

Chemicals And Materials From Renewable Resources

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Energy & Chemicals from Renewable Resources by Electrocatalysis

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The selective production of chemicals from renewable resources with contemporaneous release of energy is perhaps one of the most desired targets of sustainable chemistry. Here, we report an overview of our recent research efforts, where we have demonstrated that this can be achieved using renewable alcohols, by means of two electrochemical devices: *direct fuel cells* and *electrolyzers*. In either case, an aqueous solution of the fuel in the anode compartment is oxidized to a nonreactive electrocatalyst that promotes selectively the partial oxidation of the anolyte with high stability and fast kinetics. We have found that anode electrocatalysts based on nano-sized Pt particles, alone or promoted by Ni-Zn phases as well as by CeO₂ or TiO₂, are able to accomplish this goal in alkaline environment when used in conjunction with commercially available cathode electrocatalysts and solid or liquid electrolytes. In an electrolyzer, containing an anode electrocatalyst similar to that employable in a DAFC, the electrolyte may be either an anion exchange membrane or a solution of an alkali metal hydroxide (NaOH or KOH, for example) and the alcohol is converted to the corresponding alkali metal carboxylate, while hydrogen gas is produced at the cathode upon water reduction.

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DAFCs are attracting increasing interest as power sources for portable applications due to some unquestionable advantages over endogenous devices fed with hydrogen.¹ Alcohols, such as methanol, ethanol, ethylene glycol and glycerol, exhibit high volumetric energy density and their storage and transport are much easier as compared to hydrogen. On the other hand, the oxidation kinetics of any alcohol are much slower and still H₂-fuelled polymer electrolyte fuel cells (PEMFCs) exhibit superior electrical performance as compared to DAFCs with comparable electroactive surface areas. Increasing research efforts are therefore being carried out to design and develop more efficient anode electrocatalysts for DAFCs.

The most common DAFC is the direct methanol fuel cell (DMFC) of which there exist commercial devices with power densities spanning from a few watts to 100 W. The large majority of DMFCs, either monoplanar cells for direct use as oxidant, but these processes are generally characterized by harsh conditions and low selectivity, and as a consequence low sustainability.^{2,3}

Glycerol can be transformed by dehydration/hydrogenation reactions,⁴ into 1,2-propanediol which is an effective intermediate for the production of lactic acid. Lactic acid can be used as a building block for the development of degradable biopolymers^{5,6} and currently is used mainly as a fine chemical, with application in cosmetic, textile and food industries.

Notable efforts are therefore being carried out to design new catalytic structures for DAFC anodes that do not contain platinum or contain tiny amounts of this rare metal and, most of all, are able to oxidize primary and secondary alcohols with fast kinetics and tolerable deactivation. Within this context, DAFCs operating in alkaline media with solid electrolytes constituted by anion exchange membranes (AEMs) can provide a number of advantages, especially in view of recent successful developments in the design and production of AEMs. The drawback of traditional alkaline fuel cells—that undergo electrolyte carbonation—is, in fact, strongly minimized by the use of an anion conductive polymeric membrane, while the advantages of operating in alkaline conditions are manifold and include: a) utilization of both noble and non-noble metals as electrocatalysts; b) improved kinetics at both cathode and anode, in particular low anodic over-voltages for alcohol oxidation; c) alcohol cross-over from anode compartment to cathode compartment is reduced by electro-osmotic drag of hydrated hydroxyl ions; d) easier water management as water is formed at the anode side where an aqueous solution already exists, while the electro-osmotic drag transports water away from the cathode preventing its flooding;

and widely available (2.4 million tons per year). Moreover, the increasing demand for methyl esters as fuel additives is expected to increase the G₃ production, thus leading to further cost reductions.⁷ It is also important to stress that some EG and G oxidation products, such as glycolic acid, oxalic acid, glyceric acid, tartaric acid, meso-xalic acid, and 1,3-dihydroxyacetone, currently produced by costly and non-environmentally friendly processes, are valuable compounds that serve as versatile building blocks for the synthesis of a variety of fine chemicals and bio-sources of polymers. Indeed, G oxidation reactions are generally performed with stoichiometric oxidants, such as permanganate, nitric acid or chromic acid, and are characterized by low yields and poor selectivity.⁸ Fermentation processes exhibit higher oxidation selectivity, but have a low conversion rate. Alternatively, one may apply heterogeneous catalytic processes with molecular oxygen as oxidant, but these processes are generally characterized by harsh conditions and low selectivity, and as a consequence low sustainability.^{9,10}

Overall, these drawbacks are boosting research aimed at using other alcohols as fuels in DAFCs. Indeed, several higher molecular weight alcohols and polyalcohols have high solubility in water, low toxicity, high boiling points, high specific energy and the capacity of some of them to be renewable. Included in this group are ethanol, ethylene glycol (EG), glycerol (G) and 1,2-propanediol. Ethanol can be produced on a large scale from biomass feedstocks originating from agriculture (first-generation bio-ethanol), and forestry and urban residues (second-generation bio-ethanol). Ethylene glycol has a volumetric energy density of 5.9 kWh L⁻¹ and can be produced by heterogeneous hydrogenation of cellulose derivatives.¹¹ Glycerol has a volumetric energy density of 6.3 kWh L⁻¹ and is a by-product of biodiesel production. Glycerol is also inexpensive (0.3 US\$ kg⁻¹)

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Abstract: A symposium entitled "Chemicals and Materials from Renewable Resources" was held as part of the ACS National Meeting in August, The possibilities surrounding the use of renewable resources for chemical feedstock is well known. What appears to stand between the concept. New Chemicals and Polymers from Renewable Resources. Joseph J. Bozell The use of renewable raw materials as feedstocks for chemical production is. Processes in the chemical industry are historically based on fossil resources. Renewable Raw Materials: New Feedstocks for the Chemical Industry, First. Renewable resources in the chemical industry--breaking away from oil? Rising prices for fossil-based raw materials suggest that sooner or later renewable. It covers the main raw materials based on vegetable resources, namely (i) wood . justify their exploitation as renewable sources of chemicals and monomers. The polymerisation of furan monomers and the exploitation of some of the chemical peculiarities of the furan heterocycle have generated a wide diversity of . A renewable resource is a natural resource which replenishes to overcome resource depletion Water can be considered a renewable material when carefully controlled usage, treatment, and release are followed. . Biorenewable chemicals can provide solar-energy-powered substitutes for the petroleum-based carbon. In Europe, for instance, the use of renewable resources is also being driven by the approach for the use of renewable raw materials in the chemical industry. The biobased economy targets replacing fossil resources with renewable biological resources from land and sea to produce food, materials, chemicals and . Renewable resources have been used as industrial feedstocks throughout raw materials to products such as basic chemicals, intermediates, fine chemicals. Advances in material science and in biologically derived chemistries are changing our bio-based chemicals and fuels, sustainable food sources, energy storage, The entrepreneurs drawn to the advanced materials and renewable energy. Fuels, Chemicals and Materials from the Oceans and Aquatic Sources Sustainability Assessment of Renewables-Based Products: Methods and Case Studies." A raw material of feedstock should be renewable rather depleting wherever Starch and Cellulose are important renewable resources for chemical production. materials and processes for converting renewable and clean energy resources such as sunlight, heat, and renewable fuels into chemical and electrical energy. Request PDF on ResearchGate Renewable resources in the chemical industry Breaking away from oil? Rising prices for fossil-based raw materials suggest MIT chemical engineer Yuriy Roman develops catalysts for environmentally sustainable synthesis of materials such as fuels, plastics, and other.

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