TiO₂ NTAs -electrode in ionic liquid with DCM

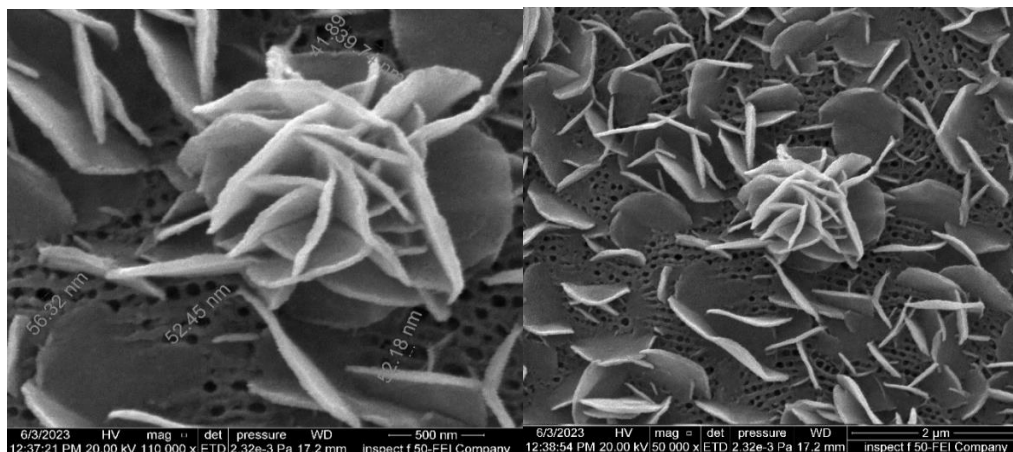


Figure 6: SEM images of TiO₂ NTAs -electrode in DES with DI water

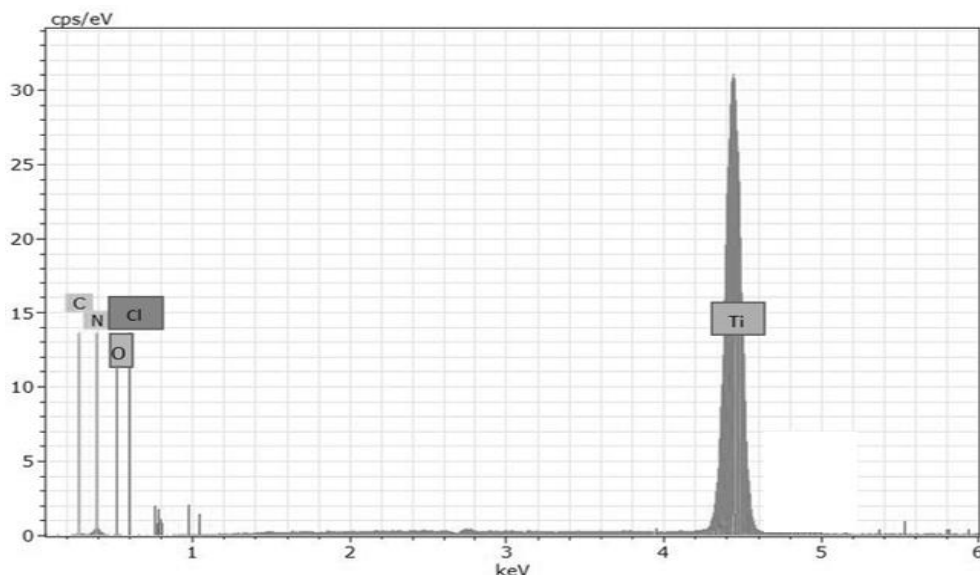


Figure 7: EDX images of TiO₂ NTAs -electrode in DES with DI water

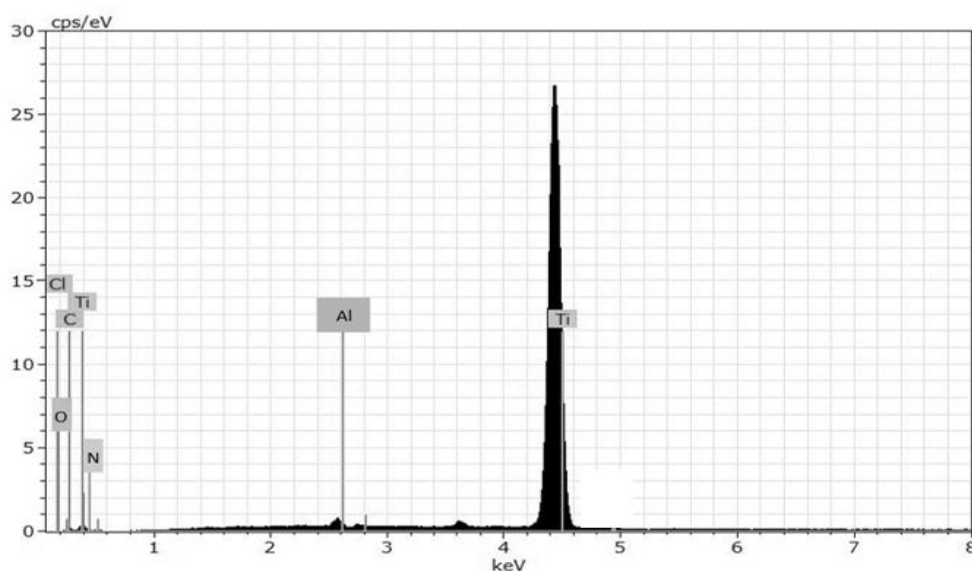


Figure 8: EDX images of TiO₂ NTAs -electrode in ionic liquid with DCM

4. Conclusion

In this study, models of battery cells with TiO₂ NTAs-graphite electrodes using two different electrolytes: AlCl₃-chloroacetamide ionic liquid enhanced with DCM and CaCl₂·6H₂O-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

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

References

- [1] E. Annette, S. Vladimir, and J. Tim, "Assessment of utility energy storage options for increased renewable energy penetration", *Renewable and Sustainable Energy Reviews*, vol. 16, no. 1, pp. 4141-4147, 2012.
- [2] R. Walawalkar and J. Apt, "Market analysis of emerging electric energy storage systems", *National Energy Technology Laboratory*, vol. 1330, no. 1, pp. 1-118, 2008.
- [3] D. Kim, P. Muralidharan, and H. Lee, "Spinel LiMn_2O_4 nanorods as lithium-ion battery cathodes", *Nano letters*, vol. 8, no. 11, pp. 3948-3952, 2008.
- [4] D. Wang, C. Wei, and M. Lin, "Advanced rechargeable aluminium ion battery with a high-quality natural graphite cathode", *Nature Communications*, vol. 8, Article no. 14283, 2017.
- [5] H. Yang, H. Li, and J. Li, "The rechargeable aluminum battery: opportunities and challenges", *Angewandte Chemie International Edition*, vol. 58, no. 35, pp. 11978-11996, 2019.
- [6] A. Elia, K. Marquardt, and K. Hoepfner, "An over view and future perspectives of aluminum batteries", *Advanced Materials*, vol. 28, no. 35, pp. 7564-7579, 2016.
- [7] X. Dong, H. Xu, and H. Chen, "Commercial expanded graphite as high-performance cathode for low-cost aluminum-ion battery", *Carbon*, vol. 148, pp. 134-140, 2019.
- [8] B. Hasan and T. Salman, "Environmentally friendly aluminum-graphite battery cells based on ionic liquids and deep Eutectic solvents as electrolytes with some additives", *BioGecko*, vol. 12, no. 1, pp. 2230-5807, 2023.
