UDC 544.1;544.41, 544.47,669.054.76,544,544.6,541.13:541.183:541.138

S. Shemet, D. Kovtunov, O. Shmychkova, T. Luk'yanenko, A. Velichenko

ANODIC TITANIUM OXIDES: FORMATION IN ETHALINE-BASED DEEP EUTECTIC ELECTROLYTES AND THEIR SEMICONDUCTOR PROPERTIES

Ukrainian State University of Science and Technologies, Dnipro, Ukraine

The feasibility of forming mesoporous anodic titanium oxide coatings in an Ethaline-based electrolyte was investigated and compared with oxide layers formed in pure Ethaline and in the conventional ethylene glycol/NH_4F/H_2O electrolyte. Electrochemical characterization demonstrated that Ethaline possesses a wide electrochemical stability window and is suitable for anodic oxidation of titanium. The anodization electrolyte was found to strongly influence the electrochemical behavior, semiconductor properties, and surface morphology of the resulting oxide films. Linear sweep voltammetry revealed that the addition of NH_4F and water promotes the formation of more protective oxide layers compared with anodization in pure Ethaline. Mott-Schottky analysis confirmed n-type semiconducting behavior for all samples, while significant differences in donor concentration and flat-band potential indicated substantial changes in the electronic structure of the anodic oxides. Profilometric measurements showed that the oxide formed in the Ethaline/NH_4F/H_2O electrolyte possessed the highest surface roughness, reflecting a different balance between oxide growth and localized dissolution compared with the conventional nanotubular TiO_2 obtained in the ethylene glycol electrolyte. The results provide a basis for further optimization of Ethaline-based electrolytes through variation in the water and fluoride contents to control the balance between oxide growth and field-assisted dissolution, enabling the development of mesoporous titanium oxide coatings with tailored functional properties.

Keywords: anodic titanium oxide, deep eutectic solvent, Ethaline, anodization, Mott–Schottky analysis, mesoporous TiO_2.

DOI: 10.32434/0321-4095-2026-168-5-22-30

Introduction

Porous anodic metal oxides represent an important class of functional materials owing to their large specific surface area, controllable morphology, and unique electrochemical and semiconducting properties [1]. Such materials have attracted considerable attention for applications in photocatalysis, photoelectrochemical energy conversion, chemical and biological sensing, water electrolysis, corrosion protection, and electronic devices [2]. Among them, anodic titanium dioxide is one of the most extensively investigated systems because its morphology and electronic properties can be tailored over a wide range through electrochemical anodization [3].

The morphology of anodic TiO_2 is primarily governed by the anodizing electrolyte. Compact oxide films are generally formed in fluoride-free electrolytes, whereas fluoride-containing electrolytes promote the

© S. Shemet, D. Kovtunov, O. Shmychkova, T. Luk'yanenko, A. Velichenko, 2026

This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

development of porous structures due to the competition between field-assisted oxide growth and fluoride-assisted oxide dissolution [4]. Conventional anodization of titanium nanotubes is typically performed in ethylene glycol-based electrolytes containing a small amount of water and ammonium fluoride. In these systems, water serves as the oxygen source for oxide formation, while fluoride ions locally dissolve the growing oxide, enabling the self-organization of highly ordered mesoporous nanotube arrays. The structural characteristics of anodic TiO_2 are known to depend strongly on anodization voltage, water content, fluoride concentration, temperature, and anodization time [5].

In recent years, increasing attention has been devoted to replacing conventional organic electrolytes with environmentally benign media in accordance with the principles of green chemistry. Deep eutectic solvents (DESs) have emerged as promising alternatives because of their low volatility, low toxicity, simple preparation, high ionic conductivity, and wide electrochemical stability window [6]. Among them, the choline chloride–ethylene glycol mixture (Ethaline) has been extensively investigated as an electrolyte for electrodeposition of metals and alloys [7], electropolishing of titanium and stainless steel [8], and the preparation of composite coatings [9]. However, despite the rapidly growing interest in DESs, their application to the anodic formation of titanium oxide remains largely unexplored.

The formation of anodic oxide films in DESs differs fundamentally from that in conventional aqueous electrolytes because oxide growth depends on the availability of oxygen-containing species within the electrolyte. The high viscosity of Ethaline, its limited water content, and the different transport properties of ionic species may significantly influence the balance between oxide growth and field-assisted dissolution [10]. Whether a fluoride-containing Ethaline electrolyte can support the formation of mesoporous titanium oxide comparable to that obtained in conventional ethylene glycol electrolytes remains an open question.

Therefore, the aim of the present work was to evaluate the feasibility of forming mesoporous anodic titanium oxide films in an Ethaline-based electrolyte containing ammonium fluoride. The electrochemical behavior during anodization, the semiconducting properties, and the surface morphology of the resulting oxide films were systematically compared with those of oxide layers produced in pure Ethaline and in the conventional ethylene glycol/NH_4F/H_2O electrolyte. The results provide new insight into the mechanisms of oxide formation in deep eutectic solvents and demonstrate the potential of DES-based electrolytes for the preparation of functional anodic titanium oxide materials.

