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Report on the thesis manuscript of Mgr. Alina MADALINA DARABUT on the subject:
« Structural characterization and functional properties of eopy/graphite composites for fuel cel bipolar plates ».

(Defense planned April 16, 2025)

Ms. Alina MADALINA DARABUT's thesis work was carried out at Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University, under supervision of Dr. Yevheniia LOBKO and avdisoring of Prof. RNDr. Vladimir MATOLIN.
This thesis focuses on the design and characterization of new bipolar plates based on epoxy/graphite composites for PEMFC (proton exchange membrane for fuel cells). The aim of this study is the production of composite bipolar plates meeting the specifications of the (DOE) with improved specific performances in terms of electrical conductivity, thermal conductivity and mechanical resistance, while allowing lightening and low cost. To achieve this objective, this work is structured around 3 parts: 1) the preparation and characterization of thermally expanded graphite fillers, 2) the synthesis of graphene oxide and its interactions with expody resin and 3) the development and analysis of the properties of epoxy/graphite composites.

The 173-page manuscript (double-sided), written in English, is structured in a classic way in three main parts, with a general introduction and a state of the art in the first part, a description of the materials and analytical methods in the second part and the results and discussion in the third part (subdivided into chapters), all completed by a general conclusion and followed by attachments. This work is at the crossroads of several scientific fields including the modification/functionalization of conductive graphite fillers, the development of expoxy/graphite composites, their physicochemical characterizations, and the analyses of their electrochemical (electronic conductivity) and mechanical properties.

The first bibliographic chapter provides a state-of-the-art review of fuel cell membranes and bipolar plates made from polymer-based composites and graphite fillers. This bibliographic update is concise, well-documented and referenced, and, without being exhaustive, provides the essential

information needed to approach the other chapters while showing the importance and difficulty of the research carried out for the study of epoxy/graphite composite materials in relation to the DOE (Department Of Enery) recommendations.

The second chapter "*Experimental*" section is devoted to the presentation of the chosen materials (epoxy resin and graphite fillers), to the modification of the fillers, the preparation of composite samples in particular to allow the characterization of the matrix/filler interfaces as well as to the description of the different analysis techniques for the morphological and structural characterization of the materials, for the study of their electrical, thermal and gas barrier properties and their electrochemical behavior in fuel cell conditions. The development protocols and characterization techniques are well described and explained.

Given the importance of the role of bipolar plates in PACs, the study carried out by the candidate on the fine analysis of the properties of the different graphite fillers but also on the expoxy/graphite interfaces is relevant for a good understanding of the conduction mechanisms (electronic and heat transfers) and transport of molecules. The sample preparations are clearly described and demonstrate know-how and a good knowledge of the difficulties of preparing these types of assemblies.

From a characterization point of view, the analysis tools used are perfectly suited for measuring the performance of composites at a laboratory scale but also under the conditions of use of the PAC.

Regarding gas permeability (H_2 and O_2), the candidate was able to develop a permeation device based on an electrochemical process. This demonstrates the strong skills acquired by the candidate in the analysis and assembly of specific experimental devices.

Note, in equations 2.14, 2.15 and 2.16, the thickness is expressed by t which can be confusing with time. It would be appropriate to use another symbol like L, which is often used.

Since the permeability device is a homemade system, one may question the reliability of the measurements. How validate the measurements made by this setup? (reference polymer film? What standard within the measurement range used?)

The third part of this manuscript that corresponds to the heart of the manuscript and dedicated to experimental results and discussions, is divided into five sub-chapters.

The investigations conducted in this third part are well-conducted, and the summaries at the end of each subchapter provide a good overview of the main results.

These five chapters are part of a coherent and progressive scientific approach, beginning with the optimization of modified graphite fillers (TEG and TEGO), the characterization of filler/hardener and filler/epoxy resin interactions, followed by the preparation of epoxy-based composite films including one type of filler, then two types of fillers, and finally the production of the finished product in the form of bipolar plates. The first two parts of this chapter therefore deal with thermally modified graphite fillers (TEG) and then oxidized graphite fillers (TEGO).