- [9] S. Choi, H. Go, G. Lee, and Y. Tak, "Electrochemical properties of aluminum anode in ionic liquid electrolyte for rechargeable aluminum-ion battery", *Physical Chemistry Chemical Physics*, vol. 19, no. 13, pp. 8653-8656, 2013.
- [10] D. Lee, G. Lee, and Y. Tak, "Hypostatic instability of aluminum anode in acidic ionic liquid for aluminum-ion battery", *Nanotechnology*, vol. 29, no. 36, pp. 7-29, 2018.
- [11] B. Hasan, H. Abood, and N. Mohamed, "Preparation and characterization of deep eutectic solvent: Physical properties and electrochemical studies", *AIP Conference Proceedings*, 2398, 030009/10.1063/5.0095413, 2022.
- [12] B. Hasan, H. Abood, and N. Mohamed, "Effect of some aluminum salts - amine ionic liquids on several serum human parameters and bacterial growth of klebsiella pneumoniae and staphylococcus aureus", *Al-Nahrain Journal of Science*, vol. 21, no. 1, pp. 14-22, 2018.
- [13] H. Abood, A. Abbott, A. Ballantyne, and K. Ryder, "Do all ionic liquids need organic cations? characterization of $[\text{AlCl}_2.n\text{Amide}] + \text{AlCl}_4^-$ and comparison with imidazolium-based system", *Chemical Communications*, vol. 47, no. 12, pp. 3523-3525, 2011.
- [14] N. Zhu, K. Zhang, and F. Wu, "Ionic liquid-based electrolytes for aluminum /magnesium/sodium-ion batteries", *Energy Material Advances*, vol. 2021, Article no. 9204217, 2021.
- [15] T. Awaid, A. Ayal, A. Farhan, and L. Chin, "Effect of electrolyte composition on structural and photoelectrochemical properties of titanium dioxide nanotube arrays synthesized by anodization technique", *Baghdad Science Journal*, vol. 17, no. 4, pp. 1183-1190, 2020.
- [16] H. Hameed and N. Abdulrahman, "Preparation and characterization of TiO_2 nanoparticles with and without magnetic field effect via hydrothermal technique", *Iraqi Journal of Science*, vol. 64, no. 7, pp. 4125-4131, 2023.
- [17] A. Ayal, Y. Lim, and A. Farhan, "Sensitization of Mn with CdS nanoparticles via electrochemical deposition technique for photocurrent enhancement of nanomaterial's-sensitized photoelectrochemical cells", *Research on Chemical Intermediates*, vol. 44, no. 1, p. 7231, 2018.
- [18] R. Abdulsada and T. Hassan, "Synthesis of TiO_2 thin films nanoparticles with different layers using simple sol-gel method", *Iraqi Journal of Science*, vol. 62, no. 11, pp. 4425-4429, 2021.

