

Materials for electrochemical energy conversion and storage

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WARSAW UNIVERSITY OF TECHNOLOGY

Outlin Conversion

- 1. Introduction to technologies for Energy "Production" Conversion
- 2. Energy conversion through electrochemical processes **Fuel cells**
- 3. Hydrogen -> **Syntetic fuels** -> fuel cells

STORAGE

- 1. Introduction to Energy Storage technologies
- 2. Hydrogen vs Batteries
- 3. Supercapacitors
- 4. Chemical storage of hydrogen



Forms of Energy



Basing on: https://www.geeksforgeeks.org/energy-conversion/



Conventional

The production of electricity and heat through the **combustion of fuels**, which include, for example, hard coal, lignite, oil, gas, biogases, biomass (plant and animal), peat

Non-conventional

Obtaining electricity and heat from alternative sources, including: flowing waters, geothermal waters, wind, sun, sea tides, green fuels, nuclear reactions, and ambient heat.





Energy distribution systems



- Classic system, a few or a dozen large or very large sources generate energy.
- Energy is transported to consumers over long distances through transmission and distribution networks.
- Electrical energy is usually produced from conventional energy sources.



Distributed

- The generation of energy by small units or production facilities, directly connected to distribution networks or located within the consumer's power grid.
- Usually producing electricity from renewable or nonconventional energy sources, often combined with heat generation (distributed cogeneration).





Global primary energy consumption by source



Primary energy is calculated based on the 'substitution method' which takes account of the inefficiencies in fossil fuel production by converting non-fossil energy into the energy inputs required if they had the same conversion losses as fossil fuels.



Various conversion energy technologies

Energy source	Sposób generacji energii elektrycznej	Theoretical efficiency[1]	Zagrożenie dla środowiska
Water	Water turbine	90-95%	Ecosystem change, methane emission
Hydrogen, amonia, hydrocarbons	Fuel cells	40-60%	CO ₂ emission when hydrocarbon used
Coal/oil/gas	Turbine	40-45%	Emision of gasous and Particulate Matter(PM) pulutions
Nuclear power	Reactor, Turbine	40%	Radioactive waste
Wind	Wind turbine	35%	Threat to fauna
Biomas	Turbine	35%	Emission of gases and Particulate Matter(PM)
Sun	Photovolatics	15-25%	_
Geotermia	turbina	15%	Contamination of groundwater, soil cooling

Basing on: [1] https://www.mpoweruk.com/energy_efficiency.htm

Fuel Cells - principles



Fuel cells are classified primarily by the kind of electrolyte

https://www.gecos.polimi.it/research-areas/hydrogen-fue cells-and-electrochemical-energy-systems/

Fuel cell overall efficiency

Fuel Cells - principles

Fuel Cell Type	Common Electrolyte	Operating Temperature	Typical Stack Size	Electrical Efficiency (LHV)	Applications	Advantages	Challenges
Polymer Electrolyte Membrane (PEM)	Perfluoro sulfonic acid	<120°C	<1 kW - 100 kW	60% direct H ₂ ; ⁱ 40% reformed fuel ⁱⁱ	 Backup power Portable power Distributed generation Transportation Specialty vehicles 	 Solid electrolyte reduces corrosion & electrolyte management problems Low temperature Quick start-up and load following 	 Expensive catalysts Sensitive to fuel impurities
Alkaline (AFC)	Aqueous potassium hydroxide soaked in a porous matrix, or alkaline polymer membrane	<100°C	1 - 100 kW	60% ⁱⁱⁱ	MilitarySpaceBackup powerTransportation	 Wider range of stable materials allows lower cost components Low temperature Quick start-up 	 Sensitive to CO₂ in fuel and air Electrolyte management (aqueous) Electrolyte conductivity (polymer)
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a porous matrix or imbibed in a polymer membrane	150 - 200°C	5 - 400 kW, 100 kW module (liquid PAFC); <10 kW (polymer membrane)	40% ^{iv}	• Distributed generation	 Suitable for CHP Increased tolerance to fuel impurities 	Expensive catalystsLong start-up timeSulfur sensitivity
Molten Carbonate (MCFC)	Molten lithium, sodium, and/ or potassium carbonates, soaked in a porous matrix	600 - 700°C	300 kW - 3 MW, 300 kW module	50% ^v	Electric utilityDistributed generation	 High efficiency Fuel flexibility Suitable for CHP Hybrid/gas turbine cycle 	 High temperature corrosion and breakdown of cell components Long start-up time Low power density
Solid Oxide (SOFC)	Yttria stabilized zirconia	500 - 1000°C	1 kW - 2 MW	60% ^{vi}	 Auxiliary power Electric utility Distributed generation 	 High efficiency Fuel flexibility Solid electrolyte Suitable for CHP Hybrid/gas turbine cycle 	 High temperature corrosion and breakdown of cell components Long start-up time Limited number of shutdowns

