EXECUTION STAGE 2/2022

Fabrication of hybrid composite membranes from cellulose-based matrices and different N-heterocyclic compounds

Fuel cells are currently the subject of a global research trend due to the rising demand for such devices. Even though the fundamental concept was developed more than 150 years ago by Sir W.R. Grove, fuel cell (FC) technology might be one of the options for innovative and sustainable energy generation. The electrolyte membrane is a critical component for fuel cell performance and serves as a separator between the anode and cathode.

Any material can be used as a proton exchange membrane if several conditions are concomitantly satisfied:

i) high proton conductivity

ii) good thermal and chemical stability

iii) outstanding tensile strength

iv) electron insulator

Main cellulosic materials used in this step:

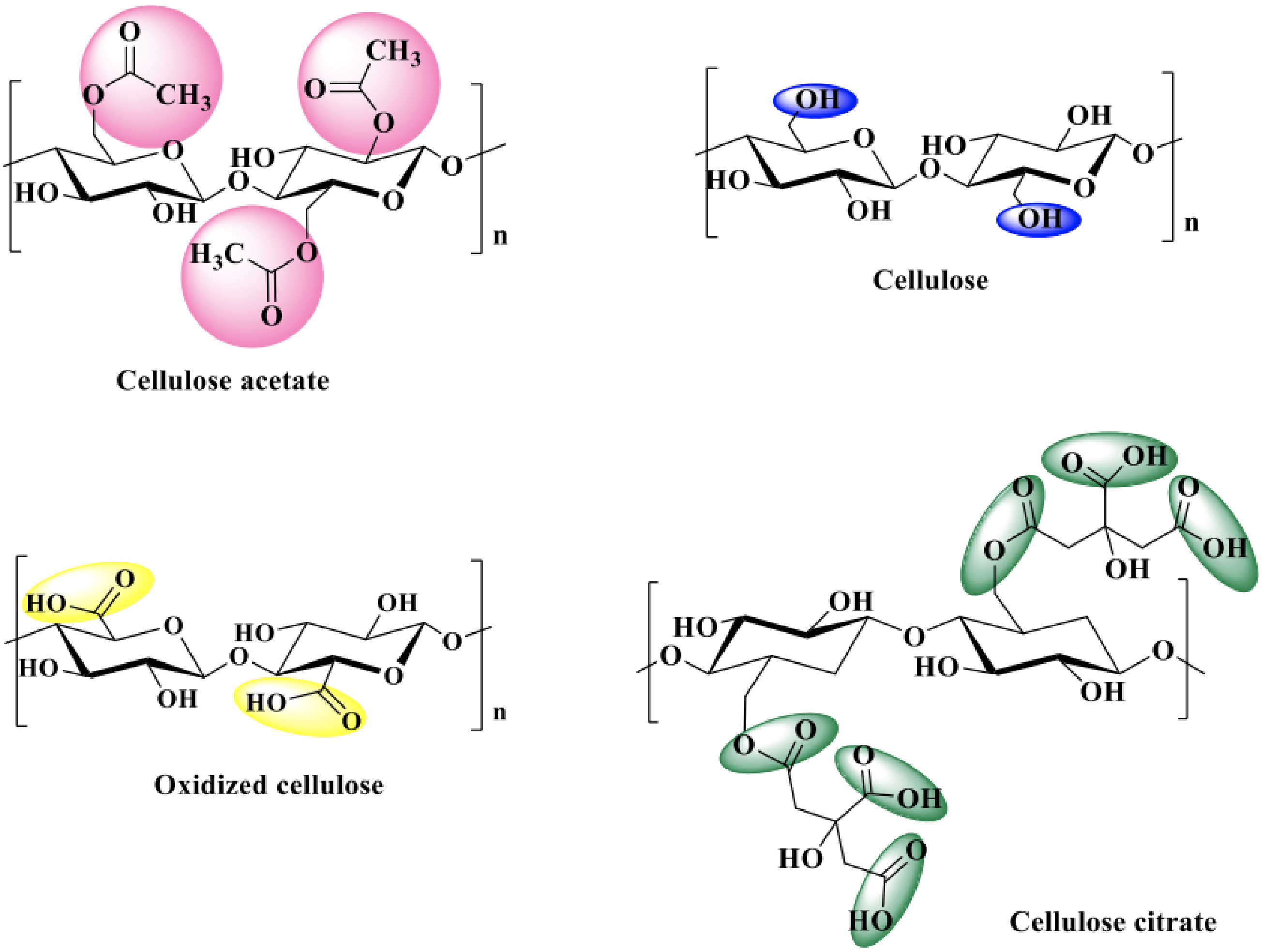

Fig. 1. Cellulose and its derivatives structures used in the execution stage 2/2022

Main heterocyclic compounds used in the execution stage 2/2022:

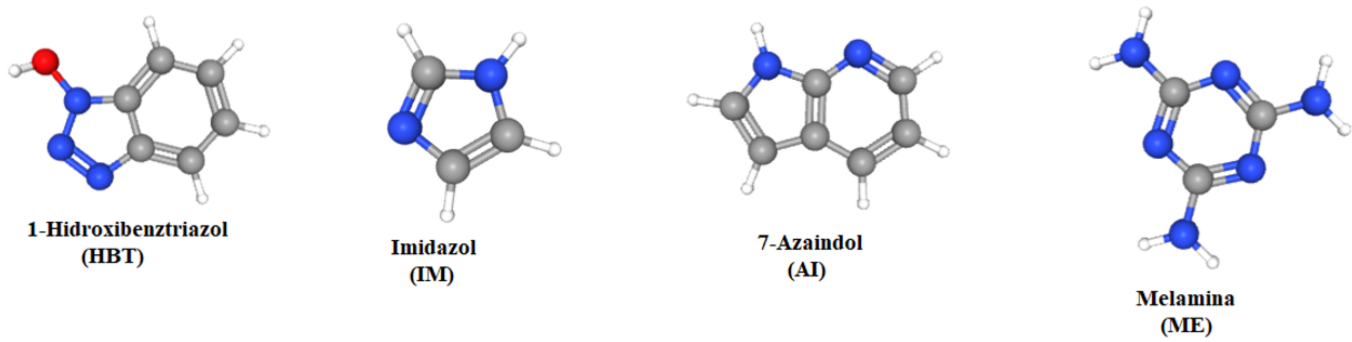

Fig. 2. Molecular structures of heterocyclic compounds used in the execution stage 2/2022

The results of molecular docking are highlighted in Figure 3, showing the best receptor-ligand complexation poses for each case (i.e. for cellulose receptor (Figure 3a) and for oxidized-cellulose receptor (Figure 3b)).