The characterization results of the TEG fillers show the significant effect of temperature on the electrical and thermal properties of the fillers with an optimum at 600 °C. Note the lack of

uncertainties on the thermal conductivity results (Figure 3.6). The interpretation of these properties in relation to the structure/morphology of the treated fillers is clear and in agreement with the literature. The choice of the temperature of 500 °C to treat the graphite particles is fully justified. Concerning the oxidized graphene fillers, here again the characterization results (SEM, EDX, TEM, XRD, FTIR) validate the effectiveness of the chosen protocol and attest both to an effect on the structure (increase in interlayer spaces, reduction in the number of layers, reduction in the size of crystallites) and an increased presence of polar functions with a much reduced C/O ratio after oxidation of the TEG particles.

Spectroscopic analyses of TEGO/hardener (amine) interactions clearly highlight the establishment of chemical reactions that evolve with temperature. In the case of TEGO/epoxy interactions, very few reactions appear to have taken place, regardless of the temperature. What are the explanations for this lack of reactivity? What about the literature data? The presence of polar functions is crucial to promote interactions with the composite components. At this stage of the study, it would have been interesting to verify with non-oxidized fillers (TEG) as a reference. Given the importance of these interfaces on the electrical and thermal properties, it would also have been interesting to test the TEGO at 600°C, despite its higher cost, which showed much higher thermal conductivities. The lack of reactivity of the epoxy resin with TEGO fillers is a limiting factor. What strategies could the candidate propose to obtain more interactions between the resin and the TEGO filler? The candidate focused on pER-1 resin. What about pER-2 using another diamine?

Section 3.3 discusses the composite material based on pER-2 and H2. This choice is puzzling given that the investigations into interactions were conducted with pER-1 and H1 resin. It is unfortunate that interactions with pER-2 were not addressed in the previous section. Subsequently, two types of composites are studied: one with a single type of filler (NG or SG or TEG) and the second combining two types of fillers (SG+TEG).

However, the absence of TEGO is questionable. Why not try oxidized fillers, which seem more appropriate for ensuring interface quality?

Regarding the first type of composite, the conductivity results are entirely consistent with the filler morphologies, since the lowest percolation threshold is achieved for TEGs with sheet-like structures, which facilitate conduction paths. Also, the through and in-plane electrical conductivity results clearly highlight the effects of filler orientation and (an)isotropy in the epoxy matrix. It is regrettable that SEM or TEM images do not allow for a clearer visualization of the dispersion and orientation quality of the TEG fillers.

For measurements at 80°C, Figure 3.27-b appears identical to Figure 3.5-b. Is this an error?

The interpretation of the results is based on the glass transition temperatures of the composites (Figure A27). The effect of fillers on the Tg of the epoxy resin is not really discussed. How can we explain the reduction in Tg with the presence of fillers, as it should provide a reinforcing and constraining effect on macromolecular chains? Is it related to an increase in free volume at the interfaces? The measurements taken at 80°C occur with the onset of the glass transition of the

materials. Has the candidate observe some changes in conductive properties due to some macrolomecular chain mobilty ? What about the stability in time because of risks of relaxation? With operating conditions of PACs, it is important to consider the effect of the presence of water, and so on the Tg of the composites. Epoxy resins are sensitive to water, so the Tg can decrease significantly. It would have been interesting to verify the impact of the presence of water on the thermal and mechanical behavior of the filled composites at 80°C, then beyond.

In the second part of this study, composites with two types of fillers are studied. In view of the previous results, this approach of combining the best SG and TEG fillers is relevant and original, especially since the DOE criteria in terms of electrical conductivity and mechanical properties were met, with a higher Tg (120°C) and for a total of 75 wt % fillers, the most promising material being TEG+SG/ER-2 (5+70/30 wt%).