Source: US DOE (2010). Fuel Cell Factsheet

High-temperature fuel cells

Molten carbonate fuel cells (MCFCs) are the one of the most promising high efficiency and sustainable power generation technologies. MCFCs convert chemical energy of **fuel (hydrogen)** into **electricity, heat and water** through electrochemical reactions.



Main features:

- 300 kW-2.8 MW units, commercially available,
- combination of heat and power with gas expansion turbine delivers up to 65% efficiency,
- fuels: natural gas, anaerobic digester gas with internal reforming, sewage gas, natural gas and biogas compatible,
- average 10 000h lifetime,
- possible to employ in electrical utilities, industrial, and military applications.



The world's largest operating fuel cell power plant (59 MW), located in Hwaseong, South Korea

Source:E4Tech http://www.fuelcelltoday.com

Materials for molten carbonate fuel cells (MCFCs)

Molten carbonate fuel cells are highly efficient **chemical to electrical energy converters** and emerges as the one of the **most promising sustainable power generation technologies**.



MCFC stacks are assemblies of **single cells**, where each single cell comprises of **porous** components:

- cathode,
- anode,
- electrolyte matrix.

The **electrolyte** – mixture of $(Li/K)_2CO_3$ or $(Li/Na)_2CO_3$ – is kept in molten state in MCFC operating conditions (600-700 °C).



Concept for materials development



Concept for materials development - fabrication

Two main factors governing the performance of molten carbonate fuel cell materials

CHEMICAL COMPOSITION

POROUS NICKEL STRUCTURE





Molten Carbonate Fuel Cell - Processes





Elemental reaction steps:

- ① Adsorption of molecules
- ② Surface diffusion
- ③ Reaction at TPB
- ④ Desorption of products

The open-porous microstructure, apart from the chemical composition, is of great importance for the fuel cel performance.



Heat treatment

GREEN TAPE

Heat treatment of green tapes can be separated in two steps: 1) removing volatile content and binder residues, 2) sintering of powders

Open-porous structure of MCFC components is obtained after sintering. Porosity level is an effect of slurry composition and parameters of heat treatment: temperature (800-1000°C), time and atmosphere (commonly 100% hydrogen). CHARACTERIZATION AND TESTING

In the present work we sintered nickel-based porous electrodes using $N_2 + 5\% H_2$ atmosphere.



Fabrication - equipment

https://www.wim.pw.edu.pl/Badania-i-nauka/Aparatura-badawcza

Tape caster





High-temperature atmospheric tube furnace Czylok, Poland



Planetary Centrifugal Vacuum Mixer Thinky ARV 930 TWIN





Programmable, atmosphere furnace Czylok FCF-V70C/R



Ultrasonic spray coater Exacta Coat SONO-TEK

> Microwave reactor MAGNUM II, ERTEC-Poland





MICROSTRUCTURE CHARACTERIZATION

PERFORMANCE TESTING



Milestone 1 Application of porogens

100

100

100

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Milestone 1 Application of porogens