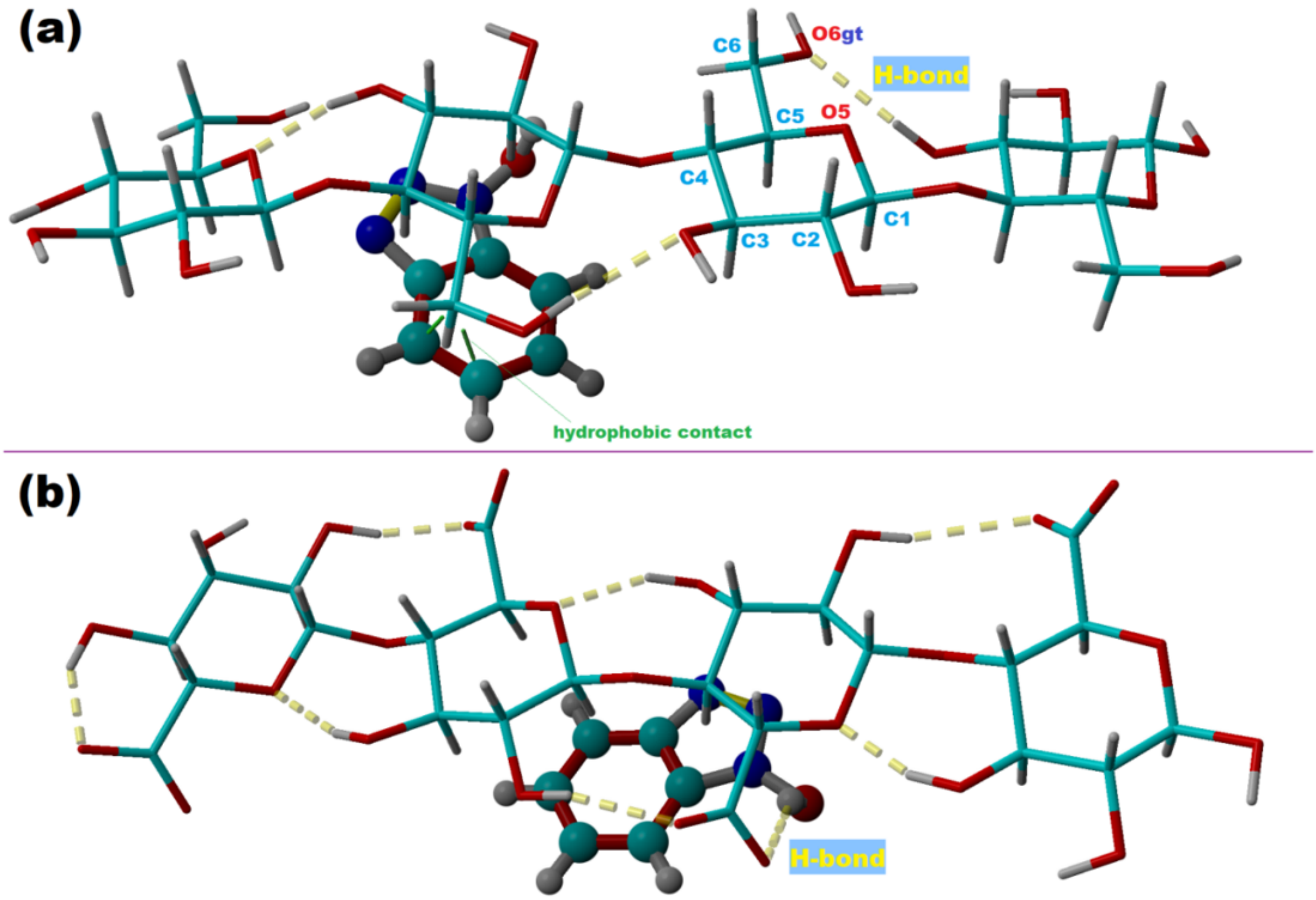

***Fig. 3**. Molecular docking outcomes highlighting the interaction between cellulose-based tetramers (receptors) and 1-Hydroxybenzotriazole compound (ligand): (a) best docking pose showing the binding mode of the ligand to the cellotetraose receptor; (b) best docking pose showing the binding mode of the ligand to the oxidized-cellotetraose receptor*

Cellulose acetate is a cellulose derivative widely used in many applications due to its good solubility in several organic solvents, so it is easily processed and subsequently can be employ for the cellulose regeneration, following a simple deacetylation process under alkaline conditions. Taking advantage of this common process for cellulose regeneration, CA films in DMF were firstly prepared, then cellulose films, which in turn were subjected to a mild oxidation in an oxidizing aqueous solution containing TEMPO, NaClO, and NaBr. Parallel, hybrid films incorporating various amounts of HOBt, following the previously presented route were fabricated, see Figure 4.

