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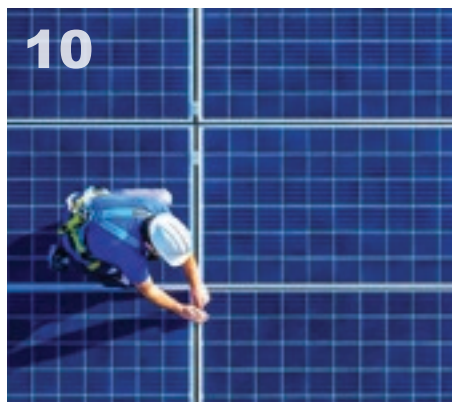
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Welcome



Alireza Hedayatpour
Managing Director
ARA Spectron
Scientific & Laboratory
Equipment Trading L.L.C

EMBRACING A SUSTAINABLE FUTURE: INNOVATIONS IN SUSTAINABLE ENERGY

As we present this special edition of "ARA Information," Sustainable Energy " we are reminded of the transformative power of sustainable innovations. The quest for greener energy solutions is no longer a mere aspiration but a necessity. This edition delves into groundbreaking research and technologies shaping the future of energy, with a focus on sustainable, renewable, and environmentally friendly options.

As we navigate the challenges of climate change and energy security, the role of Sustainable Energy technologies cannot be overstated. This edition of "ARA Information" provides a comprehensive overview of the innovations driving the Sustainable Energy sector forward. From advanced storage solutions to solar technologies and biofuel advancements, the path toward a sustainable energy future is filled with promising developments.

HARNESSING THE SUN WITH ADVANCED PHOTOVOLTAIC MATERIALS

Our energy future is increasingly being shaped by solar power advancements. "NIR Spectroscopy for Photovoltaics Materials Analysis" highlights the role of near-infrared (NIR) spectroscopy in advancing solar technologies. By providing critical insights into the reflectivity and efficiency of photovoltaic materials, NIR spectroscopy aids manufacturers in enhancing the performance of solar panels. The drive to improve polycrystalline thin-film solar cells, such as CdTe and CIGS, underscores the continuous efforts to reduce costs and improve efficiency, making solar power more accessible and competitive.

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THE PROMISE OF BIOFUELS: A RENEWABLE ENERGY SOURCE FOR TOMORROW

Biofuels remain at the forefront of the renewable energy conversation. "Biofuel Energy Source for the Future" provides an in-depth look at the evolution of biofuels from first-generation options, which relied heavily on food-based crops, to more sustainable second-generation biofuels derived from non-food biomass. These advancements not only minimize competition with food production but also offer a more climate-friendly alternative to fossil fuels. As the article explores, second-generation biofuels harness the energy-rich parts of plants that are otherwise considered waste, contributing to a circular and sustainable economy.

INNOVATIVE ANALYTICAL APPROACHES IN BIOMASS CONVERSION

The transformation of biomass into a viable energy source is complex, requiring precise analytical tools to optimize conversion processes. The article "HPLC Approaches in Biomass as Renewable Energy" underscores the significance of High-Performance Liquid Chromatography (HPLC) in analyzing biomass. This technique allows for the detailed examination of biomass composition, crucial for enhancing conversion technologies like fermentation and pyrolysis. By identifying key chemical constituents, HPLC aids in optimizing processes to increase energy yields, making biomass a cornerstone of the renewable energy landscape.

SURFACE AND POROUS STRUCTURE EFFECTS ON BINDER-FREE CARBON CATHODES IN MICROBIAL FUEL CELLS

In this study, Pasternak et al. examine the long-term effects of surface and porous structure on the performance of carbon powder cathodes in microbial fuel cells (MFCs) over 300 days. The research investigates two types of activated carbon, CWZ-22 and CWZ-35, and a modified version with silica nanoparticles, CWZ-22/Si. The study reveals how variations in surface area and pore size distribution significantly influence MFC performance, including biofilm development, power density, and cathodic fouling. The findings provide valuable insights for optimizing cathode materials in MFCs, focusing on cost-effective, durable alternatives to platinum-based cathodes.

We hope this edition inspires continued exploration and adoption of renewable energy solutions, fostering a world where clean, sustainable energy is accessible to all.

JOIN US IN THIS JOURNEY TOWARDS A GREENER FUTURE



SPECTROSCOPY APPLICATION CHALLENGE 2024

We are excited to announce that ARA Spectron's Spectroscopy Application Challenge for 2024 has officially begun.

This year, Researchers from GCC countries can participate for a chance to win 10,000.00 AED.

Submit an abstract of your spectroscopy research with a photo or video of your application for a chance to win 10,000.00 AED in cash, up to November 30th 2024.

In addition, ARA Spectron collaborates with researchers to discover, refine, and deliver new approaches to solving their problems with spectral technologies.

The researchers can benefit from the free technical support of our spectroscopy application/product managers team for this challenge up to the winner announcement time on December 15th and for their other requests anytime.



ION CHROMATOGRAPHY APPLICATION IN Bio diesel as new source of Energy



Houshang Noorizadeh
PhD in Analytical Chemistry
Chromatography Product Manager

Summary: Biodiesel is a renewable biofuel made from biological process. Its properties and impurities depend on its source and production method. Driven by the need to reduce dependence on fossil fuels, mitigate global warming, and meet growing energy demands, biodiesel and bioethanol have emerged as leading alternatives. Despite historical challenges with low-quality production causing engine problems, the establishment of international standards and quality controls has improved acceptance. The use of advanced ion chromatography systems, plays a crucial role in ensuring the purity and quality of biodiesel.

Introduction

Biodiesel is a renewable biofuel, a form of diesel fuel, derived from biological sources like vegetable oils, animal fats, or recycled greases, and consisting of long-chain fatty acid esters. It is typically made from fats.[2][1]

The physical and chemical properties of biodiesel vary depending on its source and production method. The US National Biodiesel Board defines "biodiesel" as a mono-alkyl ester.[4]

The main driving forces behind biofuels are the

declining supply of fossil fuels, the world's growing thirst for, global warming, and the desire to reduce dependence on fuel imports. Additionally, most biofuels are produced through direct manufacturing processes, are easily biodegradable, non-toxic, have low emission profiles, and can be used either pure or mixed with conventional fuels. Currently, biodiesel and bioethanol are the leading alternative fuels, guided by recent regulations such as the U.S. Department of Energy's Federal Biobased Products Preferred Procurement Program (FB4P) or the European Union's Directive.

The concept of using liquid biofuels dates back to 1895 when German engineer Rudolf Diesel developed the first engine to run on vegetable oil. At that time, engines were easily adaptable to viscous vegetable fuels with their large injectors. However, due to low oil prices, engine technology increasingly adapted to consume conventional low-viscosity fuels. As a result, vegetable oils only gained attention during times of high oil prices. Generally, bioethanol is made from sugar, starch, or lignocellulosic biomass. The microbial fermentation of biomass-derived sugars via yeast is a well-established technology commercially applied on a large scale. In contrast, starch-based biomass with its larger carbohydrates is not directly fermentable. Starch-containing feed must be converted to sugar prior to yeast fermentation. The fermentation of relatively

dilute aqueous solutions produces ethanol, which is distilled for subsequent use as fuel to yield %95 ethanol. "Anhydrous" %99 ethanol is mainly produced by physically absorbing water using molecular sieves.

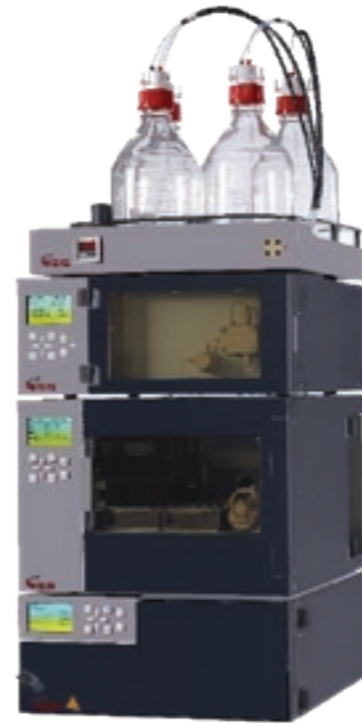
Due to the reversible nature of the reaction, a large amount of alcohol shifts the equilibrium towards the products, ensuring complete conversion to esters. After the transesterification reaction is complete, the biodiesel phase is separated from the denser glycerol phase by gravitational settling or centrifugation. The methyl esters, still containing significant residual alcohol, traces of glycerol, and unreacted caustic soda or soaps, are then washed with water. Water and water-soluble impurities, such as unreacted feedstock or mono- and diglycerides, are removed through further steps like distillation or evaporation.



Despite all the benefits mentioned at the beginning of this article, biofuels have struggled for acceptance since their inception. Reports highlighting engine problems due to low-quality biofuel discredited the promising biofuel path. Poor-quality biodiesel, often produced from raw feedstock in home plants without control, contained harmful contaminants that clogged injectors, caused severe corrosion, and blocked fuel systems. Reliable quality standards were necessary before the quality of biofuels—and thus consumer and automotive industry trust—could improve.

There are numerous international standards and test methods for analyzing biodiesel and its impurities, many of which utilize ion chromatography for this purpose.

ASTM D 6751 | ASTM D 4806 | ASTM D 5798
 ASTM D 512 | ASTM D 7318 | ASTM D 7319
 ASTM D 4806 | EN 14213/14214 | EN 14108
 EN 14109 | EN 14538



Experimental

The 2600A Inorganic Anion/Cation Analyzer, an ion chromatography system supplied by ARA Scientific company (German), includes two double piston high-pressure pumps, a fully automated injection system, two high-resolution polymeric column, an anionic suppressor, two highly sensitive conductivity detector and instrument control and data processing software.

(a) Alkali metal and alkaline earth metal determination
 Following transesterification and subsequent processing, biodiesel may contain residual alkali and alkaline earth metals as contaminants. Sodium and

potassium residues usually result from the use of their respective hydroxides during the transesterification process, whereas calcium and magnesium residues often come from using hard water in impurity extraction or from certain adsorbents employed for impurity removal. According to Standard DIN EN 14214, the maximum allowable cumulative concentration for both sodium and potassium (alkali metals) and magnesium and calcium (alkaline earth metals) is 5 mg/kg. These cations can be effectively and precisely measured in a single ion chromatography analysis.