TPB + Thin film mechanism





Multi-modal porosity of the cathode is beneficial for MCFC operation

Samih Haj Ibrahim, Tomasz Wejrzanowski, Pawel Sobczak, Karol Cwieka, Aleksandra Lysik, Jakub Skibinski, Graeme John Oliver, Insight into cathode microstructure effect on the performance of molten carbonate fuel cell, Journal of Power Sources 491 (2021) 229562

Milestone 1 Application of porogens



Figure 4. a) Reconstruction of the 3D microstructure of the cathode after operation, b) illustration of pore infiltration by the electrolyte – pores (transparent), NiO (green), electrolyte (yellow).

FIB-SEM



Nieprzewodzący spiek LiAlO₂

Przewodząca żywica z dodatkiem nanorurek węglowych



T. Wejrzanowski, J. Gluch, S. Haj Ibrahim, K. Cwieka, J. Milewski, E. Zschech, Advanced Engineering Materials 20 (2018) 1700909.

<u>μ-CT</u>

Milestone 2 Application of nickel foam support





Pore size distribution in foam suport (250g/m²)



Pore size distribution in foam suport (480g/m²)



Lp.	Surface density [g/m^2]	Support thickness [<i>mm</i>]	Top layer thickness [<i>mm</i>]
1	250	0,5	0,4
2	480	0,5	0,4
3	250	0,5	0,3
4	480	0,5	0,3
5	250	0,5	0,6
6	480	0,5	0,6

	Open porosity [%]		
	Archimedes	μ-ХСТ	
Foam 250 g/m ²	89,02	80,19	
Foam 480 g/m ²	81,60	78,60	
Top layer	67,35	n.a.	

Milestone 2 Application of nickel foam support





Mechanical testing





T. Wejrzanowski, K. Cwieka, J. Skibinski, T. Brynk, S. Haj Ibrahim, J. Milewski, W. Xing, Metallic foam supported electrodes for molten carbonate fuel cells, Materials & Design 2020







Patent: Pat.241140 "Elektroda węglanowego ogniwa paliwowego o zwiększonej wytrzymałości mechanicznej"



Patent: P.430869 Katoda węglanowego ogniwa paliwowego z warstwą spieku srebra

Milestone 4 Hybrid MCFC/SOFC = COFC (Carbonate oxide fuel cel)









Komorowska, G.; Wejrzanowski, T.; Jamroz, J.; Jastrzębska, A.; Wróbel, W.; Tsai, S.-Y.; Fung, K.-Z. Fabrication and Characterization of a Composite Ni-SDC Fuel Cell Cathode Reinforced by Ni Foam. Materials 2022, 15, 4891. https://doi.org/10.3390/ ma15144891

Gabriela Komorowska, Jan Jamroz, Tomasz Wejrzanowski, Kamil Dydek, Rafał Molak, Wojciech Wróbel, Shu-Yi Tsai, Kuan-Zong Fung, Thermal treatment and properties of Ni-SDC cathode for high temperature fuel cells, Materials Science for Energy Technologies 6 (2023) 105-113

Multiscale modelling

Atomic scale



Czelej, K., Cwieka, K., Wejrzanowski, T., Spiewak, P., Kurzydlowski, K.J., Catal. Commun. (74) 2016



Gas flow

Liquid electrolyte infiltration

Haj Ibrahim S., Neumann M., Klingner F., Schmidt V., Wejrzanowski T., Materials and Design 133 (2017)

S. Haj Ibrahim, T. Wejrzanowski, P. Sobczak, K. Cwieka, A. Lysik, J Skibinski, G.J. Oliver, Journal of Power Sources 491 (2021) 229562.