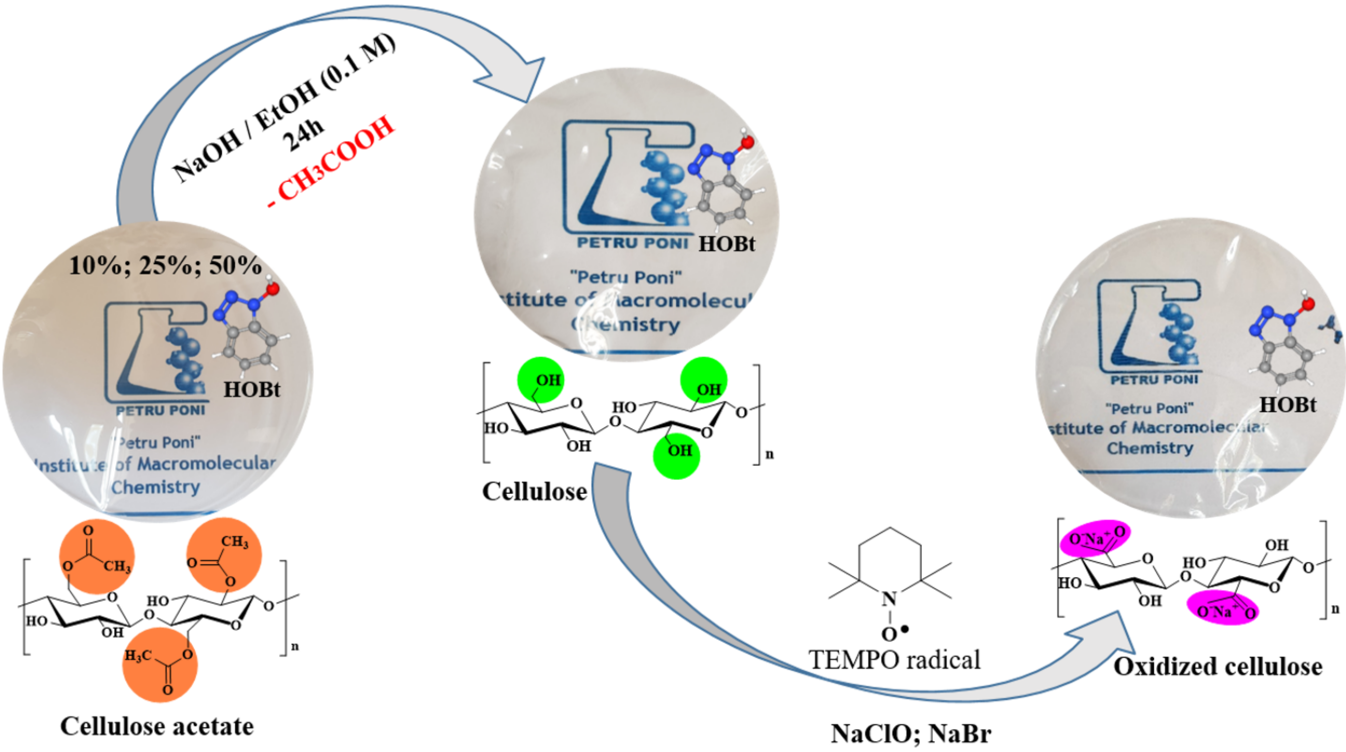

***Fig. 4**. Schematization of the cellulose acetate films conversion to cellulose and subsequently to oxidized cellulose, and visual appearance of the hybrid membranes made from different cellulosic supports with a initial load of 10%; 25% and 50% (wt.) HOBt*

HOBt was chosen to serve as a proton solvent in Nafion membranes, replacing water. The concept of employing nitrogen-bearing heterocycles was first presented some years ago. The benefits of employing such compounds come from their great self-dissociation capacity, which allows them to operate as both a proton donor and acceptor, which is a necessary attribute for good proton conductivity. Furthermore, many heterocycles containing nitrogen have great thermal stability; however, HOBt should be handled carefully, especially when anhydrous, belonging to the category of compounds that, in specific circumstances, pose an explosion danger. However, in prior works in the subject, the authors frequently lamented the inability to introduce a large quantity of heterocycles into the cellulose structure due to its insolubility. Tritt-Goc et al. determined that the greatest achievable level of imidazole in microcrystalline cellulose - imidazole composites corresponds to a molar ratio of 5.0, glucose/imidazole molar weight. By utilizing a cellulose-derivative, such as cellulose acetate, with excellent solubility in organic solvents, it is able to increase the quantity of heterocycle added to the hybrid composite in a systematic and controlled manner. Therefore, the three dosages of HOBt incorporated as a percentage by weight of the CA matrix (10%, 25%, and 50%) resulted in different molar ratios of glucose/HOBt units of 8.1, 3.32, and 1.66, respectively. The protocol was specially designed to determine the impact of the amount of HOBt introduced into the cellulose matrix on the general properties of the resulting films, see Figure 2. Conductometric titration was used to further characterize the oxidized films and establish their level of oxidation following exposure to the oxidizing solution. Thus, it was shown that because the oxidation of cellulose occurs gradually, on the surface of the cellulose film, the addition of HOBt had no effect on the process. All cellulose-HOBt hybrid samples contained roughly 340 ± 18 mmol/kg of carboxylic groups (the median value of three independent experiments), which is comparable to the sample of pure cellulose used as a reference.