Sample Preparation

The samples are first extracted using dilute nitric acid, followed by dialysis. After these steps, they are directly injected into the ion chromatography (IC) system for analysis (figure 1).

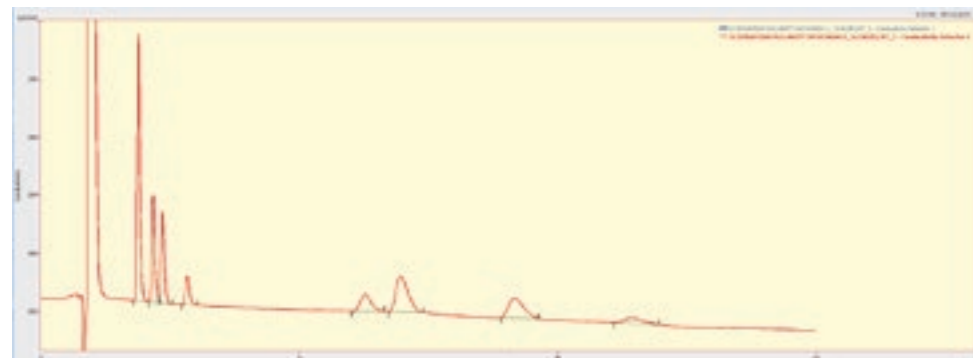


Figure 1: Analysis of alkali metals and alkaline earth metals (lithium, sodium, ammonium, potassium, calcium, magnesium, barium and strontium) in biodiesel by ion chromatography
 Eluent composition: 4mM Methane Sulfonic Acid
 Flowrate: 1 ml/min
 Temp.: 40 °C
 Detection: none suppressed conductivity

(b) Chloride and sulphate determination

Biodiesel contamination with inorganic anions such as chloride and sulfate can impair engine function by causing the formation of salts that obstruct filters and fuel injectors. Moreover, these salts can lead to corrosion of vehicle components that are in contact with the fuel. To mitigate these effects, the ethanol specification ASTM D 4806 restricts the levels of sulfate and chloride to 4 mg/L

and 40 mg/L, respectively.

ASTM D 7319 outlines a method involving direct injection and suppressed ion chromatography for quantifying chloride and sulfate anions. In this technique, chloride and sulfate are separated using an anion exchange column after being directly injected, and their concentrations are measured through suppressed conductivity detection.

Sample Preparation

To analysis of the inorganic anion add hydrogen peroxide solution to the ethanol sample. Next, directly inject this prepared sample into the ion chromatography system. The entire analysis process can be automated using the automatic sample injection system. Figure 2 show the chromatogram for this analysis which is determined acetate, formate, chloride, nitrate and sulfate .

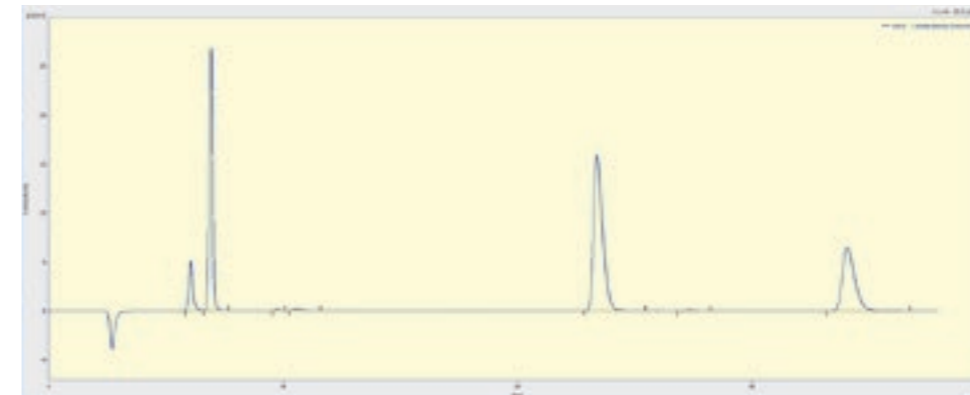


Figure 2: determination of anions in biodiesel with ion chromatography
 Eluent composition: 3.6 mM Na₂CO₃
 Flowrate: 0.8 ml/min
 Temp.: 40 °C
 Detection: suppressed conductivity



Conclusion

The application of ion chromatography in biodiesel analysis is critical for ensuring the quality and purity of this renewable biofuel. Biodiesel, derived from biological sources, presents varying physical and chemical properties depending on its production methods, making accurate testing essential. Ion chromatography, particularly through methods outlined in ASTM standards, effectively measures impurities such as alkali and alkaline earth metals, as well as inorganic anions like chloride and sulfate. This technology helps address contamination issues that can impair engine performance and cause corrosion, ensuring that biodiesel meets stringent quality standards. The advanced ion chromatography systems, including the 2600A Inorganic Anion/Cation Analyzer, provide precise and reliable results, supporting the broader adoption of biodiesel as a viable alternative fuel by enhancing its quality control processes.

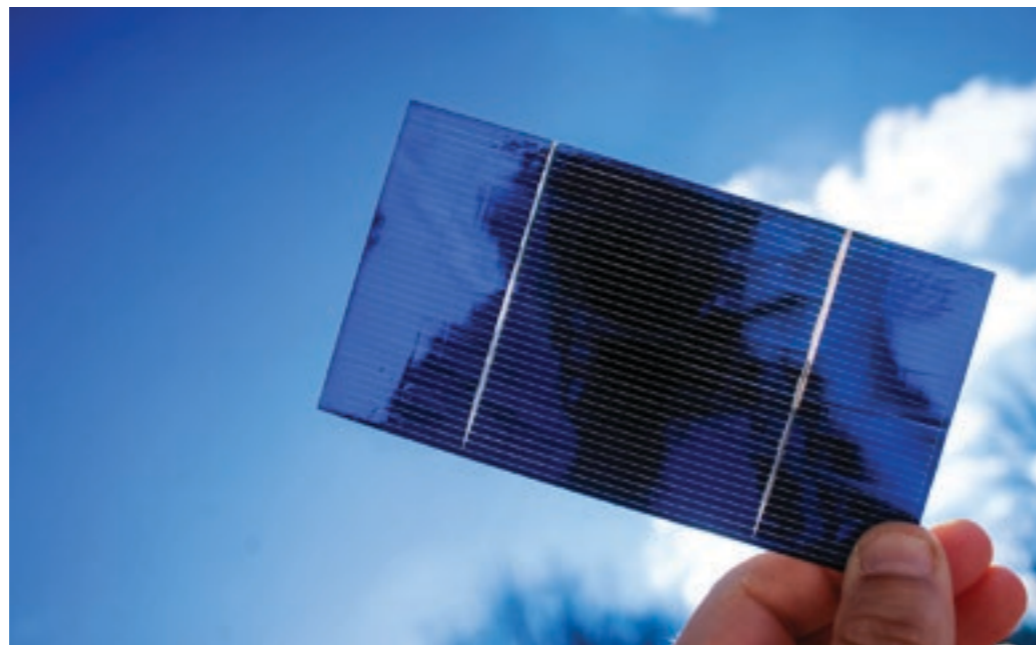
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5. www.Shodex.com

INSPECTION OF thin-film solar cell processing by laser induced breakdown spectroscopy and neural network



Mitra Amoli Diva
PhD in Analytical Chemistry
Spectroscopy Application Manager

Abstract:

LASER SCRIBING IS used in the manufacturing process of thin-film solar cells. Selective material ablation is required to remove the desired layers while minimizing the damage caused to the rest of the structure with the aim of improving efficiency of solar cells and reducing production costs. To that end, laser induced breakdown spectroscopy (LIBS) assisted by artificial neural networks (ANN) was implemented as monitoring tool during laser scribing. The performance of this method to identify transition between layers presented low error and high precision. Therefore, the feasibility of using plasma emission spectra for inspection of solar cell processing was demonstrated.

Introduction:

A growing need in alternative energies has led to an increase in the demand of photovoltaic devices. Solar cells based on thin-films are flexible, light and economic and require a small amount of raw material

to be produced. Laser processing is implemented in solar cell manufacturing due to its high speed and reliability to reduce production costs and to improve performance of solar cells. Laser-Induced Breakdown Spectroscopy (LIBS) is an analytical technique based on ablating a small portion of a sample with a highly focused laser beam to create a plasma plume. Plasma emission is optically collected and spectrally resolved for subsequent analysis. Each sample presents characteristic plasma emission spectra which can be used as "fingerprints" for sample classification. LIBS spectra analyzed by artificial neural networks (ANN) have been used for classification of diverse sample types producing reliable results [2-4].

The objective of this study was to employ plasma emission induced during laser machining of thin-film solar cells as a feedback signal to inspect the process. Artificial neural networks were used to analyze LIBS spectra to identify transitions between layers and to improve selective ablation of laser processing.



Experimental:

Fig. 1 shows a schematic of the experimental setup. A diode-pumped, solid-state Nd:YVO₄ laser (Super Rapid, Lumera Laser) was used. Its characteristics were: wavelength of 532 nm, pulse width of 7 ps, energy per pulse of 30 μJ and repetition rate of 50 kHz. The spot size on the surface was ca. 35 μm. Plasma emission was acquired with a 0.75x microscope objective coupled to a spectrometer (USB2000+, Ocean Optics). An acquisition window of 100 ms was used. A notch filter for 532 nm was needed to protect the spectrometer from reflected laser light. A simplified diagram of a CIS-based solar cell is depicted in Fig. 2a. The layers and thicknesses are, from top to bottom:

- Zinc Oxide (ZnO) of ca. 2 μm (front contact)
- Cupper-Indium-Diselenide or CIS (CuInSe₂) of ca.
- Molybdenum of ca. 0.5 μm (back contact)
- Glass substrate of ca. 5 mm

The samples used in this investigation emulate the conditions faced during industrial manufacturing of solar cells.

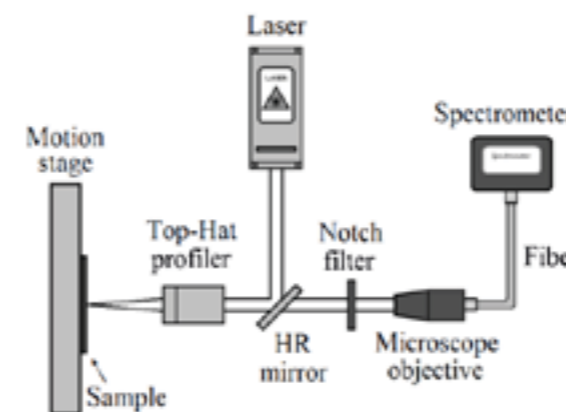


Figure 1. Experimental setup used for laser processing of solar cells and simultaneous plasma emission acquisition.

