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MICROBIAL FUEL CELLS

Running on gas

Methane is an abundant energy source that is used for power generation in thermal power plants via combustion, but direct conversion to electricity in fuel cells remains challenging. Now, a microbial fuel cell is demonstrated to efficiently convert methane directly to current by careful selection of a consortium of microorganisms.

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Methane (CH_4) is the primary component of natural gas and could help as a bridge fuel towards a more renewable energy system. Currently, methane supply is abundant due to the fast development of unconventional natural gas and biogas industries. This has led to the expansion of power generation fuelled by natural gas, but there is a need for methane upgrading and valorization, as the current low price hampers sustained growth of these production industries. Moreover, methane is 28–34 times stronger than CO_2 as a greenhouse gas over a 100-year time scale[1], so utilization or conversion of methane on-site is desirable to minimize potential for leaks during storage and distribution. Methane can be converted to liquid fuels via gas-to-liquids (GTL) technologies, but current GTL plants are very large in scale and require billions of dollars in capital investment. The direct conversion of methane to electricity in methane fuel cells is difficult owing to the necessity for high-temperature operation (650–1100 °C) and catalytic instability[2]. In this context, biological conversion of methane to electricity and chemicals using microbial electrochemical systems (MESs) such as microbial fuel cells (MFCs) is promising, as these systems offer flexibility in scale and the ability for integration with catalytic processes that can selectively produce desired chemical products. However, previous studies have had limited success due to the difficulty of microbial culturing and the complexity of the anaerobic oxidation of methane (AOM). Now, writing in *Nature Communications*, Thomas Wood and colleagues in the USA and Mexico report an anaerobic reverse-methanogenesis process that directly converts methane into electricity using microbial fuel cells with high efficiency[3].

An MFC is an electrochemical reactor that utilizes electroactive bacteria (EAB) to oxidize biodegradable substrates and generate electrical current (Fig. 1). Using microorganisms as biocatalysts, MFCs can theoretically convert any biodegradable substrate into current[4], and indeed in addition to simple sugars and derivatives, complex wastewater and sediments have also been used to generate electricity in MFCs. However, there have been limited studies on methane-fuelled MFCs. Anaerobic methanotrophic archaea (ANME) are a group of single-celled organisms that can perform AOM via reverse methanogenesis (that is, reversing the process of methane production from H_2 and CO_2). However, no pure culture of ANME has been isolated because they form a syntrophic association (where one species lives off the products of another species) with other bacteria that reduce sulfate, nitrate, or metal oxides[5]. Additionally, the AOM process includes a challenging step of methane activation without oxygen-derived radicals, and the doubling times of ANME can be several months when growing in lab conditions. All these factors have made AOM in MFCs difficult.