Material and methods

All chemicals were analytical reagent grade. Ethaline deep eutectic solvent was prepared by mixing choline chloride and ethylene glycol in a molar ratio of 1:2. The mixture was heated at 70^0C in ultrasonic bath until a homogeneous, clear, colorless liquid was obtained (near 30 min). The prepared DES was allowed to cool to room temperature and stored in a sealed container prior to use. Analytical-grade reagents were used without further purification. For the preparation of the fluoride-containing electrolyte, NH_4F (0.3 wt.%) and deionized water (5 vol.%, where applicable) were added to the freshly prepared Ethaline under continuous stirring until complete dissolution. Composites were obtained by the original method, which includes the stages of preliminary preparation of the titanium substrate etching in 3% HF. The technical titanium grade was VT1-0. Coatings were obtained on titanium foil with an area of 1 cm^2. Three types of anodic titanium oxide electrodes were prepared for comparison. The first sample was obtained by anodization of titanium foil in pure ethaline at a constant potential of 15 V for 3 h. The second sample consisted of conventional TiO_2 nanotube arrays prepared in an ethylene glycol-based electrolyte containing 0.3 wt.% NH_4F and 2 vol.% H_2O at a constant potential of 60 V for 3 h [5]. The third sample was fabricated in ethaline containing 0.3 wt.% NH_4F and 5 vol.% H_2O by anodization at a constant potential of 30 V for 3 h. All anodizations were performed under potentiostatic conditions. During oxidation, the current density exhibited the characteristic transient behavior, passing through a maximum before gradually decreasing to a quasi-steady value. To ensure comparable synthesis conditions, the maximum current density was maintained below 10 $mA \cdot cm^{-2}$ in all experiments. Three types of anodically treated titanium electrodes are hereafter referred to as Sample 1, Sample 2, and Sample 3.

The surface morphology and roughness were characterized using a Micron-alpha 3D optical profilometer (Ukraine). Representative surface images and line profiles were used to evaluate the roughness factor of the anodic oxide films.

The electrochemical properties of the materials were studied in a 1 M $HClO_4$ aqueous solution using quasi-stationary voltammetry and electrochemical impedance spectroscopy with a VersaSTAT 3A Potentiostat Galvanostat (USA). All potentials were measured and are reported versus an Ag/AgCl/KCl (sat.) reference electrode.

Results and discussion

The electrochemical behavior of titanium during anodic processes is strongly influenced by the polarization conditions. In particular, the passivation of titanium electrodes depends on the electrolyte composition, with electrolyte anions exerting a particularly pronounced effect. The growth of the oxide film and the oxidation rate of titanium and its alloys are governed by the transport of ions through the oxide layer to the reaction zone, i.e. to the electrolyte/electrode interface. The principal factor controlling oxide film growth during anodic polarization is the electric field strength across the oxide layer (the potential drop per unit film thickness), which determines the generation of mobile ionic species and their migration rate toward the reaction zone [11,12].

Despite the extensive body of research on the formation of porous anodic titanium oxide, important questions regarding its formation and the possibilities for controlling this synthesis remain unresolved.

Fig. 1 compares the cyclic voltammograms recorded on a Pt disk electrode and a Ti foil electrode in pure ethaline. Despite the substantial difference in the electrochemical properties of these substrates, the voltammograms are remarkably similar over the potential range from −1.1 to +1.1 V (vs. Ag/AgCl). The absence of additional oxidation or reduction peaks and the close agreement of the current responses indicate that no significant Faradaic processes occur within this potential window. In particular, no evidence of pronounced titanium passivation or platinum surface oxidation is observed under these conditions. These results demonstrate the wide electrochemical stability window of ethaline and confirm that the solvent does not interfere with the electrochemical behavior of the substrate. Therefore, ethaline can be considered an appropriate solvent for controlled anodic oxidation of titanium after the introduction of oxygen-containing species (e.g. water), which act as the oxygen source for oxide formation.

The anodization conditions were selected to ensure comparable maximum current densities (≤10 mA·cm^{-2}), thereby minimizing the influence of excessive Joule heating and dielectric breakdown while allowing direct comparison of oxide films formed in conventional and deep eutectic solvent electrolytes.

Figure 2a shows the first linear sweep voltammograms of Samples 1−3 recorded in 1 M $HClO_4$. Perchloric acid was selected as the supporting electrolyte because ClO_4^- ions exhibit negligible specific adsorption on titanium oxide surfaces and do not participate in oxide dissolution or complex formation. Consequently, the recorded anodic response