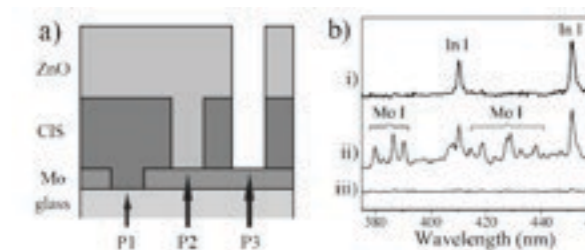


Figure 2. a) Simplified diagram of a thin-film solar cell based on CIS. P1, P2 and P3 represent the processing steps of layer separation. b) Reference spectra of i) CIS layer, ii) Mo layer with In impurity and iii) glass substrate.

Solar cells processing consists of scribing channels on the multi-layer structure to produce conductive paths between adjacent cells. The processing steps considered are:

- P1, removal of Mo film from glass substrate.
- P2, removal of CIS layer from Mo film.
- P3, removal of ZnO and CIS layers from Mo film.

Results of laser processing of thin-film solar cells are expected to present narrow channels with clean edges in order to maximize useful raw material and to increase area of light collection. Implementation of an inspection method is recommended to improve selective ablation. Characteristic plasma emission of each layer can be used to identify desired channel depth to guarantee that just the targeted layers are removed, minimizing the damage produced to the rest. Multiple pass scribing was conducted on the same track to gradually increase channel depth. Simultaneously, plasma emission was acquired. Spectra presented a combination of features of various layers due to contamination of films and interaction of laser with the edges of channels. Therefore, a robust classification algorithm was implemented.

The artificial neural network developed was based on a 3-level structure consisting of input, hidden and output layers. A feed-forward perceptron with sigmoidal activation function was used. The inputs of the ANN consisted of 480 test spectra acquired during each scribing pass in the spectral band of 375-500 nm. Training procedure based on back-propagation algorithm was applied using 60 reference spectra corresponding to the desired channel depth of processing steps P1, P2 and P3. Spectra shown in Fig. 2b represent the signal to be detected by the algorithm in order to assure selective ablation. The network produced a single output indicating if test spectra belonged to the same class of reference spectra. When this occurred, the system considered that the desired channel depth was reached and laser scribing was stopped to avoid over processing.

Results and discussion:

Table 1 shows the results of evaluating the performance of applying artificial neural networks for the identification of the desired channel depth for processing steps P1, P2 and P3. Metrics of classification performance showed low error and high sensitivity, precision and specificity for identification of transition between layers for all the processing steps evaluated. However, the efficiency of identifying the desired channel depth can be improved. To this end, the enhancement of the neural network used and the implementation of different classification methods, e.g. linear correlation or PCA-SIMCA, are envisioned as future work to compare performance results and select the methods that enhances removal selectivity.

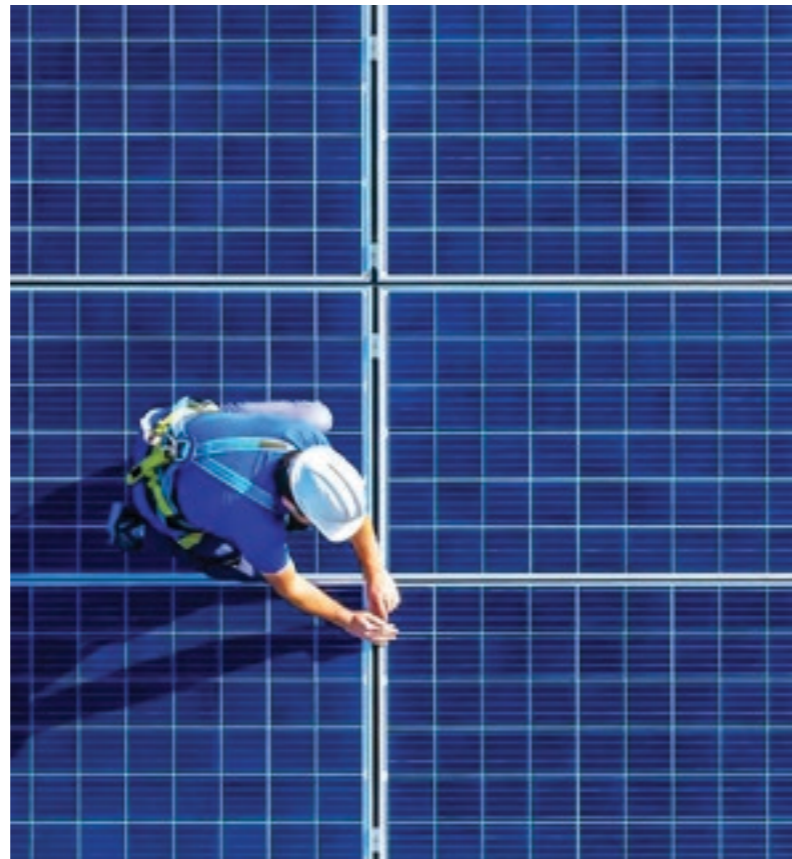


Table 1. Classification performance of ANN

Metrics	P1	P2	P3
Classification error	0.05	0.07	0.13
Sensitivity	0.98	0.98	0.96
Precision	0.99	0.96	0.92
Specificity	0.96	0.96	0.92

Conclusion:

Laser-induced breakdown spectroscopy assisted by artificial neural networks was implemented to accurately identify the transition between layers during laser scribing of thin-film solar cells to enhance selective ablation. Low classification error and high precision were observed for the studied processing steps indicating reliable identification results of transition between layers. This technique has the potential to be applied as an online inspection method of solar cell processing to improve the quality of selective machining.



Reference:

D. Diego-Vallejo, H. J. Eichler, D. Ashkenasi, Proceedings of ISOT'12, Intl. Symposium on Optomechatronic Technologies, 2022

NIR SPECTROSCOPY FOR Photovoltaics Materials Analysis



Mitra Amoli Diva
PhD in Analytical Chemistry
Spectroscopy Application Manager



Abstract:

COMPACT, MODULAR SPECTROMETERS are attractive tools for photovoltaic materials research and production. Some applications include evaluation of solar cell materials and quality control in solar cell module production. Here NIR spectroscopy was evaluated as a method to measure the reflection of materials used in photovoltaic panels (modules). Since, the manufacturers of thin film photovoltaic panels need NIR reflectivity analysis of several proprietary coated glass samples, the measurements were conducted from 1200-2100 nm under ambient lab lighting conditions.

Introduction:

Polycrystalline thin-film solar cells have reached a levelized cost of energy that is competitive with all other sources of electricity. The technology has significantly improved in recent years, with laboratory cell efficiencies for cadmium telluride (CdTe), perovskites, and copper indium gallium diselenide (CIGS) each exceeding 22 percent. Both CdTe and CIGS solar panels are now produced at the gigawatt scale. However, there are ongoing challenges, including the continued need to improve performance and stability while reducing cost. Advancing polycrystalline solar cell technology demands an in-depth understanding

of efficiency, scaling, and degradation mechanisms, which requires sophisticated characterization methods. These methods will enable researchers and manufacturers to improve future solar modules and systems. This article provides researchers with an overview of the thin-film solar cell characterization. Because the absorbance characteristics of photovoltaic panels are so critical to solar cell efficiency, determining the reflectivity at panel edges and elsewhere is a good indicator of the light loss at those areas. The use of anti-reflective coatings and glass dopants are among many materials manufacturers may evaluate to improve energy conversion efficiency.

Experimental Conditions:

Five coated glass samples were analyzed with an Ocean Optics NIR spectrometer that was customized with a -100 μm entrance slit and optimized for the range from 2100-1200 nm. (A preconfigured NIRQuest2.2+, which covers 2200-900 nm, would be the spectrometer of choice today.) The sampling setup comprised a tungsten halogen light source, 400 μm reflection probe and an optical stage. A specular reflection standard was used as a reference. Spectrometer operating software completed the setup. The glass samples were placed on the sample holder uncoated side down, to ensure the probe measured the reflection from the coating through the glass. The optical stage positioned the probe at 90° to measure specular reflectance. Measurements were taken under overhead lighting

conditions. The high-powered tungsten halogen light source provided continuous illumination from 360-2000 nm. The distance from the tip of the reflection probe to the surface of the sample was measured at ~ 7.0 cm for each sample, to simulate production conditions. Ocean Optics NIRQuest+ spectrometers have an enhanced optical bench design for high-sensitivity performance, allowing for low limits of detection at NIR wavelengths from 900-2500. NIRQuest+ has great thermal stability and can be used in the lab (Fig. 1) or on the line, such as on a conveyor belt, as its higher sensitivity allows users to capture the necessary spectra over shorter integration times. Also, at longer wavelengths, as in the evaluation of solar panel materials, NIRQuest+ measures diffuse reflection at low noise levels, resulting in cleaner spectra at wavelengths where distinct spectral features can be difficult to capture.

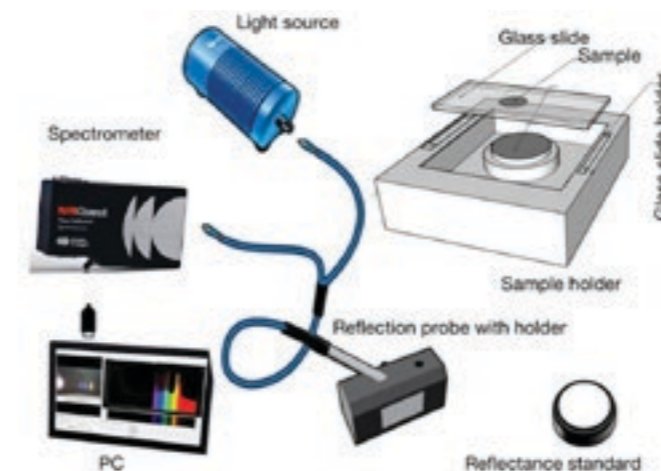


Fig. 1 Example of experimental set up for a laboratory reflection spectroscopy.