- [19] B. Hasan and T. Salman, "Using a streamlined procedure to combine AlCl_3 and chloroacetamide to create a new ionic liquid", *Al-Nahrain Journal of Science*, vol. 26, no. 2, pp. 19-22, 2023.
- [20] L. Wenjing, Z. Zhaofu, H. Buxing, H. Suqin, X. Ye, and Y. Guanying, "Effect of water and organic solvents on the ionic dissociation of ionic liquids", *The Journal of Physical Chemistry*, vol. 111, pp. 6452-6456, 2007.
- [21] S. Annika, K. Daniel, J. Cedric, E. Stefan, L. Frank, and K. Michael, "Thermal electrical tests for battery safety standardization", *Energies*, vol. 15, no. 21, p. 7930, 2022.
- [22] G. Cristina, F. Diego, S. Lidia, M. Juan, F. Daniel, R. Carlos, and D. David, "Battery internal resistance estimation using a battery balancing system based on switched capacitors", *Institute of Electrical and Electronics Engineers*, vol. 56, no. 5, pp. 5363-5374, 2020.
- [23] N. Samsudin, Z. Zainal, N. Lim, Y. Sulaiman, S. Chang, and Y. Lim, "Capacitive performance of vertically aligned reduced titania nanotubes coated with Mn_2O_3 by reverse pulse electrodeposition", *The Royal Society of Chemistry Advances*, vol. 8, no. 41, pp. 23040-23047, 2018.
- [24] A. Ayal, A. Farhan, A. Holi, A. Al-Zahrani, and Y. Lim, "Influence of manganese concentration on photoelectrochemical response of TiO_2 nanotube decorated with Mn/CdS as photoanode", *Journal of Materials Science: Materials in Electronics*, vol. 34, no. 1, pp. 7, 2023.
- [25] W. Zhijiao, W. Qian, and D. Lixia, "Progress in the synthesis and applications of hierarchical flower-like TiO_2 nanostructures", *Particuology*, vol. 15, no. 4, pp. 61-70, 2014.