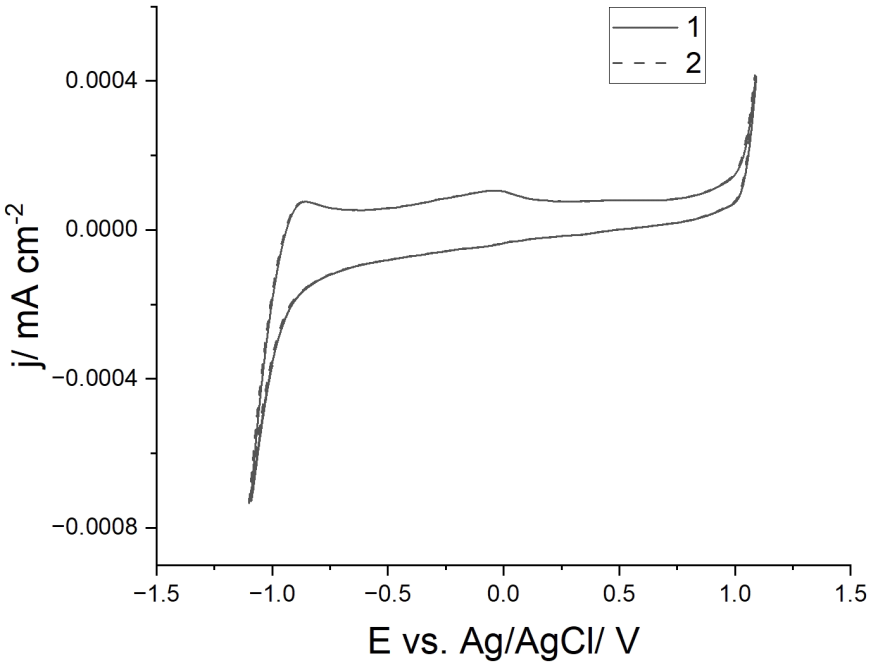


Fig. 1. Cyclic voltammograms on a Pt disk electrode (1) and on a Ti foil electrode (2) in Ethaline. Potential scan range: −1.1 to +1.1 V. Scan rate: 100 mV·s^{-1}

primarily reflects the intrinsic electrochemical properties of the anodically formed surface layers.

The electrochemical response of the as-prepared electrodes (Fig. 2a) differs markedly from that observed after electrochemical oxidation (Fig. 2b), indicating stabilization of the anodic oxide layer during the initial polarization.

The anodization electrolyte strongly affects the electrochemical behavior of the resulting titanium oxide films. Figure 2a represent the anodic oxidation and passivation of the titanium surface. Sample 1, prepared in pure ethaline, exhibits the earliest increase in anodic current at approximately 0.096 V, indicating active anodic dissolution of titanium followed by the formation of a passive oxide film. The polarization curve displays a characteristic passivation peak and subsequent current decrease, reflecting the gradual development of the protective oxide layer. This behavior is consistent with the formation of only a thin passive film during anodization in pure ethaline, leaving a significant fraction of the metallic titanium surface electrochemically accessible. In contrast, Samples 2 and 3 exhibit substantially more positive potentials (0.41 and 0.87 V, respectively), indicating that these surfaces are already covered with oxide films formed during anodization. Consequently, the anodic current is mainly associated with further oxidation of the pre-existing oxide, i.e. oxygen incorporation and thickening of the oxide layer, rather than oxidation of metallic titanium. The different positions of these features demonstrate that the anodization electrolyte strongly influences the structure and electrochemical properties of the oxide films.

The polarization behavior changes markedly after the oxide films have been established (Fig. 2b). At higher anodic potentials, the electrochemical response is governed by charge transport through the oxide layer rather than by oxidation of metallic titanium. At 1.7 V, the anodic current density reaches $1.90 \cdot 10^{-4}$ mA·cm^{-2} for Sample 2, $1.13 \cdot 10^{-4}$ mA·cm^{-2} for Sample 1, and $7.56 \cdot 10^{-5}$ mA·cm^{-2} for Sample 3. The highest current observed for Sample 2 indicates the highest electronic conductivity of the oxide film, which is attributed to the highly defective mesoporous nanotubular oxide formed in the conventional ethylene glycol/NH_4F electrolyte. Sample 1, anodized in pure ethaline, exhibits a lower current, consistent with the presence of a relatively thin passive oxide layer. In contrast, Sample 3 shows the lowest current density, indicating the formation of the least conductive oxide layer, whose structural and electronic properties differ substantially from those of the conventional nanotubular oxide.

Surface morphology was further evaluated by 3D optical profilometry. Representative surface images of the three samples are shown in Fig. 3. Significant differences in surface topography are observed depending on the anodization electrolyte. Sample 1 exhibits a relatively smooth and homogeneous surface, whereas Samples 2 and 3 display a progressively more developed surface morphology.

Representative line profiles extracted from the profilometric data are presented in Fig. 4. Sample 1 shows only minor height variations along the scanned region, indicating a relatively smooth surface. Sample 2 exhibits a moderately developed surface profile, consistent with the formation of a mesoporous TiO_2 layer. The largest height fluctuations are observed for Sample 3, indicating the development of a highly rough oxide surface.

The electrochemical behavior also correlates with the surface morphology. The calculated roughness factors were 4.08, 2.99, and 7.30 for Samples 1, 2, and 3, respectively. The highest roughness factor