Results:

The reflection spectra for the samples demonstrated that reflection values increased as a function of wavelength comparably across all five samples, peaking at about 2000 nm (Fig. 2). Also, the gap between the least reflective and most reflective samples was relatively narrow at the lower and upper ranges of the wavelength range, with the greatest variation observed near 1700 nm. Spectra were captured without averaging or boxcar smoothing functions applied. Reflectance intensity of the coated samples ranged from ~%25 at lower wavelengths to as much as %80 at higher wavelengths. These values are relative to the response of the specular reflectance standard, which has nearly "flat" reflectivity across all NIR wavelengths.

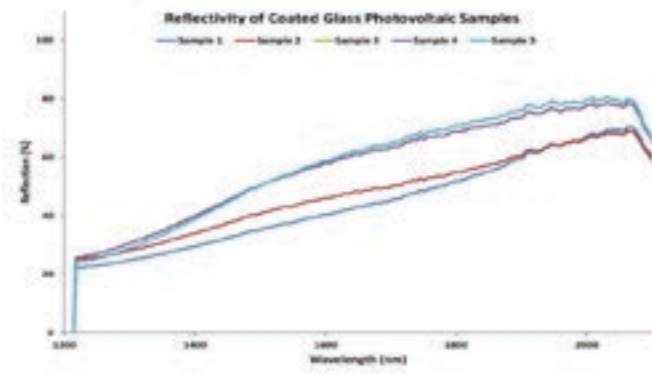


Fig. 2. NIR specular reflection measurements reveal spectral differences in coated glass samples evaluated for use in photovoltaic panels.

Conclusion:

As developers of photovoltaic materials seek improvement in cell efficiency, the need for convenient analytical tools to evaluate glass coatings, dopants and other materials is great. Optical sensing systems such as NIR spectrometers can be configured for both research lab and process line applications. NIR spectroscopy can be used to determine the specular reflectivity of coated glass samples relative to each other and to know reflectance standards. As a result, the solar light-capturing efficiency of the sample coatings can be inferred using Ocean Optics spectrometers and accessories.



Reference:

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Farid Sheikh-Hasani
MSc of polymer chemistry
Particle & Polymer Testing Product Manager

Introduction:

BIOFUELS are renewable energy sources derived from plant, algal, or animal biomass. Unlike fossil fuels such as petroleum, coal, and natural gas, biofuels can be replenished readily. Here are some key points about biofuels:

Types of Biofuels:

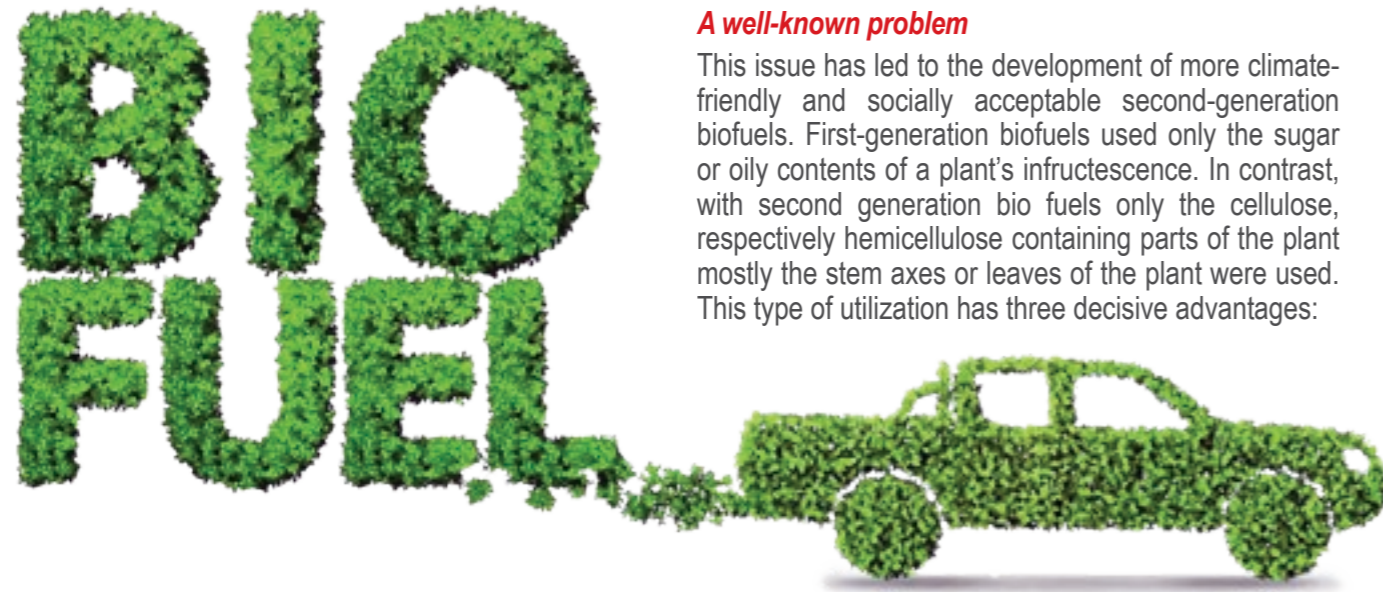
Liquid Biofuels: These are used primarily for transportation. The most common liquid biofuel is ethanol (ethyl alcohol), produced by fermenting starch or sugar. In the United States, ethanol is mainly made from corn, while in Brazil, it comes from sugarcane.

Solid Biofuels: Examples include wood, which can be burned directly for heat or used in power plants to generate electricity.

Environmental Benefits:

Biofuels are considered environmentally friendly because they reduce greenhouse gas emissions and dependence on finite fossil fuel resources and offer a promising alternative to traditional fossil fuels, contributing to a more sustainable energy future that everyone is talking about them. They are at present the only renewable alternative in the mobility sector and already today make up 6.1 % of the fuel consumption in Germany.

However, in the past months and years biofuels had the reputation to generate a social and environmental dilemma. For example, in developing countries large areas were cleared and used for sugar cane biofuel monocultures or similar and therefore were at the same time unintentionally in competition with the production of food.



A well-known problem

This issue has led to the development of more climate-friendly and socially acceptable second-generation biofuels. First-generation biofuels used only the sugar or oily contents of a plant's infructescence. In contrast, with second generation bio fuels only the cellulose, respectively hemicellulose containing parts of the plant mostly the stem axes or leaves of the plant were used. This type of utilization has three decisive advantages:

1. Non-competition with Food Production: The infructescence, such as corn kernels, can still be used for food production.
2. Energy-Rich Parts of the Plant: Cellulose-containing parts are energy richer.
3. Cost-Effectiveness: Cellulose or hemicellulose parts are more readily available and cheaper than nutrient-rich parts like monosaccharides, proteins, or lipids.

Bio fuels of the second generation are additionally more climate friendly than fuels of fossil energy sources like crude oil or natural gas, because during its growth, the plant draws from the atmosphere exactly the amount of the climate gas carbon dioxide, which is later released during the combustion in engines.

Production of bioethanol

Bio ethanol is produced and obtained via biocatalysts' (fermentation) and bio process technology. The pretreatment of raw materials for bioethanol production is a crucial step that enhances the accessibility of lignocellulosic biomass (LCBs) for further processing. In order to run such well-engineered bio process technology plants, as a rule, a preparation of the lignocellulose containing residual material is required. Not only the degree of the comminution (particle size) due to the installed technical components of

the plant, like valves and the built-in measurement instrumentation and control systems play a part, but rather what seems even more important is the produced by the comminution high surface and the associated residence time and fermentation period in the bio-fermenter. Hereby the used microorganisms and enzymes are given the opportunity in a time and resource saving approach to achieve the highest possible plant effectiveness.

The importance of the final fineness

Physical (mechanical) pretreatment includes milling (e.g., two-roll milling, ball, cutting or hammer milling), irradiation (gamma ray, electron beam, microwave) and other (e.g., hydrothermal, expansion, extrusion or pyrolysis) methods. After physical pretreatments, the reduction in particle size and crystallinity of lignocellulosic biomass has an impact on the increase of specific surface area and reduction of the degree of polymerization. However, the particle size has to be optimized (very small particles are not desirable) because of high energy consumption during milling and negative impact on the pretreatment. Many of the mentioned size-reduction physical methods are not economically feasible due to the very high energy demands. Extremely decisive though for the production of bio ethanol is the achievable final fineness. While the levels of size reduction and densification are dictated by the end use of the biomass, they are also limited by feedstock type and inherent material properties, equipment, and facility conditions. Here due to the utilized patented FRITSCH sample exhaustion, it is possible to produce sufficiently large amounts of bio mass with a particle size distribution from up to smaller than 250 μm , which then can be transferred to the fermentation plants without any problems. The attainment of the required final finenesses depends mainly on the type of commodities, as well as the regulating factors of the machines (sieve inserts / comminution principle). So inevitably the available sieve passage surface with the used 100 μm sieves are multiply reduced in comparison with the standard sieves, resulting in a high degree of physical strain on the sample material. This physical strain usually becomes noticeable through the generation of heat in the instrument, as well as a reduced throughput.

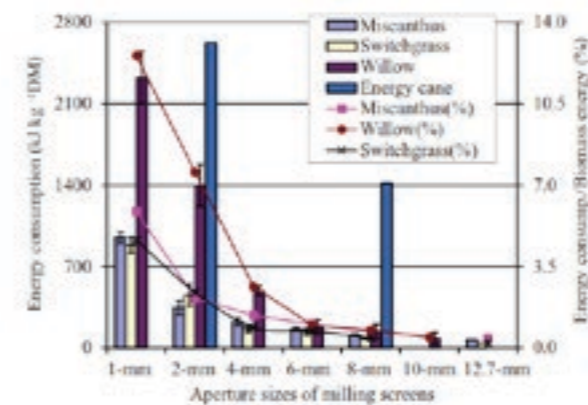


Figure 1 Specific energy requirement of biomass size reduction. Note: The right y-axis refers to the percentage of specific energy consumption of size reduction to biomass inherent heating value (PIHV).



Effective comminution of raw materials

For the comminution of the residual plant matter in many pilot plant stations and pilot installations FRITSCH Cutting Mills are utilized. Here especially the PULVERISETTE 19 in combination with the sample exhauster the cyclone separator. Advantages of this system are: easiest handling during cleaning and the exchange of the cutting tools and occupational safety thanks to the use of highly efficient vacuuming and particle separation via a high-performance Cyclone separator

All these problems can be avoided due to the directed high-volume flow of the exhaust system adapted to the Cyclone with 3840 l/min and 259 mbar negative pressure.