In fact, this feature can also be seen by comparing the visual aspect of the films before- and after-oxidation, which remain colorless in contrast to a sample of pure HOBt that under the identical oxidation conditions turns reddish-brown. To assess the possibility of HOBt leaking or washing during regeneration processes, we conducted a series of experiments in which quantities of film with the same thickness (0.025 ± 0.005 mm), accurately weighed using a balance with 10 mg precision, were exposed to the alkaline environment. After 24h, the films were thoroughly cleaned with water, dried, and reweighed. Following these tests, we discovered that the hybrid films do actually lose HOBt after being exposed to an alkaline environment. The actual HOBt content after regeneration was determined to be: 7.8 ± 0.3% (sample C-HOBt10), 21.3 ± 0.6% (sample C-HOBt25), and 41.7 ± 1.6% (sample C-HOBt50). Additionally, the films that had been regenerated and additionally exposed to oxidation were weighed once more, but this time no additional mass losses due to HOBt washing (leakage) were noted. In this way, we can consider that HOBt is not affected under any kind of exposure for 5 min to the oxidizing solution; this only leads to oxidation on the surface of the cellulose. Moreover, using an analyzer equipped with a conventional CHN detector, the regenerate and oxidized samples were also examined in terms of their elemental nitrogen content. The average of three determinations representing the nitrogen content for each sample correlates quite well with the findings from the gravimetric analysis of the films following regeneration and oxidation. The samples of regenerated cellulose therefore had the following nitrogen percentages: 1.96% (sample C-HOBt10), 5.98% (sample C-HOBt25), and 11.68% (sample C-HOBt50). The nitrogen content in the further oxidized films was similar to that in the cellulosic films, as shown in the following examples: 1.925% (Cox-HOBt10 sample), 5.86% (Cox-HOBt25 sample), and 11.55% (Cox-HOBt50 sample) respectively.

Summary of progress (achieved deliverables, result indicators, dissemination of results, justification of differences, if applicable):

Website project: https://icmpp.ro/projects/l2/about.php?id=37

According to the project proposal, the following deliverables were provided for the year 2022:

- 2 scientific works sent for publication;
- 2 oral presentations and 4 posters by participating in conferences;
- Initiation of a special issue by the project director as "*Guest editor*" at "**Energies**" journal.

I would like to mention that all these deliverables have been fulfilled 100%, as follows:

Published papers

1. M.E. Culica, R. Rotaru, D. Bejan, A. Coroaba, T. Mohan, S. Coseri*****, *Cellulose surface modification for improved attachment of carbon nanotubes*, **Cellulose**, **2022**, 29, 6057–6076. **IF = 6.123**; https://doi.org/10.1007/s10570-022-04640-4

2. M.E. Culica, A.L. Chibac-Scutaru, M. Asandulesa, V. Melinte, C. Cojocaru, S. Coseri*****, *Convertible cellulosic platforms with manageable loads of 1-hydroxybenzotriazole: their preparation and conductive behavior*, **Cellulose**, **2022**, 29, 9847-9863. **IF = 6.123**; http://dx.doi.org/10.1007/s10570-022-04865-3

3. M. Asandulesa, A.L. Chibac-Scutaru*****, M.E. Culica, V. Melinte, S. Coseri*****, *Cellulose-based films with enhanced load of nitrogen containing heterocycles: the impact on the surface morphology and proton conductivity*, **Applied Surface Science**, **2023**, 607, 1550771. **IF = 7.392**; https://doi.org/10.1016/j.apsusc.2022.155077

***** *corresponding author*

Papers under review

1. Y. Liu, S. Zhang*, L. Li, S. Coseri, *Cellulose nanofibers extraction from unbleached kraft pulp for paper strengthening*, **Cellulose**, **2022** (*under review*)

Oral communications at conferences

1. G. Biliuta, R.I. Baron, S. Coseri, *Oxidation of cellulose under mild and selective conditions employing phthalimide N-oxyl radical*, Congresul internațional pregătim viitorul promovând excelența, Ediția a XXXII-a, February 28 - March 2, **2022**, Iasi, Romania.