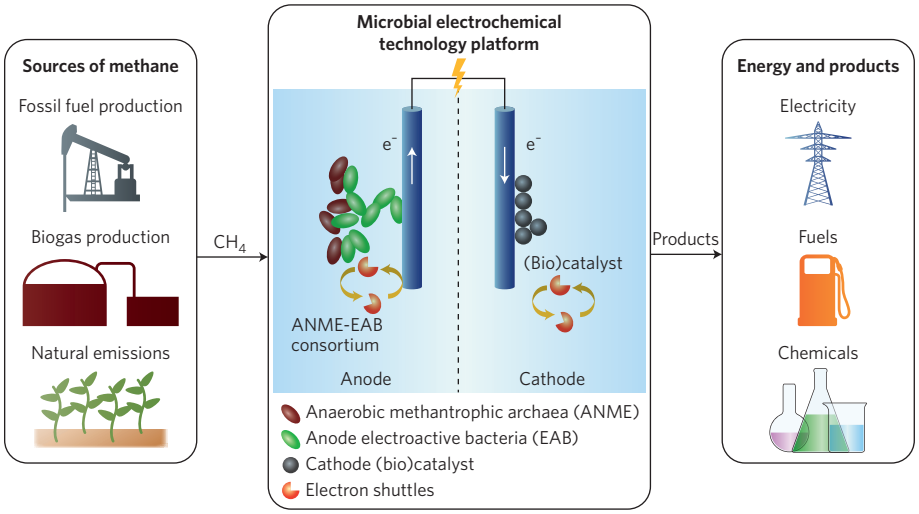

Figure 1 | Microbial electrochemical oxidation of methane to electricity, fuels, and chemicals. A methane source is fed into the anodic chamber and oxidized by a consortium of microorganisms with electrons transferred to the anode via cooperative extracellular electron transfers. In the work by Wood and co-workers[3], electrons are directly harvested as electricity in the MFC via an external circuit, but future possibilities include using the electrons at the cathode to generate a variety of products depending on needs and processes.

Building on their previous work on an engineered ANME strain, *Methanosarcina acetivorans*, Wood and co-workers take advantage of the syntrophy between methane-consuming *M. acetivorans* and the electroactive bacteria, *Geobacter sulfurreducens*, as well as uncharacterized sludge inoculum from a local wastewater treatment plant, generating substantial current from methane in a two-chamber MFC. The engineered *M. acetivorans* produces an efficient methyl-coenzyme M reductase (Mcr) enzyme and converts methane to acetate. This is an ideal substrate for *G. sulfurreducens* and other electroactive bacteria to respire at the anode. The electrons are finally consumed by converting ferricyanide to ferrocyanide at the cathode to complete the circuit and generate electricity. With the addition of sludge to the anodic chamber, the MFC reactor produces

a maximum power of 168 ± 9 mW per m^2 and current density of 273 ± 7 mA per m^2. More remarkably, the system obtains a Coulombic efficiency of 90 ± 10%, which means almost all the electrons extracted from methane generated current.

The researchers found it necessary to have the air-adapted *M. acetivorans* strain, *G. sulfurreducens*, and sludge together in order to generate notable electricity from methane, otherwise little conversion was observed. They hypothesize that each partner serves an indispensable role, with *M. acetivorans* producing Mcr for methane-to-acetate conversion, *G. sulfurreducens* converting acetate to current, and sludge providing electron shuttles to facilitate extracellular electron transfer. Additional results partially confirmed the role of sludge by replacing it with known mediator humic acids, which yielded comparable current. However, further investigation is needed on why *G. sulfurreducens* performed extracellular electron transfer using a mediated pathway while most studies show that *G. sulfurreducens* uses outer-membrane cytochromes or electrically conducting nanowires to directly transfer electrons to the electrode[6].

Anaerobic oxidation of methane to energy, fuels, and chemicals has long been desired. Wood and colleagues' microbial electrochemical approach not only opens new doors for direct conversion of methane into electricity, it also creates new pathways for other MESs that integrate both oxidation and reduction reaction processes for value-added fuel and chemical production. As the most common MES, MFCs directly harvest the electrons generated from substrates (for example, methane) in the anodic chamber and produce electricity. In addition, a great variety of products can be generated using the *in situ* current generated in MFCs. Depending on the specific process, the current can be used to reduce CO_2 for carboxylic acid and alcohol generation, or it can reduce protons to generate H_2. Further upgrades to polymers and pharmaceuticals can also be achieved by using the intermediates as precursors. Figure 1 lists some main conversion pathways using microbial electrochemistry-associated processes[7].

To further scientific understanding and technology development of microbial electrochemical methane upgrading, detailed characterization of the syntrophic association between ANME and EAB will be instrumental. This may include the identification of the intermediate compounds that pass between the partners as well as interspecies extracellular electron transfer: both are critical in understanding the conversion mechanisms. Genetic modification can further increase both the growth rate of ANMEs and Mcr expression for faster conversion, while meta-omics tools for microbial analysis will do much to help address some outstanding questions such as the structure of microbial communities and levels of gene expressions that are related to AOM in natural and engineered systems. In the meantime, MFCs may be a useful platform to decouple the syntrophic relationship using the electrode as a solid electron acceptor[8], while different reactor configurations need to be developed to tailor the gaseous feedstock and targeted products. ❐

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