The use of two polyester filter cassettes ensures a constant high vacuum performance according to dust Protection class M. This is additionally supported by the permanent automatic, electromagnetic pulse Cleaning at the filter during continuous vacuum operation.



HPLC APPROACHES IN BIOMASS AS RENEWABLE ENERGY



Houshang Noorzadeh
PhD in Analytical Chemistry
Chromatography Product Manager

Summary: Biomass, a versatile and carbon-neutral source derived from organic materials, holds significant potential as an alternative to fossil fuels. The quantitative analysis of biomass is a very important phase in the biomass feedstocks conversion to fuels and chemicals. This article explores the role of HPLC in enhancing the utilization of biomass for renewable energy production. HPLC serves as a critical analytical technique in this context, allowing for the detailed analysis of biomass composition. By identifying and quantifying various chemical constituents, such as sugars, lignin, and other biopolymers, HPLC aids in understanding the potential energy yield and improving conversion processes like fermentation and pyrolysis.

Introduction

The growing demand for sustainable and eco-friendly energy solutions has directed significant attention towards biomass as a renewable energy source. Biomass, derived from organic materials such as plants, agricultural residues, and waste, presents a promising alternative to fossil fuels due to its abundance and carbon-neutral properties. However, the complexity and variability of biomass feedstocks pose challenges in optimizing their conversion processes into usable energy forms.

High-Performance Liquid Chromatography (HPLC) has emerged as a vital analytical tool in the study and utilization of biomass for renewable energy. HPLC enables detailed analysis and quantification of the diverse chemical constituents within biomass. This capability is crucial for understanding the composition and potential energy yield of different biomass types, as well as for monitoring the efficiency of various conversion processes, such as fermentation and pyrolysis.



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Through the application of HPLC, researchers can identify and measure the concentrations of key components, including sugars, lignin, and other biopolymers. This information is essential for enhancing biomass conversion technologies and developing more efficient and cost-effective methods for producing biofuels and other bio-based products. By providing precise and reliable data, HPLC supports the advancement of biomass as a cornerstone of the renewable energy landscape, contributing to a more sustainable and resilient energy future.

Biofuel is a general term used for the bioethanol and biodiesel. Bioethanol is the majority (~90%) of the biofuel used worldwide. It is considered as an ECO-friendly automobile fuel produced from sugar and starch in plants. Ideally the main source of biofuel is none-food source such as wood, algae, and inedible part of crops.

There are different biofuel production methods already used in industries, and the others that are under development. Most starting product is polysaccharide which needs to be broken down to monosaccharide in order to produce ethanol through fermentation process. Throughout the production, it is important to analyze various components generated. They are for quality

assurance purpose of raw material, final product, byproduct, and impurities, as well as for understanding of degradation mechanism and for recovery monitoring of final product. HPLC analysis is the most frequently used qualification and quantification method. Several methods using different HPLC systems and columns are introduced as below:

1. Saccharides in wood
2. Separation of hexose and pentose
3. Hydrolyzed dextran I
4. Hydrolyzed dextran II
5. Fermentation inhibitors (Organic acids)
6. Fermentation inhibitors (Furfurals)
7. Biodiesel composition analysis
8. Biomass (Lignin)
9. Biomass (Xylan)
10. Impurities (Glycerides)
11. Impurities (Organic acids)

Experimental

The following is needed for the Analysis of biomass composition: ISS Carb. Analyzer, ISS GPC Analyzer and ISS Organic Acid Analyzer including: high pressure pump, injection system, columns, guard columns, data acquisition system and chemicals.



Results and discussion

Several HPLC methods is described here to show capability of liquid chromatography system as robust technique for separation different component in biomass, byproducts, final product and other similar samples.

1. Saccharides in wood

Polysaccharide hydrolyzation is a prerequisite for biomass production: As oligomers need to be further processed into monosaccharides in order to produce bioethanol. Separation of oligosaccharides and monosaccharides can be achieved under simple HPLC conditions using proper HPLC column (figure 1). It works under size exclusion and ligand exchange modes.

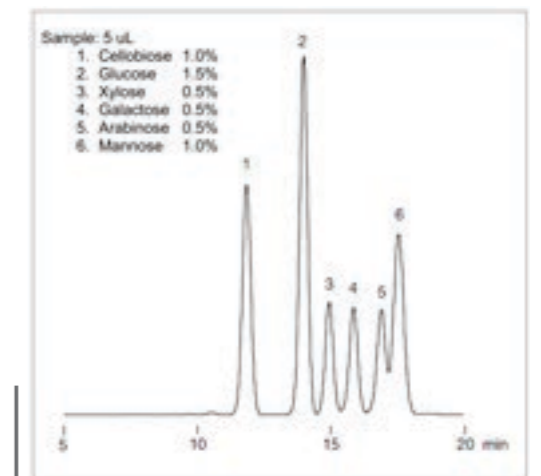


Figure 1: Separation of oligosaccharides and monosaccharides, Column Temperature: 85°C Detector: RI

2. Separation of hexose and pentose

Both hexose and pentose are the source of bioethanol. However, there is less number of enzymes that can decompose pentose compared to the enzyme that can decompose hexose. An amino column can be used to separate several hexose and pentose under isocratic elution (figure 2).

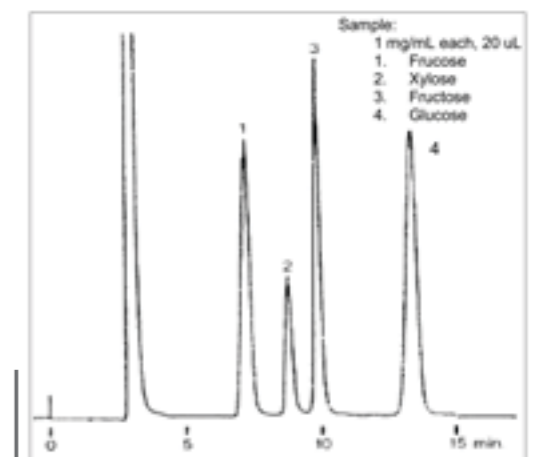


Figure 2: separate several hexose and pentose under isocratic elution, Column Temperature: 30°C Detector: RI

3. Hydrolyzed dextran I

Hydrolyzation process can be monitored by analyzing oligosaccharides with different molecular sizes. As shown in figure 3 and figure 4 size exclusion HPLC columns are suitable for the separation of polysaccharides under size exclusion mode. The same column can be also used to separate oligosaccharides from ethanol.

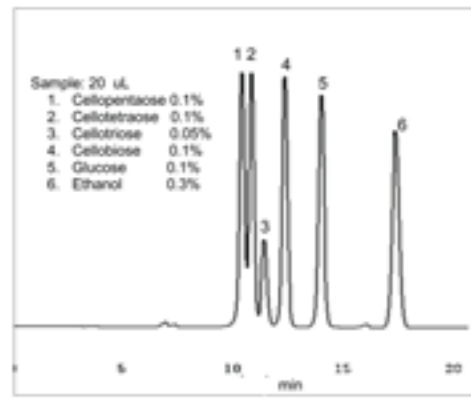


Figure 3: separation of polysaccharides with size exclusion Column, Column Temperature: 80 °C Detector: RI

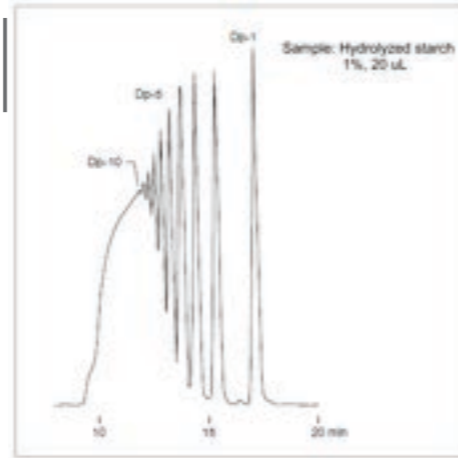


Figure 4: separation of polysaccharides with size exclusion Column, Column Temperature: 80 °C Detector: RI

4. Hydrolyzed dextran II

Amino HPLC column is also suitable for hydrolyzation process monitoring. Figure 5 shows gradient method provides better separation compared to an isocratic method. Evaporative light scattering detector (ELSD) is feasible for the detection of saccharides under gradient separation mode.

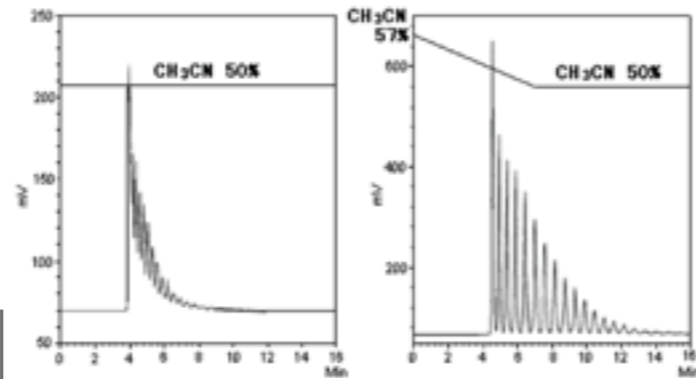


Figure 5: Sample: Hydrolyzed starch 20, %0.5 μ L, Eluent: (A) $\text{CH}_3\text{CN}/\text{H}_2\text{O}=50/50$, (B) 0 to 7min $\text{CH}_3\text{CN}/\text{H}_2\text{O}=43/57$ to 50/50 (Linear gradient), 7 to 16min $\text{CH}_3\text{CN}/\text{H}_2\text{O}=50/50$, Flow Rate: 1.0 mL/min Column Temperature: 30 °C, Detector: ELSD

5. Fermentation inhibitors (Organic acids)

Organic acids are one of biomass hydrolyzation byproducts. They prevent microorganism (i.e., enzyme) growth, and thus inhibit fermentation process. Figure 6 shows the column works under size exclusion and ion exclusion modes. It is suitable for the simultaneous separation of saccharides, organic acid, and alcohol. Elution time of organic acids can be controlled by optimizing the sulfuric acid concentration. For a better separation of DP4 and DP3, slower flow rate (0.6 mL/min instead of 1.5 mL/min) is recommended.