2. A.L. Chibac-Scutaru, M.E. Culica, M. Asandulesa, S. Coseri, C*arboxylic groups enriched cellulose surfaces for advanced proton exchange membranes*, Polymer Network Group-PNG2022, June 12-16, **2022**, Rome, Italy.

3. I.S. Trifan, V. Melinte, A.L. Chibac-Scutaru, S. Coseri, *Effect of functionalization degree of celulose derivatives on their properties and photopolymerization profile*; XXXVI-a National Chemistry Conference, October 4-7, **2022**, Calimanesti-Caciulata, Valcea, Romania.

4. M.E. Culica, A.L. Chibac-Scutaru, V. Melinte, S. Coseri, *Versatile composite films based on cellulosic derivatives and they photocatalytic behavior*, International Chemical Engineering and Material Symposium, SICHEM 2022, November 17-18, **2022**, Bucuresti, Romania.

5. I.A. Duceac, S. Coseri, *Advances in magnetic nanocomposites: synthesis and characterization of new chitosan/pullulan/MNPs materials*, International Chemical Engineering and Material Symposium, SICHEM 2022, November 17-18, **2022**, Bucuresti, Romania.

6. I.S. Trifan, V. Melinte, A.L. Chibac-Scutaru, S. Coseri, *Photopolymerization profile of modified cellulose*, ICMPP - Open Door to the Future Scientific Communications of Young Researchers, MacroYouth 2022, November 18, **2022**, Iasi, Romania.

Poster communications at conferences

1. M.E. Culica, A.L. Scutaru, M. Asandulesa, S. Coseri, *Cellulose-derived platforms for emergent energetic applications*, Polymer Network Group-PNG2022, June 12-16, **2022**, Rome, Italy.

2. M.E. Culica, A.L. Scutaru, S. Coseri, *Tuning cellulose surfaces for better, more efficient and robust proton exchange membranes in fuel cells,* Polymer Network Group-PNG2022, June 12-16, **2022**, Rome, Italy.

3. M.E. Culica, A.L. Chibac-Scutaru, S. Coseri, *Insights on the cellulose-based surfaces with conductive properties,* XXXVI National Chemistry Conference, October 4-7, **2022**, Calimanesti-Caciulata, Valcea, Romania

4. M.E. Culica, A.L. Chibac-Scutaru, V. Melinte, S. Coseri, *Cellulose-based films with controlled load of 1-hydroxybenzotriazole applied in fuel cell technology,* XXXVI National Chemistry Conference, October 4-7, **2022**, Calimanesti-Caciulata, Valcea, Romania

5. A.L. Chibac-Scutaru, M.E. Culica, V. Melinte, M. Asanduleasa, S. Coseri, *Influence of 1-hydroxybenzotriazole loading on surface morphology and proton conductivity of cellulose-based films,* XXXVI National Chemistry Conference, October 4-7, **2022**, Calimanesti-Caciulata, Valcea, Romania

Initiation of a special issue by the project director as "*Guest editor*" at "**Energies**" journal.

[Energies] New Special Issue proposal – Accepted on 08.06.2022

Energies Editorial Office (June 8, 2022 11:23 AM)

To: "Sergiu Coseri" <coseris@icmpp.ro>

CC: "Allen Liu" <allen.liu@mdpi.com>

Dear Dr. Coseri,

Thank you very much for proposing a Special Issue: Natural polymers application in fuel cell technology. After our careful consideration, we believe it to be a promising topic and want to move forward with it. As such, your proposal has been approved and assigned to Allen Liu for further processing. They will contact you for further details regarding this Special Issue.