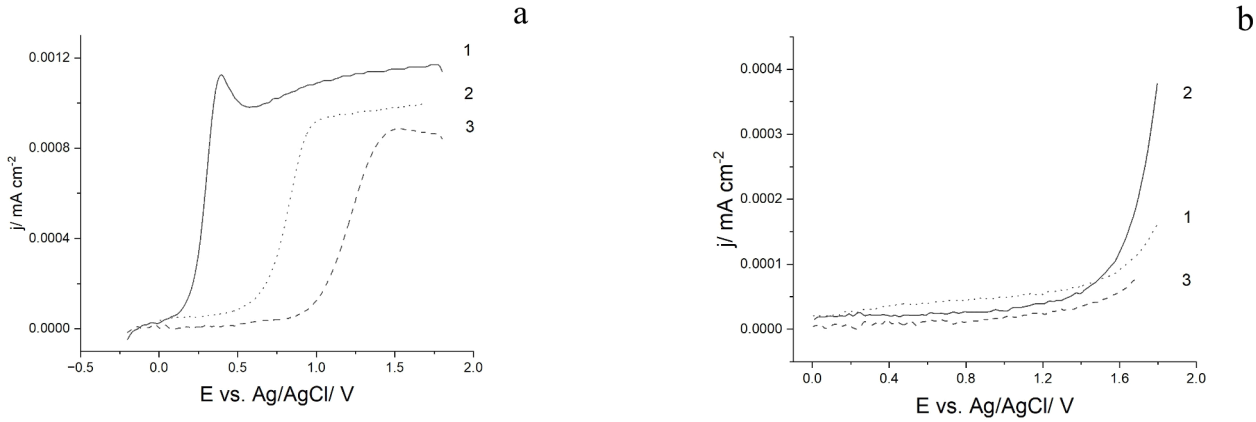


Fig. 2. Linear sweep voltammograms of Samples 1–3 recorded in 1 M $HClO_4$ at a scan rate of 100 mV s^{-1}: (a) as-prepared electrodes; (b) electrodes after electrochemical oxidation

obtained for Sample 3 indicates that anodization in the ethaline/NH_4F/H_2O electrolyte produces the most developed surface. This result agrees well with the electrochemical measurements, where Sample 3 exhibited the highest oxygen evolution overpotential and the lowest anodic current density after electrochemical oxidation, suggesting the formation of the most protective oxide layer.

Impedance measurements were carried out in a 1 M $HClO_4$ aqueous solution in order to investigate the semiconducting properties of the samples involved.

If the surface region of the semiconductor electrode in the investigated potential range is depleted of majority carriers, the experimental data obtained by measuring the electrode capacitance should be linear in coordinates of C^{-2} vs. E and follow the Mott–Schottky equation [13]:

$$C^{-2} = \frac{2}{e\varepsilon\varepsilon_0 N}\left(E - E_{fb} - \frac{kT}{e}\right), \quad (1)$$

where C is the capacitance of the electrode; ε is the electron charge; N is the carrier concentration; E_{fb} is the flat-band potential; k is the Boltzmann constant;

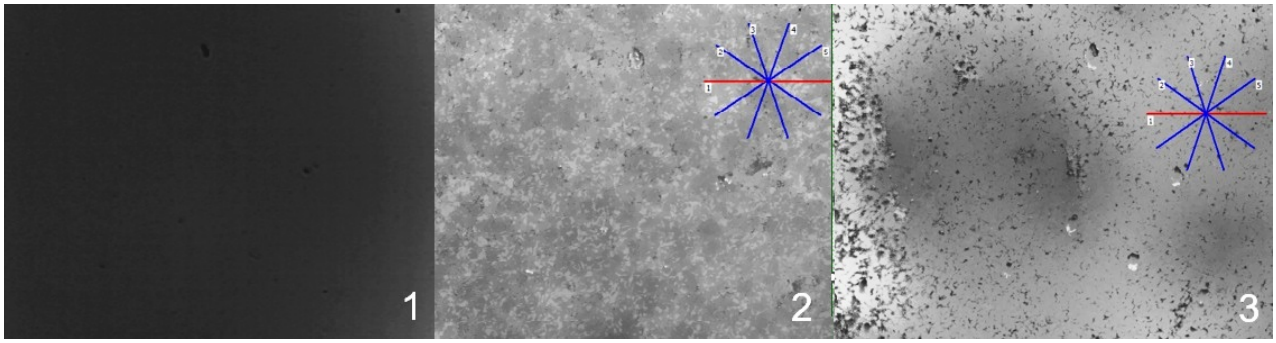


Fig. 3. Surface images of Samples 1–3 obtained by 3D optical profilometry. The radial lines indicate the directions used for surface profile analysis

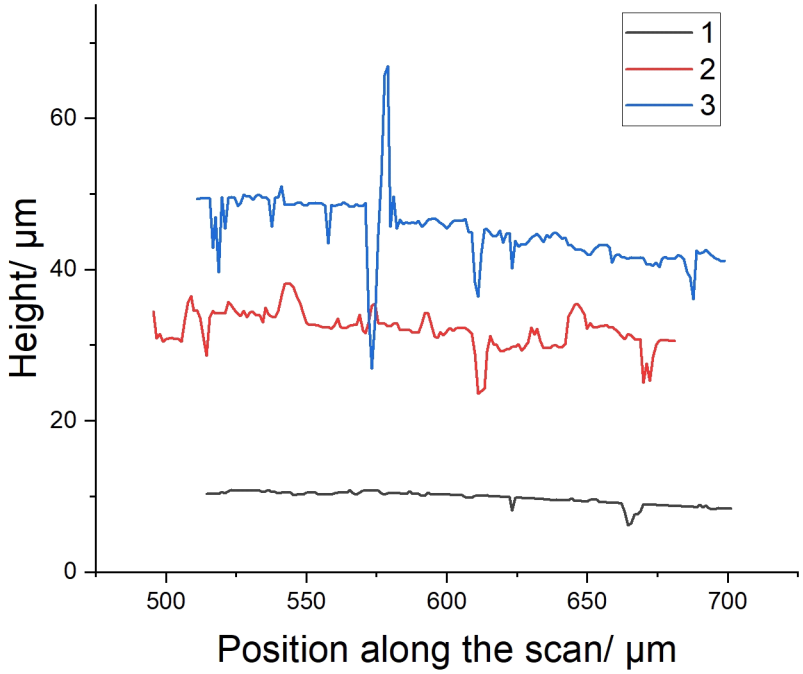


Fig. 4. Representative surface line profiles of Samples 1–3 measured by 3D optical profilometry over the selected scan region (500–700 μm)

T is the absolute temperature; ε is dielectric constant; and ε_0 is the electric constant.