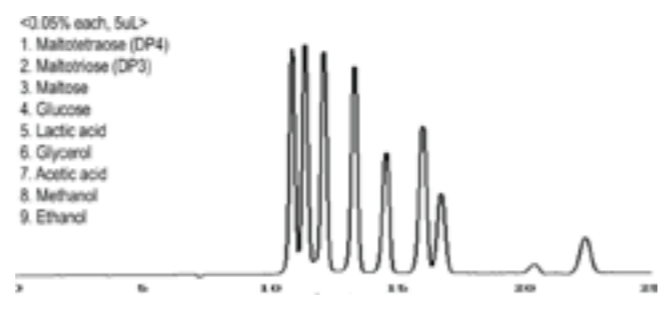


Figure 6: size exclusion and ion exclusion Columns use for organic acid separation, Temperature: 75 °C Detector: RI



6. Fermentation inhibitors (Furfurals)

Depending on the type of biomass and processing mechanisms, furfural and -5hydroxymethylfurfural (-5HMF) may be generated. They are considered as fermentation inhibitors. Figure 7 demonstrates using a combination of size exclusion and ion exclusion separation modes are suitable for the separation of cellulosaccharides and furfurals.

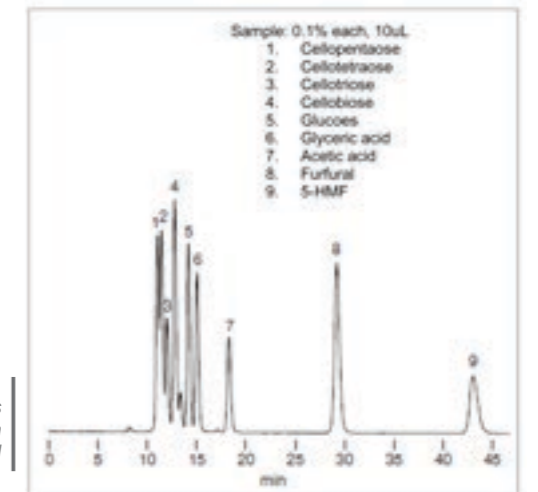


Figure 7: separation of cellulosaccharides and furfurals, Flow Rate: 0.6 mL/min Column Temperature: 75 °C Detector: RI

7. Biodiesel composition analysis

Fatty acid methyl esters are the components of biodiesel. They were analyzed using a polymer-based reversed-phase column. The chromatogram in figure 8 shows good separation between components.

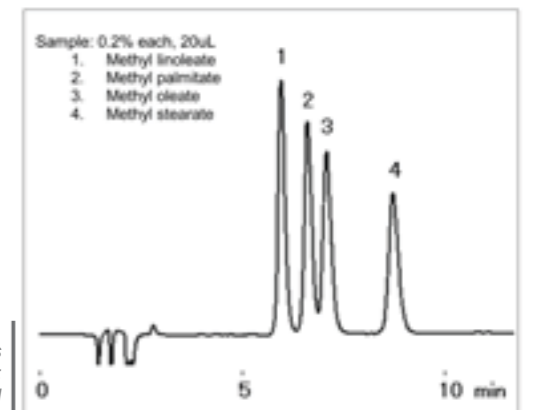


Figure 8: Fatty acid methyl esters separation, Column Temperature: 40 °C Detector: RI

Lignin is present in the cell wall of wood and other plants. Although it is an undesired component for the production of biofuel, the degradation products of lignin have potential use in biopolymers. Figure 9 shows GPC column is suitable for a wide range of MW determination analysis.

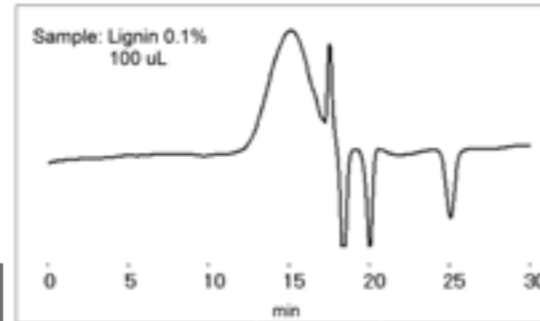


Figure 9: Lignin Analysis with GPC Column, Column Temperature: 50 °C, Detector: RI

9. Biomass (Xylan)

Xylan is a type of hemicellulose and present in most plants' cell wall. Hemicellulose, as well as cellulose, is used as a biofuel source. Hemicellulose is easily decomposed by weak acid or weak base and enzymes. GPC column is suitable for the MW determination and/or for Xylan decomposition monitoring (figure 10).

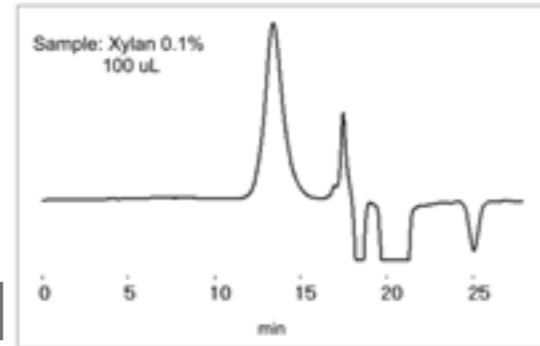


Figure 10: Xylan decomposition monitoring Column Temperature: 50°C Detector: RI

10. Impurities (Glycerides)

Glycerides are one of impurities found in biodiesel. Figure 11 shows the separation works under size exclusion mode to separate mono-, di- and tri-palmitins.

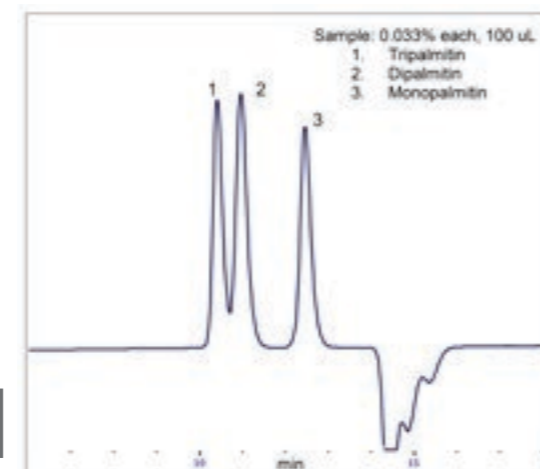


Figure 11: Glycerides analysis using size exclusion column, Column Temperature: 30 °C Detector: RI

11. Impurities (Organic acids)

Acetic, propionic, and formic acids are impurities of biofuel. They may cause fuel tank corrosion.

Strong anion exchange column provides simultaneous separation of organic acids, oxyhalides, and other anions. Figure 12 shows separation of 14 anions with this type of column.

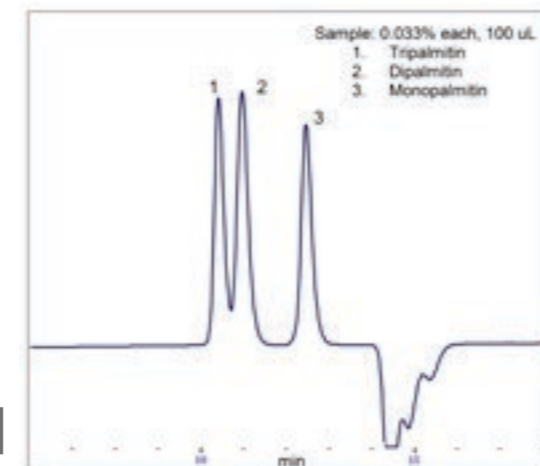


Figure 12: separation of organic acids, oxyhalides, and other anions, Column Temperature: 45 °C, Detector: Suppressed conductivity



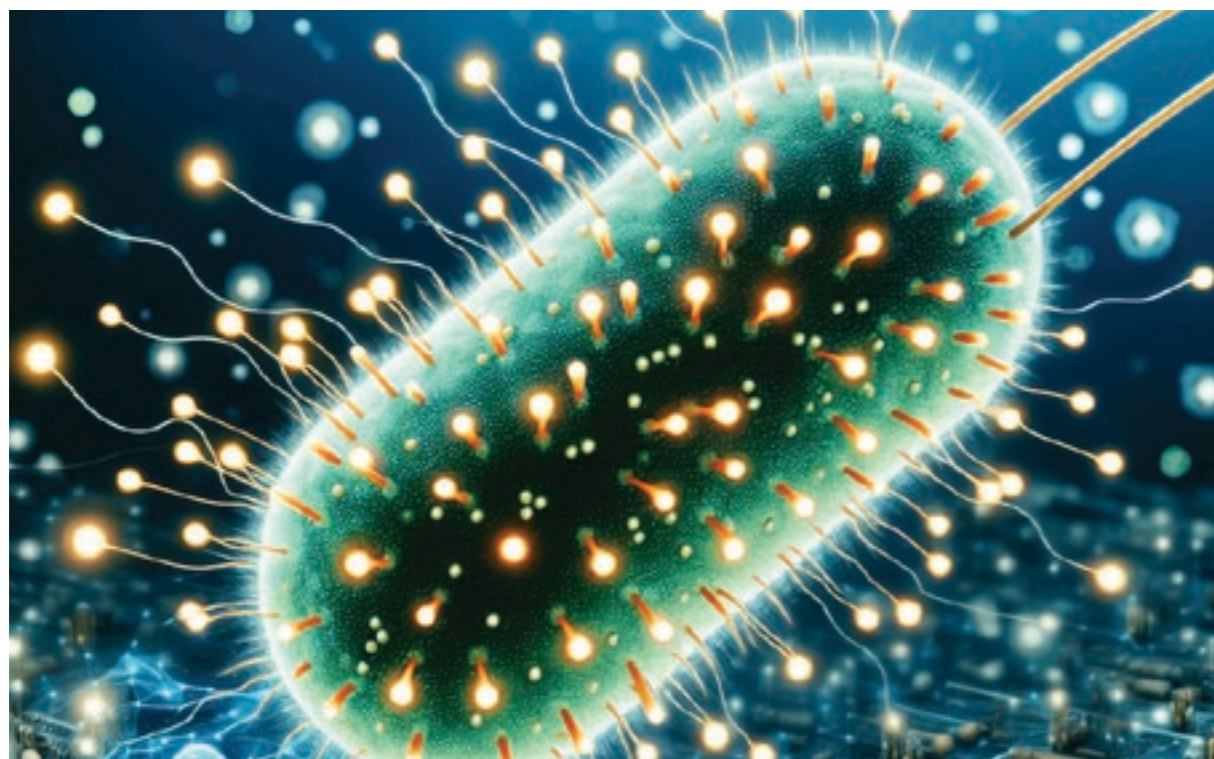
Conclusions:

HPLC systems offer a number of separation modes to analyze various components generated during biomass production. Presented methods include the analysis of raw material, final products, byproducts, impurities, as well as methods for saccharification/hydrolyzation monitoring.