Microstructure modeling – general concept



Molten Carbonate Fuel Cell Modeling capillary effect



a)

Wejrzanowski T., Haj Ibrahim S., Cwieka K., Milewski J., Kurzydlowski K.J., Journal of Power Technologies 96 (2016)

Haj Ibrahim S., Neumann M., Klingner F., Schmidt V., Wejrzanowski T., Materials and Design 133 (2017)

Ref

b)

Cathode

P1+P2

Syntectic fuels The concept



Hierarchical porous materials – 3D printing The concept



Fabrication of hierarchical open porous materials by application of 3D printing



Schematic illustration of hierarchical open-porous microstructure of catalytic materials fabricated via 3D printing



Multiscale modeling of reactive flow in hierarchical microstructure.

3D printing of hierarchical open-porous materials by FDM (Fused Deposition Modeling)



ABS-Ni 25% granulate

ABS-Ni 25% filament

distribution of Ni particles

SEM analysis

Porous structures in FDM 3D printing technology

SEM images for prints after heat treatment:



E. Mackiewicz, T. Wejrzanowski, B. Adamczyk-Cieślak, G.J. Oliver "Polymer–Nickel Composite Filaments for 3D Printing of Open Porous Materials", Materials 2022, 15, 1360

Impregnation of 3D printed structures



E. Mackiewicz, R. Nowacki, G. Komorowska, T. Wejrzanowski "Impregnation of composite 3D prints obtained by material extrusion technology as an effective method of preserving the spation of composite 3D prints obtained by material extrusion technology as an effective method of preserving the spation of composite 3D prints obtained by material extrusion technology as an effective method of preserving the spation of composite 3D prints obtained by material extrusion technology as an effective method of preserving the spation of composite 3D prints obtained by material extrusion technology as an effective method of preserving the spation of composite 3D prints obtained by material extrusion technology as an effective method of preserving the spation of the material obtained by material extrusion technology as an effective method of preserving the spation of the spation of the material extrusion technology as an effective method of preserving the spation of the material extrusion technology as an effective method of preserving the spation of the spation of the material extrusion technology as an effective method of preserving the spation of the material extrusion technology as an effective method of preserving the spation of the spation of the material extrusion technology as an effective method of the spation of technology as an effective method of the spation of technology as an effective method o

Porous 3D printed materials – Direct Ink Writing (DIW)

Preparation of silica-nickel 3D structures using Direct Ink Writing technique



Mackiewicz, E., Wejrzanowski, T., Nowacki, R., Jaroszewicz, J., Marchewka, J., Wilk, Ł., Bezkosty, P., & Sitarz, M. (2023). 3D hierarchical porous structures printed from a silica-nickel composite paste. *Applied Materials Today*. <u>https://doi.org/10.1016/j.apmt.2023.101859</u>

R. Nowacki, E. Mackiewicz, G. Komorowska, T. Wejrzanowski, J. Marchewka, Ł. Wilk, M. Sitarz, M. Pietrowski, Exploring the Properties of DIW 3D Printed SiO2-Ni Structures Impregnated by Ruthenium: Influence of Sintering Atmosphere and Initial Tests for Catalytic Applications, 2025 (submitted)

Porous 3D printed materials – Direct Ink Writing (DIW)



At 400 °C CO₂ conversion reached almost 75% and 66% for Ar_Ru and H₂+N₂_Ru, respectively

Monolithic catalysts - tests

R. Nowacki, E. Mackiewicz, G. Komorowska, T. Wejrzanowski, J. Marchewka, Ł. Wilk, M. Sitarz, M. Pietrowski, Exploring the Properties of DIW 3D Printed SiO2-Ni Structures Impregnated by Ruthenium: Influence of Sintering Atmosphere and Initial Tests for Catalytic Applications, 2025 (submitted)

Storage of Energy - Technologies



A.A. Kebede at al.., A comprehensive review of stationary energy storage devices for large scale renewable energy sources grid integration, Renewable and Sustainable Energy Reviews, 159, 2022, 112213, ISSN 1364-0321, <u>https://doi.org/10.1016/j.rser.2022.112213</u>.