When $N>10^{20}$ cm^{-3}, the capacitance of the space-charge layer becomes comparable to the Helmholtz capacitance (approximately 20 $\mu F \cdot cm^{-2}$). Because these capacitances are connected in series, the $1/C^2$ plot is significantly shifted toward more negative potentials. Therefore, to determine the true flat-band potential, a positive Helmholtz correction must be applied to the extrapolated potential:

$$C^{-2} = C_H^{-2} + \frac{2}{e\varepsilon\varepsilon_0 N}\left(E - E_{fb} - \frac{kT}{e}\right), \quad (2)$$

so

$$E_{fb} = E_{C^{-2}=0} + \frac{e\varepsilon\varepsilon_0 N}{2C_H^2} - \frac{kT}{e}. \quad (3)$$

Figure 5 presents the Mott–Schottky plots of the investigated anodic TiO_2 films, while the corresponding semiconductor parameters are summarized in Table. All samples exhibit positive slopes, confirming the n-type semiconducting behavior of the anodic titanium oxide films. The donor concentrations calculated from the slopes are in the range of $1.57 \cdot 10^{21}$ to $5.40 \cdot 10^{21}$ cm^{-3}, indicating a high density of electrically active donor defects.

Sample 1 exhibits a donor concentration of $1.65 \cdot 10^{21}$ cm^{-3} and the most negative flat-band potential (−1.31 V vs. Ag/AgCl). The highly negative flat-band potential suggests that the oxide possesses electronic properties close to those of relatively stoichiometric TiO_2. Since anodization in pure ethaline produced only a thin oxide layer, as evidenced by the electrochemical measurements, the electronic response may also be influenced by the underlying titanium substrate. Charge transfer between the metallic substrate and the thin oxide film can therefore contribute to the experimentally determined donor concentration.

Sample 2, prepared in the conventional ethylene glycol/NH_4F/H_2O electrolyte, exhibits the highest donor concentration ($5.40 \cdot 10^{21}$ cm^{-3}) and a flat-band potential close to −0.03 V. This behavior is consistent with the formation of a highly defective mesoporous TiO_2 nanotube layer containing a large concentration of oxygen vacancies and Ti^{3+}-related donor states [14,15]. The large thickness and porous morphology of the nanotube layer may additionally promote spatial non-uniformity of charge transport, with electrochemical reactions occurring predominantly at the outer surface while the inner regions of the pores contribute less efficiently to the measured capacitance.

Sample 3 demonstrates intermediate semiconductor characteristics, with a donor concentration of $1.57 \cdot 10^{21}$ cm^{-3} and a flat-band

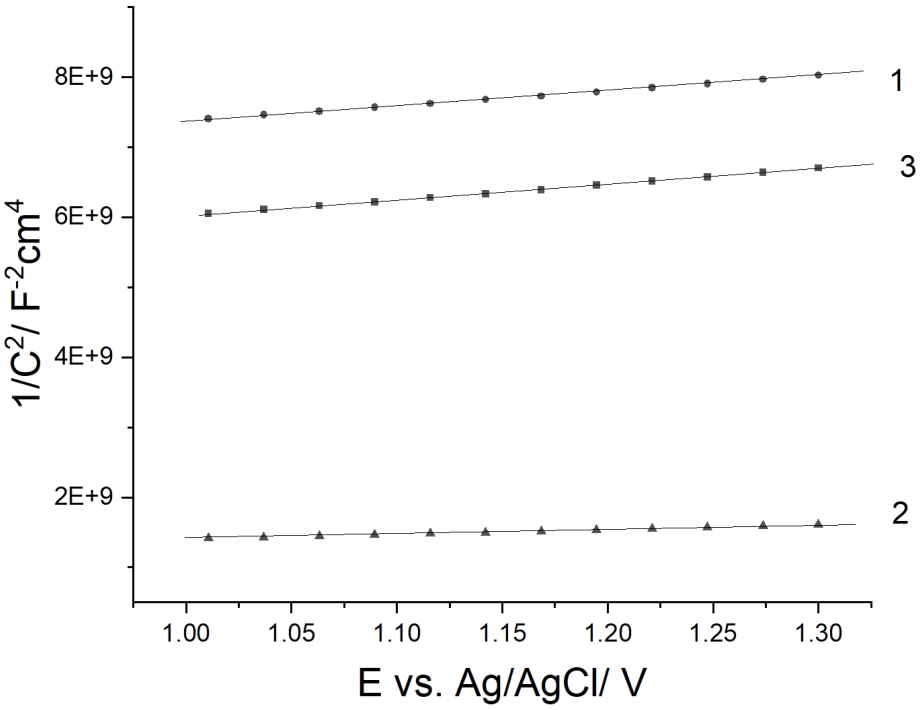


Fig. 5. Mott–Schottky plots of Samples 1–3 recorded in a 1 M $HClO_4$ aqueous solution. Frequency: 50 kHz

Semiconductor properties of TiO_2 in a 1 M $HClO_4$ aqueous solution

Sample	N/cm^{-3}	E_{fb}/V
1	$1.65 \cdot 10^{21}$	–1.31
2	$5.40 \cdot 10^{21}$	–0.03
3	$1.57 \cdot 10^{21}$	–0.57

potential of −0.57 V. Together with its high roughness factor and the electrochemical data, these results indicate the formation of a well-developed oxide layer possessing a lower defect density than the nanotubular oxide formed in the conventional electrolyte, while remaining more defective than the oxide produced in pure ethaline. Unlike Sample 1, the thicker oxide layer formed in the ethaline/NH_4F/H_2O electrolyte effectively screens the influence of the metallic titanium substrate on the measured semiconductor properties.