Concentration and composition of mobile phase, temperature, and/or flow rate influence the separation performance of particular HPLC Analyzers. Therefore, for the specific set of target analysis, optimization of HPLC condition is highly recommended.

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THE EFFECT OF Surface and Porous Structure on Long-Term Performance of Carbon Powder Cathodes Without Binder, During a -300day Trial in Microbial Fuel Cells



Grzegorz Pasternak et. al
Researcher at Faculty of Chemistry, Wrocław
University of Science and Technology

Abstract:

COMPACT, MODULAR SPECTROMETERS The performance of microbial fuel cell (MFC) highly depends on the selection of appropriate electrode materials, in particular- cathodes. Herein, two different activated carbons (CWZ22- and CWZ35-) without binder, as well as the activated carbon modified with silica nanoparticles (CWZ22-/Si), were used to improve the performance of air cathodes. Nearly one year of operation of materials varying in surface area and microporous structure revealed significant differences in their dynamic behavior. This is the first work in which the pore size distribution and surface area are demonstrated to have a long-term impact on cathodic fouling, and, depending on these properties, this impact may be either positive or negative on MFC performance.

Introduction

The microbial fuel cell (MFC) is a bio-electrochemical reactor in which organic matter is oxidized by electroactive bacteria and converted to electricity. The typical MFC design comprises anode and cathode compartments, while more practical MFC designs use an air-cathode instead of a cathodic chamber. The air-cathode MFC consists of an anode chamber, separator, and cathode material in direct contact with air. In recent years, multiple pilot studies have emerged, in which MFCs were tested to treat urine, domestic, swine and brewery wastewater. In many cases, these studies were carried out over a short-term period of days rather than months. However, some examples of long-term studies have also been reported.

The cathode material is, in most configurations with an air-cathode, the key limiting factor in MFC performance. The component that decreases the activation energy of oxygen reduction reaction (ORR) in the most efficient cathodes is platinum. However, its high cost, combined with poor stability in the presence of contaminants

in wastewater, resulted in the development of new cathode catalysts to replace platinum. Among various cathodic catalysts, activated carbon (AC) is constantly attracting attention due to its low cost, large surface area, good catalytic properties, and ease of modification. Furthermore, AC can be obtained from many precursors, including food and post-industrial wastes.

the aim of this work was to investigate the long-term effect of the carbon surface properties, as well as the modification of the carbon surface with a silane/siloxane-based nanoparticle coating on the MFC performance. The study focused on commercially available activated carbons as the cathodes. Their efficiency and stability were assessed by electrochemical studies, surface and structural properties, and thermogravimetric analysis, providing insights into long-term operation and fouling of low-cost, commercially available materials for MFCs. This will help to provide indications for selecting the appropriate materials for upscaling projects.

Materials and Methods

2.1 Cathodes materials and module preparation

The cathodes were made of three types of carbon materials: activated carbons CWZ22- and CWZ35- (Grand Activated, Poland), produced by gas-steam activation of charcoal and CWZ22- modified by mixing with silane-siloxane microemulsion to achieve %1.8 (w/w) of final silicates concentration. This modified cathode was labelled within this manuscript as CWZ22-/Si.

2.2 Construction and operation of the MFC

This study used a single-chamber air-cathode MFC. The working volume was 20 cm³ and the anode chamber was separated from the cathode by a cation exchange membrane (CMI7000-, USA). A square-shaped anode was prepared from carbon veil with 316LSi steel wire. The MFCs were inoculated with a mixture (1:1) of two activated sludge collected from the aerobic chambers of the wastewater treatment plant.



2.3 Real time temporal monitoring and electrochemical experiments

Closed circuit voltage (CCV) was measured in real time and recorded with 3 min interval by a KEYSIGHT DAQ970A data acquisition system. Polarisation experiments were performed in three-electrode mode using a MultiPalmSens4 potentiostat (Palmsens BV, Netherlands). The anode was used as working electrode (WE), the cathode as counter electrode and the saturated Ag/AgCl electrode as reference electrode, placed in the anode chamber. Power and polarisation curves were obtained using the linear sweep voltammetry (LSV) technique in the potential range from open circuit potential to 0.0 V WE vs Ag/AgCl, at a scan rate of 1 mV s⁻¹. Based on the obtained experimental data, the maximum power density, current density, and optimal resistance were extracted.

Electrochemical impedance spectroscopy (EIS) was used to analyse the internal resistance of MFCs equipped with different cathode materials. The EIS experiments were carried out for the whole cell with the anode as a working electrode, while the cathode served as a counter and reference electrode. MultiPalmSens4 potentiostat (Palmsens BV, Netherlands) was used to perform the EIS. The applied alternating current with an amplitude of 10 mV had a frequency range of 100 kHz to 10 mHz. All EIS spectra were recorded when the MFC was in open circuit voltage (OCV) mode.

2.4 Performance of MFC

COD removal and coulombic efficiency and Energy production and efficiency were considered. The experimental data were analysed and visualised graphically using OriginLab 2019. Current, power, and internal resistance were calculated according to Ohm's law. $R=UIQ$, $P=U \times IW$, where U – voltage (V); I – current (A); P – power (W); R – resistance (Ω).

Results and Discussion

3.1 Real-time monitoring of MFC power performance

The MFC was supplied with three different carbon cathode materials. During nearly one-year operation of the microbial fuel cells, the power density output was monitored in real time. Fig. 1a shows the real time data of the highest performing MFCs for each cathode type. The highest power density of 18.8 W m⁻³ (377 μ W) was recorded for CWZ35- after 100 days of operation and resulted from the ongoing biofilm development due to the increased cathode performance. This was later proven through polarisation experiments. From this moment, a gradual decrease in the output power of MFCs with the CWZ35- cathode was observed. In contrast to these results, a further increase in the power density of MFCs was observed for CWZ22- and CWZ22-/Si, modified with silica nanoparticles. The highest power density obtained after 197 days of operation for CWZ22- was equal to 27.8 W m⁻³ (557 μ W) (Fig. 1b.), while the modified CWZ22-/Si showed a maximum real-time power density lower by %22 after 183 days (when compared to CWZ22-). In the 7th month of operation, a significant decrease in the power of CWZ22-/Si was observed.

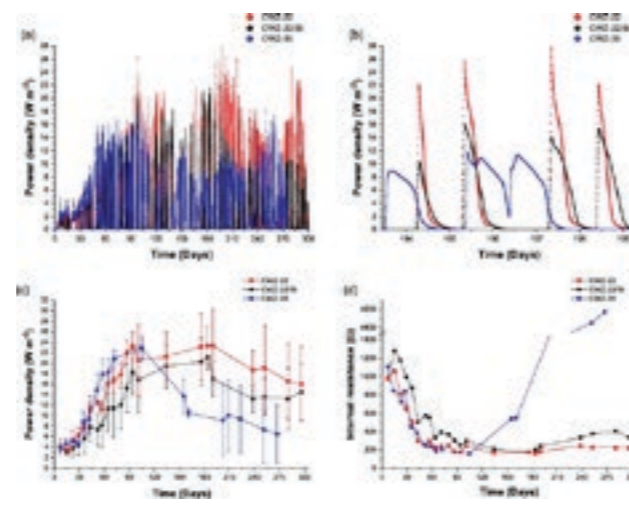


Figure 1: Real-time temporal power density output (a) and the characteristics of exemplary feeding cycles (b). Graph of the changes in: power density (c) and internal resistance (d) during operation. For clarity, the error bars were removed from the plot (d). Electrochemical characteristics

3.2 Long-term efficiency

Fig. 1c. shows the values of the maximum power densities extracted from the LSV data. After 105 days of operation, CWZ35- reached the highest power density of 22.8 $2.2 \pm W m^{-3}$. This trend was reversed in the following period and a significant decrease in power efficiency was observed. Furthermore, the power density of one of the CWZ35- replicates has decreased rapidly by more, starting with the %50 drop compared to the previous measurement. In contrary to CWZ35-, CWZ22- and CWZ22-/Si were displayed by a relatively high-power density from day 90 to the end of the experiment. Overall, this material has shown a reduction in the maximum power density of %31 during the -300day test, which was the lowest value compared to the materials available in the literature, at a similar operating time. Modifying CWZ22 with silica nanoparticles did not improve maximum power density but maintained high long-term performance. Moreover, an increasing trend of CWZ22-/Si performance was observed in the last stage of the experimental period, while the nonmodified CWZ22- displayed a decreasing trend. CWZ22-/Si reached a maximum power density of $2.4 \pm 21.1 W m^{-3}$ after 184 days of operation. A similar tendency can be observed for internal resistance (Fig. 1d).