The permeabilities to dihydrogen and dioxygen were measured for a composite film with 85 wt% of SG fillers and for different catalyst concentrations (Pt). Why this choice of composite when the previous study shows an interest in the TEG+SG/ER-2 composite film (5+70/30 wt%)? Here again, the candidate should provide additional information on her motivation in the selection of materials. Furthermore, no information is given on the thickness of the samples, the reproducibility (number of samples tested?), the measurement conditions (temperature, humidity)? The linear evolution of the permeation fluxes with pressure is consistent with a constant permeability coefficient (Eq. 2.16). Please note that the unit of P is incorrect ($cm^3(STP).cm^{-2}.s^{-1}Pa^{-1}$). It takes into account the thickness and must be expressed in $cm^3(STP).cm.cm^{-2}.s^{-1}Pa^{-1}$. Also, the permeability data in Table 3.11 are expressed in different units. For comparison, it would be appropriate to convert the values into the same unit, such as Barrer (10^{-10} $cm3(STP).cm.cm^{-2}.s^{-1}.cmHg^{-1}$), the conventional unit for gas permeabilities of polymers. According to the calculations, the value of P to O_2 for 0.4 $mg.cm^{-2}$ Pt would be $7.3x10^{-10}$ $cm^3(STP).cm^{-2}.s^{-1}Pa^{-1}$. This value would correspond to 9732 Barrer, which is not an excellent barrier, contrary to what the candidate claims. Also, comparing this value with the DOE is not relevant since the measurement conditions are probably different and knowing that the DOE recommends a permeance (P/L) (according to the given unit) and not a permeability coefficient P (independent of the thickness). This part dedicated to the study of gases is debatable and should be reviewed with further clarifications and corrections.

The last part is devoted to the study of bipolar plates made from different types of fillers (Gr, CF, EG, etc.) and resins (mainly PR). A comparison of the performance of these plates is made with commercial plates (CGBP). For homemade plates, despite much lower performance in electrical conductivity, the power densities nevertheless remain quite high. Through this study, the candidate succeeded in optimizing the performance of the PACs by resizing and modifying the geometries of the gas flow channels. However, there are still some questions about the very nature of the PCBP1 and PCBP2 bipolar plates? The lack of details on the materials tested would indicate a certain

confidentiality. Is this the case? And if so, why not mention it? The study focused on Epoxy resin? Why phenolic resins (PR)? Table 3.13, however, gives a result for SG/ER (90/10 wt.%). What about TEG+SG/ER composites? We would have liked to see initial tests of manufacturing bipolar plates with these composites. This last part, supposed to meet the final objective of the thesis work, leaves us at the end with an optimized format of bipolar plates but without the epoxy resin-based composites of the study.

GENERAL OPINION

The manuscript, written in English, is well-structured, with a well-conducted bibliographic study, clear text illustrated with graphs, tables, and diagrams, making it easy and enjoyable to read.

Through this research, Ms. Alina Madalina Darabut has acquired solid experience in the design and characterization of epoxy-graphite composite bipolar plates for the development and improvement of fuel cells.

Substantially, the candidate has successfully drawn on multidisciplinary skills in the physical chemistry of organic/inorganic materials, with strong theoretical support and characterization tools and methods perfectly suited to the research being conducted. Overall, through this systematic and balanced study, both from a fundamental and applied perspective, the analysis of experimental data from electrochemical measurements (intensity-potential curves, chronopotentiometry, impedance, etc.), thermal and mechanical measurements, and correlated with the morphological properties of the fillers, the structural properties of the composites, the quality of filler dispersion and epoxy/graphite interfaces, and their electrical and mechanical behaviors, is fairly well discussed and argued, and the interpretation of the results demonstrates the candidate's good mastery of the subject. All of these results therefore demonstrate the very strong potential that these epoxy/graphite composites offer for bipolar plates. It should be noted, however, that although the manuscript provides a coherent and well-synthesized whole of the numerous works carried out, certain parts suffer from a lack of information on the analysis conditions and the choice of materials, which may vary from one part to another and also some verification (gaz permeability, reproducibility).

In conclusion, it appears that Ms. Alina MADALINA DARABUT has carried out substantial and high-quality research on a complex subject with a relevant and structured scientific approach. The results of this research constitute an important contribution to the understanding and optimization of bipolar plates, which play a crucial role in the development of fuel cells.

For all these reasons, I strongly recommend the defense of this defense for the doctoral degree of the Faculty of Mathematics and Physics, Charles University (Prague), in the Physics of Surfaces and Interfaces branch of the study.

Done in Mont-Saint-Aignan (France), March 28, 2025

Stéphane Marais, Professeur des Universités