Overall, the Mott−Schottky analysis confirms that the composition of the anodizing electrolyte strongly influences the electronic structure of the resulting titanium oxide films. Whereas anodization in the conventional fluoride-containing ethylene glycol electrolyte produces a highly defective nanotubular oxide with the highest donor concentration, the deep eutectic solvent based on ethaline enables the formation of oxide layers with intermediate electronic properties. These results demonstrate that ethaline-based electrolytes provide a promising platform for tailoring the semiconductor characteristics of anodic titanium oxide through optimization of electrolyte composition and anodization conditions.

The semiconductor properties obtained from the Mott−Schottky analysis correlate well with the electrochemical behavior and surface morphology discussed above, confirming that the anodizing electrolyte governs both the structural and electronic properties of the resulting titanium oxide films.

Conclusions

Three types of anodic titanium oxide films were successfully prepared by potentiostatic anodization in pure Ethaline, a conventional ethylene glycol/NH_4F/H_2O electrolyte, and an Ethaline/ NH_4F/H_2O electrolyte. Their electrochemical behavior, semiconductor properties, and surface morphology were systematically compared.

Cyclic voltammetry demonstrated that Ethaline possesses a sufficiently wide electrochemical stability window and does not induce significant parasitic electrochemical reactions on either titanium or platinum within the investigated potential range, making it a suitable medium for anodic oxidation studies.

Linear sweep voltammetry in perchloric acid revealed pronounced differences in the electrochemical behavior of the as-prepared oxide films. The oxide formed in pure Ethaline exhibited the lowest onset potential and highest anodic current, indicating the formation of a relatively thin and less protective oxide layer. The addition of NH_4F and water promoted the formation of significantly more protective oxide films, shifting the anodic oxidation toward more positive potentials.

Mott−Schottky analysis confirmed that all anodic films behave as n-type semiconductors. The semiconductor properties strongly depended on the anodizing electrolyte. The nanotubular oxide formed in the conventional electrolyte possessed the highest donor concentration, whereas the oxide synthesized in the Ethaline-based electrolyte exhibited intermediate electronic characteristics together with the highest surface roughness, indicating a different mechanism of oxide growth.

The combined electrochemical, profilometric, and semiconductor characterization demonstrates that fluoride-containing Ethaline electrolytes are capable of producing functional anodic titanium oxide films with properties distinct from both compact oxides formed in pure Ethaline and conventional nanotubular TiO_2 prepared in ethylene glycol. These results highlight the potential of deep eutectic solvents as alternative electrolytes for tailoring the structure and electronic properties of anodic titanium oxide coatings.

Conflict of interest

A. Velichenko is an Editorial Board Member of the journal but was not involved in the peer-review process or the decision-making regarding this manuscript. All other authors declare no conflict of interest.

Acknowledgements

The authors gratefully acknowledge the Center for Shared Use of Scientific Equipment «Functional Materials Science and Innovative Materials» of the Ukrainian State University of Science and Technologies for providing access to the scientific instrumentation used in this work.

Funding

This work was supported by Ministry of Education and Science of Ukraine (grant number 0124U000536).

REFERENCES

1. *Schabikowski M., Stroz A., Kruk A.* Beyond oxidation: engineering functional anodised metal matrices through molecular and surface modifications // Int. J. Mol. Sci. – 2025. – Vol.26. – No. 16. – Art. No. 7809.

2. *Chakravorty A., Roy S.* A review of photocatalysis, basic principles, processes, and materials // Sustain. Chem. Environ. – 2024. – Vol.8. – Art. No. 100155.

3. *Corrosion* behavior of anodized nanoporous TiO_2 films in oxidizing environments: a study on electrochemically engineered titanium surfaces / Gajagouni S.P., Barsoum I., Cho S.O., Alfantazi A. // Nanoscale Adv. – 2025. – Vol.7. – No. 23. – P.7579-7587.

4. *Electrochemically* obtained titanium oxide: influence of the synthesis method on physicochemical and semiconductor properties / Shmychkova O., Knysh V., Luk'yanenko T., Velichenko A. // Adv. Mater. Sci. Res. – 2024. – Vol.69. – P.1-78.

5. *Design*, fabrication and functional properties of titanium suboxide-based composites with low noble metal content for electrocatalytic applications / Knysh V., Zhemela H., Shmychkova O., Luk'yanenko T., Velichenko A. // J. Electrochem. Sci. Eng. – 2025. – Vol.15. – Art. No. 2708.

6. *Protsenko V.* Using deep eutectic solvent-assisted plating baths to electrodeposit composite coatings: a review // Coatings. – 2024. – Vol.14. – No. 4. – Art. No. 375.