When analysing the curves obtained for all materials in the first month, it was observed that the high R_{int} (Fig. 1d.) was caused by the ohmic resistance of the cathodes (Fig. 2.). In the third month, CWZ-22 and CWZ-35 were limited by anode mass transfer, while the overall performance of CWZ-22/Si was further limited by cathode ohmic resistance. The average current observed for CWZ-35 was 1.96 ± 0.45 mA. It should be noted that from the sixth month of operation, the cathode polarisation curves for all MFCs showed a positive potential at maximum currents. Thus, the overall efficiency of all MFCs were limited by the anode operation, which was probably affected by the incapability of the cathode to accept electrons to the active sites. Nevertheless, CWZ-22/Si had a lower rate of cathodic voltage drop, compared to CWZ-22, starting from the sixth month of operation

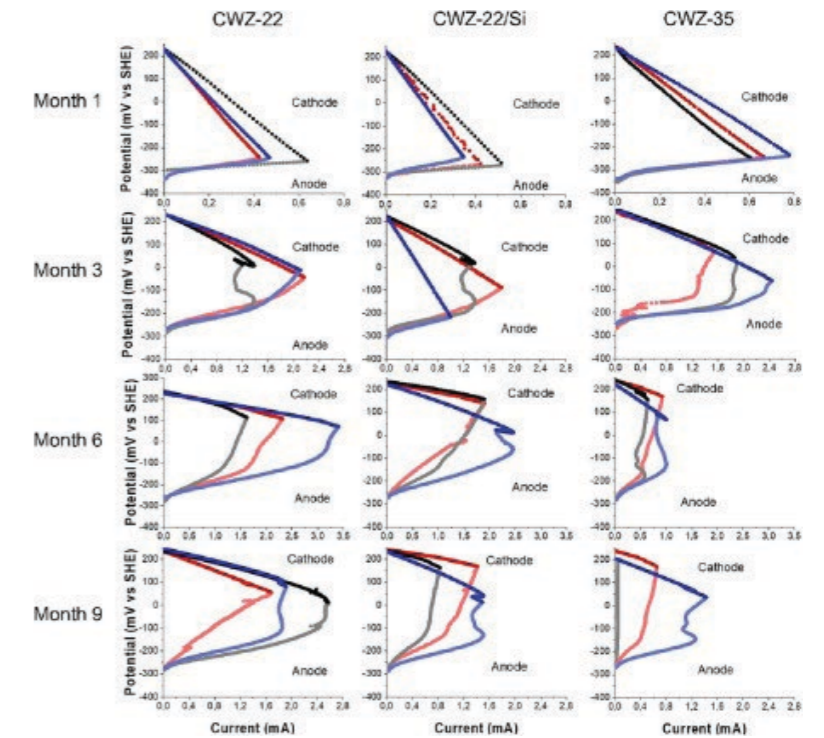
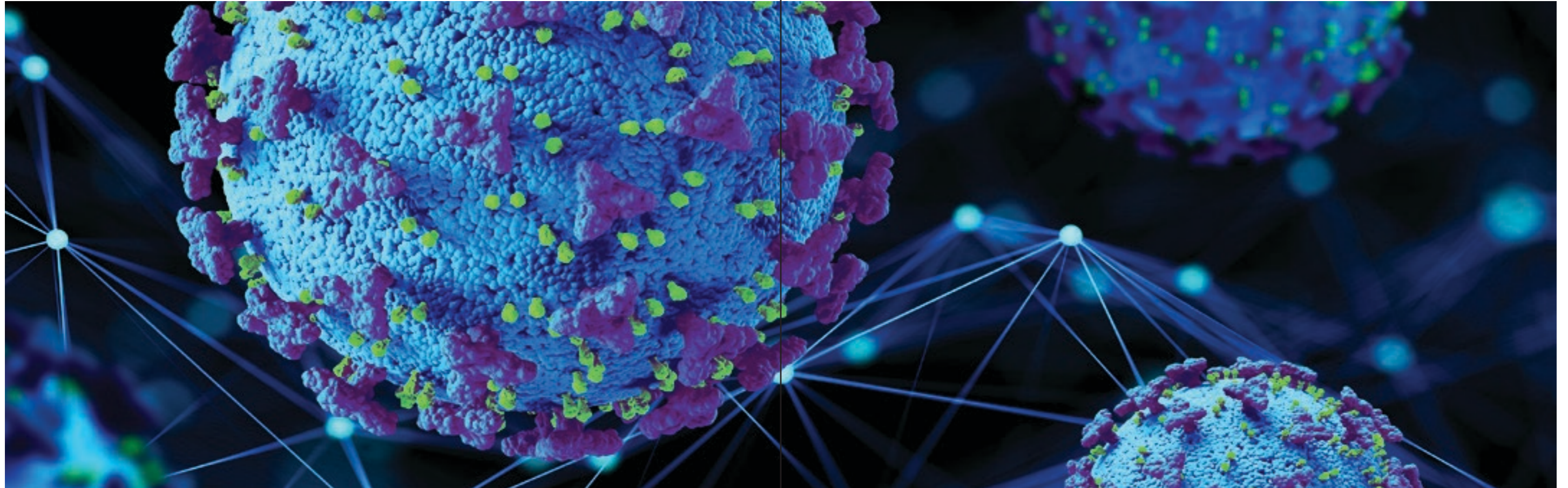


Figure 2: Polarisation curves of anodes and cathodes for all of the MFCs along the operational period. Each plot represents individual replicates.

until the end of the experiment. The average currents for CWZ-22 and CWZ-22/Si were 2.44 ± 0.90 mA and 1.97 ± 0.13 mA, respectively, in the sixth month of work. At month 9, the analysis of the polarisation curves showed a deterioration in the performance of all MFCs due to a significant increase in the anode mass transfer losses and the cathode ohmic resistance. Furthermore, from the sixth month of operation, a strong overshoot phenomenon was observed on the polarisation curves of the CWZ-22/Si and CWZ-35. This phenomenon was probably caused by the blockage of the pores by ions diffusing into the cathode, dominated by sodium and calcium, which hindered the access of oxygen to the active sites and slowed down the flow of electrons. For the CWZ-22, only a slight overshoot phenomenon was observed, proving a well-established MFC system. A

possible reason for the increase in losses may be the build-up of a thick biofilm layer on the anode, which limits the diffusion of the substrate, causing a negative gradient

towards deeper layers, accompanied by the membrane biofouling phenomenon, which limits proton transfer.



3.3 Electrochemical impedance spectroscopy

The experimental data acquired by EIS experiments was fitted to the equivalent circuit model according to, where the circuit element RA corresponded to the anode, RC to the cathode, and RM+E corresponded to the resistance of the membrane and electrolyte. Constant phase element (CPE) imitates the capacitive behaviour of the electrical double layer due to several factors such as: electrode surface roughness and porosity, the presence of biofilm, and the changes in the biofilm thickness. Additionally, at the end of the equivalent circuit model, a Finite Length Warburg element marked as WS was applied. The Nyquist plots obtained with the EIS in the successive stages of operation are shown in Fig. 3a. The acquired EIS spectra of the MFCs showed three semicircles. Fig. 3b. presents the results of the analysis of individual

impedance components using an equivalent circuit model. The EIS experiment in 3 months of operation showed that CWZ-35 and CWZ-22 indicated a similar sum of impedances of $78.6 \pm 17.3 \Omega$ and $70.1 \pm 16.2 \Omega$, respectively, while the lowest RC was detected in CWZ-35. CWZ-22/Si exhibited the highest anode and cathode impedance in this period. A different trend was observed in the 6th month, when CWZ-35 showed the highest sum of impedances, the main component of which was RC. During this period, a decrease in RC and RM+E were observed for CWZ-22 and CWZ-22/Si. The sum of the CWZ-22 resistance was of 58.2Ω and was almost 30% lower than for the CWZ-22/Si. The EIS data for month 9 showed an increase of internal resistance for each MFC, with the highest values observed for CWZ-35.

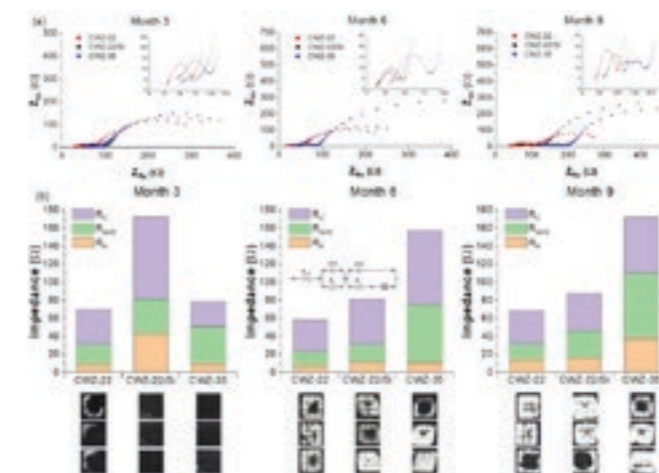


Figure 3: Nyquist plots (a) and EIS data analysis using the equivalent circuit model (b), the model is presented in the middle plot of the figure. The photographs below each bar display the intensity of the chemical fouling on the outer surface of the cathode. The white colour intensity correlates with the amount of salt precipitated over the cathode (black) surface.

The internal resistance as determined by the EIS of CWZ-22 and CWZ-22/Si decreased by 6 months of operation. It is known, that RA decreases with the development of the anode biofilm. Commonly, the cathode deterioration is associated to the chemical fouling caused by electro-osmotic drag and consequent biofilm formation. Nevertheless, here we are showing that a certain level of chemical fouling is beneficial for the MFC operation. The reduction of RM+E could have resulted from multiple factors including improved release of electron shuttles to the electrolyte. In contrast to these results, the internal resistance of CWZ-35 increased with each successive measurement due to increases in RA, RC and RM+E. The data displayed on Fig. 3, showed that the RC and RM+E had the highest effect on the MFC efficiency deterioration and

its correspondence with the outer cathode surfaces and salt accumulation. In the third month of operation, small amounts of precipitated salts were observed only for the CWZ-22 cathodes. However, in the sixth month, a similar degree of (visual) inorganic fouling was observed for all MFCs, which was accompanied by the lowest internal resistance values of CWZ-22 and CWZ-22/Si. Therefore, we conclude that electroosmosis of salts to the cathode had a positive effect on the efficiency of CWZ-22 and CWZ-22/Si materials. In contrast, it led to a rapid increase in the CWZ-35 RC, which was also revealed in polarisation experiments. In the second half of the experimental period, despite the increase in cathode coverage by salts, the CWZ-22 and CWZ-22/Si efficiencies were not limited by the cathode resistance.

3.4 Coulombic and energy efficiency

The efficiency of the substrate degradation was evaluated by determining the COD removal ability and the coulombic efficiency of the MFCs. The highest values were observed for MFCs equipped with CWZ22- cathodes. Therefore, this material is revealed to be the most attractive and cost-effective to produce a high-performance cathode in MFCs with good long-term properties. Additionally, the results suggest that the use of silica nanoparticles as a low-cost additive to improve the long-term cathodic performance is not an appropriate strategy. In contrast, the CWZ35- showed the highest power and current densities in the short-term period, while the poorest long-term performance among all tested materials.

Conclusions

The performance of the two different types of activated carbons as the air-cathode materials for MFCs and the effect of modification with silica nanoparticles on long-term properties were evaluated in a -300day trial. The results show that the pore size distribution and resulting vulnerability to chemical fouling is the crucial decisive factor to maintain the high performance of the MFC setup aimed to be operated in years.

Reference:

https://www.palmsens.com/publications/?_publication_sort=date_desc.

ARA INFORMATION



Showroom & Training Center:

Flat 929, Tamani Arts Offices Building
Al Asayel St., Business Bay Dubai, U.A.E.



+971 (0) 4 4515339 | +971 (0) 50 378 8520



+971 (0) 4 4516309



www.ara.ae | info@ara.ae