Storage of Energy – Technologies





Power-to-Gas: The Case for Hydrogen White Paper



B. Dunn, at al., Electrical Energy Storage for the Grid: A Battery of Choices, Science 334, 6058 (2021), 928. <u>DOI:</u> <u>10.1126/science.1212741</u>

Hydrogen vs batteries





Notes: To be understood as approximate mean values taking into account different production methods. Hydrogen includes onboard fuel compression. Excluding mechanical losses.

TRANSPORT & Y T © in ENVIRONMENT ⊕ transportenvironment.org Sources: Worldbank (2014), Apostolaki-losifidou et al. (2017), Peters et al. (2017), Larmanie et al. (2012), Umweltbundesamt (2019), National Research Council (2013), Ricardo Energy & Environment (2020), DOE (no date), ACEA (2016).

https://creativecommons.org/

Hydrogen vs batteries



- Energy density (0.5 kWh/l 0.5 kWh/kg)
- Battery power density (>500 W/kg)
- Electrical efficiency (>90%)
- Durability (warranty 10-15 years)
- Low charging speed
- Currently high battery purchase price
- Availability of raw materials (lithium, cobalt)
- High technological maturity

Hydrogen (fuel cells)

- Hydrogen energy density (30 MPa 0.6 kWh/l 33 kWh/kg)
- Fuel cell power density (<100 W/kg)
- Electrical efficiency (40-50%)
- Fuel cell durability (warranty 6 years)
- High charging speed
- Currently high fuel cell purchase price
- Availability of raw materials (precious metals)
- Medium technological maturity



Emerging new battery technologies

Solid State Batteries



Flow Batteries



Garnet-Type Solid-State Electrolytes: Materials, Interfaces, and Batteries Chengwei Wang et al. *Chemical Reviews* **2020** *120* (10), 4257-4300 DOI: 10.1021/acs.chemrev.9b00427 https://wysokienapiecie.pl/1254brakujace-ogniwo-energetyki/ https://www.azom.com/article.aspx? ArticleID=22278

Anoda

Na-ion Batteries

Li/Na-air Batteries



https://debuglies.com/2018/07/24/newproblem-with-lithium-oxygen-batteries/



Hydrogen or/and batteries ?



Source: Toyeta, Hyundai, Daimler

Maybe something else? Supercapacitors

Supercapacitor: An advanced energy storage device.

- > High power density (higher than batteries)
- > Wide operating temperature range
- Long cycle life (over 10 years)
- > Fast Charging
- > Less weight
- Low cost



Typical construction of supercapacitor devices

Applications of supercapacitor devices







Trams in Germany powered by supercapacitors use 30% less energy than their equivalents in other regions.

Ref: Supercapacitors take charge in Germany By Philip Ball Feature Editor Yury Gogotsi03, (2012)

Types and Classification of Supercapacitor

Objectives

A novel route for binder-free fabrication of porous electrodes

- Microwave-assisted hydrothermal method
- Fast and energy efficient
- Processing time few minutes
- Synthesis of various metallic/carbon compounds
- Novel porous nano architectures
- ➢ High surface area
- High electrochemical activity





Types of supercapacitor devices



Ragone plot showing the specific power vs. specific energy of various energy storage devices.

Nickel Hydroxide phases and electrochemical characteristics



Determination of layered nickel hydroxide phases in materials disordered by stacking faults and Interstratification Mater. Chem. A, 2023, 11,789



Microwave-assisted hydrothermal synthesis of $\alpha\beta$ -Ni(OH)₂ nanoflowers on nickel foam for ultra-stable electrodes of



Muhammad Saleem Akhtar, Tomasz Wejrzanowski et al. Microwave-assisted hydrothermal synthesis of $\alpha\beta$ -Ni(OH)2 nanoflowers on nickel foam for ultra-stable electrodes of supercapacitors https://doi.org/10.1016/j.electacta.2024.145284

Novel 2D hexagonal nanoflakes Cerium/Nickel Sulfide in situ grown on nickel foam - Anode