7. *Deep* inside of the mechanism of electrochemical surface etching of $\alpha + \beta$ Ti6Al4V alloy in room-temperature deep eutectic solvent Ethaline / Kityk A., Svec P., Soltys J., Pavlik V., Hnatko M. // J. Mol. Liq. – 2023. – Vol.375. – Art. No. 121316.

8. *Kityk A., Pavlik V., Hnatko M.* Green electropolishing using choline chloride-based deep eutectic solvents: a review // J. Mol. Liq. – 2023. – Vol.392. – Art. No. 123519.

9. *Electrochemical* corrosion behavior of Ni–TiO_2 composite coatings electrodeposited from a deep eutectic solvent-based electrolyte / Protsenko V.S., Butyrina T.E., Bobrova L.S., Korniy S.A., Danilov F.I. // Coatings. – 2022. – Vol.12. – No. 6. – Art. No. 800.

10. *Wang H., Xinchen K., Buxing H.* Electrocatalysis in deep eutectic solvents: from fundamental properties to applications // Chem. Sci. – 2024. – Vol.15. – No. 26. – P.9949-9976.

11. *Effect* of specific electrochemical settings and anion types on titanium oxide layer properties after anodization in near-neutral electrolytes for dental applications / Mehta K., Kaiser F., Stahlhut P., Wolf-Brandstetter C. // Electrochim Acta. – 2025. –Vol.541. – Art. No. 147405.

12. *Byvaltsev S.V.* The mechanism of oxide film formation for drawing titanium // Mater. Today: Proc. – 2019. – Vol.19. – P.1949-1952.

13. *Template* synthesis for the creation of photo- and electrocatalysts / Knysh V., Shmychkova O., Luk'yanenko T., Velichenko A. // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2023. – No. 3. – P.86-93.

14 Roy P., Berger S., Schmuki P. TiO_2 nanotubes: synthesis and applications // Angew. Chem. Int. Ed. – 2011. – Vol.50. – P.2904-2939.

15. *Defect* chemistry of titanium dioxide (rutile). Progress toward sustainable energy / Bak T., Sherif S.A., Black D.S., Nowotny J. // Chem. Rev. – 2024. – Vol.124. – No. 21. – P.11848-11914.

Received 17.06.2026
Revised 20.07.2026
Accepted 03.08.2026
Published 28.10.2026

АНОДНІ ОКСИДИ ТИТАНУ: ФОРМУВАННЯ В ГЛИБОКИХ ЕВТЕКТИЧНИХ ЕЛЕКТРОЛІТАХ НА ОСНОВІ ETHALINE ТА НАПІВПРОВІДНИКОВІ ВЛАСТИВОСТІ

С. Шемет, Д. Ковтунов, О. Шмичкова, Т. Лук'яненко, О. Величенко

Досліджено можливість формування мезопоруватих анодних оксидних покриттів титану в електроліті на основі Ethaline та проведено їх порівняння з оксидними шарами, сформованими в «чистому» Ethaline та традиційному водному електроліті на основі етиленгліколю з NH_4F і H_2O. Електрохімічні дослідження показали, що Ethaline характеризується широким вікном електрохімічної стабільності та є придатним середовищем для анодного окиснення титану. Встановлено, що склад електроліту анодування суттєво впливає на електрохімічну поведінку, напівпровідникові властивості та морфологію поверхні сформованих оксидних плівок. Методом лінійної вольтамперометрії показано, що додавання NH_4F і води сприяє формуванню більш захисних оксидних шарів порівняно з анодуванням у «чистому» Ethaline. Аналіз за методом Мотта-Шотткі підтвердив n-тип провідності всіх досліджених зразків, тоді як суттєві відмінності у концентрації донорів і потенціалі плоских зон свідчать про значні зміни електронної структури анодних оксидів. Профілометричні дослідження показали, що оксид, сформований в електроліті Ethaline/NH_4F/H_2O, характеризується найбільшою шорсткістю поверхні, що відображає інший баланс між ростом оксидної плівки та її локальним поле-асистованим розчиненням порівняно з традиційним нанотрубчастим TiO_2, отриманим в електроліті на основі етиленгліколю. Отримані результати створюють підгрунтя для подальшої оптимізації електролітів на основі Ethaline шляхом варіювання вмісту води та фторид-іонів з метою керування співвідношенням між ростом оксидної плівки та її поле-асистованим розчиненням, що відкриває можливості для розроблення мезопоруватих оксидних покриттів титану із заданими функціональними властивостями.

Ключові слова: анодний оксид титану; глибокий евтектичний розчинник; Ethaline; анодування; аналіз Мотта-Шотткі; мезопоруватий TiO_2.