Kind regards,
Mr. Allen Liu
Assistant Editor
E-mail: allen.liu@mdpi.com

--

MDPI Branch Office, Beijing
Energies Editorial Office
E-mail: energies@mdpi.com
http://www.mdpi.com/journal/energies

MDPI
Postfach, CH-4020 Basel, Switzerland
Office: St. Alban-Anlage 66, 4052 Basel

MDPI | Journals | Topics | Information | Author Services | Initiatives | About | Sign In / Sign Up | Submit

Search for Articles: Title / Keyword | Author / Affiliation | Energies | All Article Types | Search | Advanced

Journals / Energies / Special Issue Proposal

IMPACT FACTOR 3.004 | CITESCORE 4.7 SCOPUS

energies

Submit to *Energies*

Review for *Energies*

Thank you for sending the Special Issue proposal. One of our editors will screen it and come back to you soon.

Journal Menu

- *Energies* Home
- Aims & Scope
- Editorial Board
- Reviewer Board
- Topical Advisory Panel

Special Issue Proposal Application

If you would like to propose a Special Issue topic for this journal, please complete and submit the following form. Our editors will get back to you shortly. For your Special Issue to form a cohesive article collection, we typically expect at least ten papers to be published, including research papers, communications, and review articles.

Personal Information

IMPACT FACTOR 3.252 CITESCORE 5.0

energies

Submit to Special Issue

Submit Abstract to Special Issue

Review for *Energies*

Edit a Special Issue

Journal Menu

- *Energies* Home
- Aims & Scope
- Editorial Board
- Reviewer Board
- Topical Advisory Panel
- Instructions for Authors
- Special Issues
- Topics
- Sections & Collections
- Article Processing Charge
- Indexing & Archiving
- Editor's Choice Articles
- Most Cited & Viewed
- Journal Statistics
- Journal History
- Journal Awards
- Society Collaborations
- Conferences
- Editorial Office

Journal Browser

volume

issue

Go

> Forthcoming issue
> Current issue

Vol. 15 (2022) Vol. 14 (2021) Vol. 13 (2020) Vol. 12 (2019) Vol. 11 (2018) Vol. 10 (2017) Vol. 9 (2016) Vol. 8 (2015) Vol. 7 (2014) Vol. 6 (2013) Vol. 5 (2012) Vol. 4 (2011) Vol. 3 (2010) Vol. 2 (2009) Vol. 1 (2008)

Affiliated Society:

PTZE

Special Issue "Natural Polymers Application in Fuel Cell Technology"

- **Print Special Issue Flyer**
- **Special Issue Editors**
- **Special Issue Information**
- **Keywords**
- **Published Papers**

A special issue of ***Energies*** (ISSN 1996-1073). This special issue belongs to the section "**D2: Electrochem: Batteries, Fuel Cells, Capacitors**".

Deadline for manuscript submissions: **31 May 2023** | Viewed by 72

Share This Special Issue

Special Issue Editor

Dr. Sergiu Coseri E-Mail Website SciProfiles

Guest Editor

"Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy, 41 A, Grigore Ghica Voda Alley, 700487 Iasi, Romania

Interests: polysaccharides; cellulose; bio-based materials

Special Issues, Collections and Topics in MDPI journals

Special Issue Information

Dear Colleagues,

Fuel cells are electrochemical, environmentally friendly appliances operating in clean, simple, and efficient conditions, which aim to convert chemical energy into electricity. With the technological surge in the field of information science, electronic miniaturization, and the continuing need for mobility, there have been growing demands for portable energy sources, such as fuel cells. Great achievements are reported on this matter, especially in terms of highly selective proton conductivity, extraordinary mechanical and chemical resistance, lower costs, and environmentally friendly characteristics.

Therefore, we believe that a Special Issue of the most recent research papers dealing with natural polymers as a key material for fuel cell applications can benefit the scientific community.

Potential topics include, but are not limited to:

- Proton exchange membranes;
- Cellulose-based membranes for fuel cell;
- Proton conductivity;
- Biobased membranes;
- Supramolecular architectures for ionic conductivity;
- Nanocellulose.

Dr. Sergiu Coseri
Guest Editor