Comparative CV curves of bare Ni foam and 2D nanoflakes @ Ni foam







Exceptional performance due to its 2D morphology, achieving a **high capacitance** of 5286 Fg⁻¹ with an **high energy density** of approximately 222.09 Wh/kg and a power density of 687.19 W/kg at a current density of 2.5 Ag⁻¹



Novel 2D hexagonal nanoflakes Cerium/Nickel Sulfide anode + GNP cathode GNP - Graphene nano-pellets

The device - Full asymmetric cell

The 2D nanoflakes @Ni foam//GNPs @Ni foam asymmetric supercapacitor exhibited an **high energy density** of 77.51 Wh/kg and a power density of 797.25 W/kg at a current density of 1 Ag⁻¹. Furthermore, the asymmetric device demonstrated **exceptional cyclic performance, retaining approximately 84%** of its initial capacitance after 10,000 continuous charging/discharging cycles



(a) CV curves of positive and negative electrodes (b) CV curves of 2D nanoflakes @Ni foam//GNPs@Ni foam (c) GCD curves of 2D nanoflakes @Ni foam//GNPs@Ni foam at different current densities (d) Cyclic performance of asymmetric supercapacitor

To be published

Hydrogen storage – new concepts

NEW PROJECT:

Cost- and resource-efficient storage of hydrogen at ambient temperature and at a maximum pressure of 3.5 MPa, NCDR, European, 2024-2027 Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT | Germany AMAZEMET | Poland JA-Gastechnology GmbH | Germany VSB-Technical University of Ostrava, CEET; Energy Research center | Czech Republic Faculty of Sciences of Monastir, University of Monastir | Tunisia Warsaw University of Technology | Poland Institut für Nichtklassische Chemie e.V. | Germany Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V. | Germany

Aerogel H₂ storage

H_2 Unloading



HEA H_2 storage





NCBR

- 1. High-performance molten carbonate fuel cells (MCFC), 2015-2018, PBS, NCRD
- 2. Innovative matrix materials for molten carbonate fuel cells (MATRIX), 2016-2019, Poland-Taiwan bilateral project, NCRD
- 3. Improved fabrication of fuel cells for extended durability, improvement of working parameters, in particular power per volume/mass unit of the fuel cell and reduction of investment and exploitation costs by application of alternative catalytic systems in printing technology (AUGUSTINE), 2016-2019, POIR.01.02.00-00-0045/16, NCRD
- 4. Development of technology for noble metals and rare earth elements recycling for fabrication of molten carbonate fuel cell elements (RECREATE), 2017-2020, POIR. 01.02.00-00-0086/17-00, NCRD
- 5. Novel molten carbonate/ceramic composite materials for sustainable energy technologies with CO₂ capture and utilization (MOCO3), M-ERA_NET2/2016/04/2017, 2017-2020, NCRD
- 6. Development of the industrial scale of molten carbonate fuel cells and solid oxide electrolysers for integration into power-to-gas installations (TENNESSEE), 2018-2020, POIR, NCRD
- 7. Cost- and resource-efficient storage of hydrogen at ambient temperature and at a maximum pressure of 3.5 MPa, NCDR, European, 2024-2027





- 1. Study of the influence of microstructure and chemical composition on catalytic properties of open-porous components of molten carbonate fuel cells, 2018-2021, OPUS, NSC
- 2. Study of the influence of microstructure on reactive flow process in open-porous components for high-temperature fuel cells, 2018-2021, PRELUDIUM, NSC
- 3. POB Technologie Materiałowe of Warsaw University of Technology within the Excellence Initiative: Research University (IDUB) program
- 4. Hierarchical porous structures fabricated by 3D printing technology 2019-2024, OPUS, NSC
- 5. Carbonate-oxide fuel cell, 2023-2026, OPUS, NSC

International cooperation



South Africa, University of Cape Peninsula, Department of Mechanical Engineering, Cape Town

Mechanical and Aerospace Engineering, Nanyang Technological University

Prof. Choong-Gon Lee, South



Thank you !

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