ANODIC TITANIUM OXIDES: FORMATION IN ETHALINE-BASED DEEP EUTECTIC ELECTROLYTES AND THEIR SEMICONDUCTOR PROPERTIES

S. Shemet, D. Kovtunov, O. Shmychkova *, T. Luk'yanenko, A. Velichenko

Ukrainian State University of Science and Technologies, Dnipro, Ukraine

*** e-mail: o.b.shmychkova@ust.edu.ua**

The feasibility of forming mesoporous anodic titanium oxide coatings in an Ethaline-based electrolyte was investigated and compared with oxide layers formed in pure Ethaline and in the conventional ethylene glycol/NH_4F/H_2O electrolyte. Electrochemical characterization demonstrated that Ethaline possesses a wide electrochemical stability window and is suitable for anodic oxidation of titanium. The anodization electrolyte was found to strongly influence the electrochemical behavior, semiconductor properties, and surface morphology of the resulting oxide films. Linear sweep voltammetry revealed that the addition of NH_4F and water promotes the formation of more protective oxide layers compared with anodization in pure Ethaline. Mott-Schottky analysis confirmed n-type semiconducting behavior for all samples, while significant differences in donor concentration and flat-band potential indicated substantial changes in the electronic structure of the anodic oxides. Profilometric measurements showed that the oxide formed in the Ethaline/NH_4F/H_2O electrolyte possessed the highest surface roughness, reflecting a different balance between oxide growth and localized dissolution compared with the conventional nanotubular TiO_2 obtained in the ethylene glycol electrolyte. The results provide a basis for further optimization of Ethaline-based electrolytes through variation in the water and fluoride contents to control the balance between oxide growth and field-assisted dissolution, enabling the development of mesoporous titanium oxide coatings with tailored functional properties.

Keywords: anodic titanium oxide; deep eutectic solvent; Ethaline; anodization; Mott–Schottky analysis; mesoporous TiO_2.

REFERENCES

1. Schabikowski M, Stroz A, Kruk A. Beyond oxidation: engineering functional anodised metal matrices through molecular and surface modifications. *Int J Mol Sci*. 2025; 26: 7809. doi: 10.3390/ijms26167809.

2. Chakravorty A, Roy S. A review of photocatalysis, basic principles, processes, and materials. *Sustain Chem Environ*. 2024; 8: 100155. doi: 10.1016/j.scenv.2024.100155.

3. Gajagouni SP, Barsoum I, Cho SO, Alfantazi A. Corrosion behavior of anodized nanoporous TiO_2 films in oxidizing environments: a study on electrochemically engineered titanium surfaces. *Nanoscale Adv*. 2025; 7(23): 7579-7587. doi: 10.1039/d5na00883b.

4. Shmychkova O, Knysh V, Luk'yanenko T, Velichenko A. Electrochemically obtained titanium oxide: influence of the synthesis method on physicochemical and semiconductor properties. In: Wythers MC, editor. *Advances in Materials Science Research. Volume 69*. Nova Science Publishers; 2024. p: 1-78. doi: 10.52305/ZFSC2464.

5. Knysh V, Zhemela H, Shmychkova O, Luk'yanenko T, Velichenko A. Design, fabrication and functional properties of titanium suboxide-based composites with low noble metal content for electrocatalytic applications. *J Electrochem Sci Eng*. 2025; 15: 2708. doi: 10.5599/jese.2708.

6. Protsenko V. Using deep eutectic solvent-assisted plating baths to electrodeposit composite coatings: a review. *Coatings*. 2024; 14: 375. doi: 10.3390/coatings14040375.

7. Kityk A, Svec P, Soltys J, Pavlik V, Hnatko M. Deep inside of the mechanism of electrochemical surface etching of $\alpha + \beta$ Ti6Al4V alloy in room-temperature deep eutectic solvent Ethaline. *J Mol Liq*. 2023; 375: 121316. doi: 10.1016/j.molliq.2023.121316.

8. Kityk A, Pavlik V, Hnatko M. Green electropolishing using choline chloride-based deep eutectic solvents: a review. *J Mol Liq*. 2023; 392:123519. doi: 10.1016/j.molliq.2023.123519.

9. Protsenko VS, Butyrina TE, Bobrova LS, Korniy SA, Danilov FI. Electrochemical corrosion behavior of Ni–TiO_2 composite coatings electrodeposited from a deep eutectic solvent-based electrolyte. *Coatings*. 2022; 12: 800. doi: 10.3390/coatings12060800.

10. Wang H, Xinchen K, Buxing H. Electrocatalysis in deep eutectic solvents: from fundamental properties to applications. *Chem Sci*. 2024; 15(26): 9949-9976. doi: 10.1039/d4sc02318h.

11. Mehta K, Kaiser F, Stahlhut P, Wolf-Brandstetter C. Effect of specific electrochemical settings and anion types on titanium oxide layer properties after anodization in near-neutral electrolytes for dental applications. *Electrochim Acta*. 2025; 541: 147405. doi: 10.1016/j.electacta.2025.147405.

12. Byvaltsev SV. The mechanism of oxide film formation for drawing titanium. *Mater Today Proc*. 2019; 19(5): 1949-1952. doi: 10.1016/j.matpr.2019.07.048.

13. Knysh V, Shmychkova O, Luk'yanenko T, Velichenko A. Template synthesis for the creation of photo- and electrocatalysts. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2023; (3): 86-93. doi: 10.32434/0321-4095-2023-148-3-86-93.

14. Roy P, Berger S, Schmuki P. TiO_2 nanotubes: synthesis and applications. *Angew Chem Int Ed*. 2011; 50: 2904-2939. doi: 10.1002/anie.201001374.

15. Bak T, Sherif SA, Black DS, Nowotny J. Defect chemistry of titanium dioxide (rutile). Progress toward sustainable energy. *Chem Rev*. 2024; 124(21): 11848-11914. doi: 10.1021/acs.chemrev.4c00185.