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# Ammonium as a Carbon-Free Electron and Proton Source in Microbial Electrosynthesis Processes

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**Abstract:** Biogas upgrading to biomethane with microbial electrosynthesis (MES) is receiving much attention due to increasing biomethane demands and surplus renewable energy. Research has demonstrated the feasibility of MES to increase methane yield by reducing $CO_2$ in anaerobic digestion (AD). Such $CO_2$ reduction occurs at the cathode and requires the supply of both protons and electrons. The most studied sources of protons and electrons are oxidation of organic substances and water, generated at the anode. These anodic reactions, however, also imply the production of $CO_2$ and $O_2$, respectively, both with negative implications for the AD process. A source of protons and electrons without $CO_2$ and $O_2$ as by-products would be beneficial for MES-enhanced biomethane production. This opinion article discusses the possibility of ammonium to serve as a sustainable proton and electron source.

**Keywords:** microbial electrosynthesis; biogas; biomethane; proton source; ammonium oxidation

## 1. Introduction

Anaerobic digestion (AD) produces biomethane from organic waste materials, possibly with the best carbon footprint of all biofuels, and therefore has growing demand [1]. Generally, raw biogas contains between 30% and 40% $CO_2$, which limits the energy content and usage [2]. Therefore, bioelectrochemical techniques to reduce $CO_2$ to methane are studied [3,4]. Using renewable electricity in such electrochemical techniques to convert power to gas has several benefits, including carbon-neutral bioenergy generation, increased energy storage capabilities and energy security [4,5]. Microbial electrosynthesis (MES) is a promising technique, which has been demonstrated to enrich AD biogas up to 94% methane content [3]. In MES systems, microorganisms (electrotrophic methanogenic archaea) [6] present in the cathode biofilm catalyze the wanted $CO_2$ reduction reaction (Equation (1)). Reduction of 1 mol $CO_2$ to $CH_4$ requires 8 mol of electrons and 8 mol of protons.

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (1)$$

In MES the oxidation of organic substances and water electrolysis reactions at the anode are known sources of protons and electrons (p&e) [7–9]. The types and availability of oxidable organics in the MES reactor determine the amounts of p&e that can be donated to the cathodic reaction. For instance, 1 mol of acetate oxidation results in 8 mol of electrons, 8 mol of protons and 2 mol of carbon dioxide; while 1 mol of propanoate oxidation liberates 14 mol of electrons, 14 mol of protons and 3 mol of carbon

dioxide. Higher carbon content substances, such as long-chain carboxylic acids or fats, can release more protons and electrons upon oxidation, which increases the methane production quantity, but the methane content (v/v %) remains similar since they all also generate a significant fraction of carbon dioxide. Substrates with higher carbon content release more $CO_2$ (Equation (2)). The additional $CO_2$ generation is a trade-off with the extra p&e liberation/ $CO_2$ fixation into methane so that such MES can lead to enhanced methane yield but will not heavily influence the $CH_4/CO_2$ ratio in the generated biogas. Therefore, oxidation of organic substances at the anode in MES cannot explain the experimentally observed large increase in the $CH_4/CO_2$ ratio [3].

$$C_nH_{2n+1} - COOH + [2(n+1) - 2]H_2O \rightarrow (n+1)CO_2 + (6n+2)H^+ + (6n+2)e^- \quad (2)$$

Although water is a carbon-free p&e source, it has the drawback of oxygen gas evolution during water oxidation. Oxygen can obstruct the anaerobic digestion process by oxidizing the redox mediators [10]. It is not clear to what extent water serves as a p&e source in MES, but there appears to be a need for additional carbon-free p&e sources to increase the methane content in biogas.

Ammonium (pka = 9.24) is a valuable fertilizer and is also getting attention as a carbon-free fuel/energy carrier [11]. Ammonium and ammonium-producing substances are also major pollutants in nature that cause eutrophication [12]. Nitrogen in organic compounds present in AD feeds ends up as ammonium that can inhibit methanogenesis [13]. Conventional ammonium removal technologies consume considerable amounts of energy [14]. Ammonium removal by a microbial fuel cell (MFC) has been suggested as a viable option that involves energy recovery [15,16]. We propose here to take this a step further by recovering the energy potential of ammonium present in organic wastes and wastewater fed AD by using it as a p&e source for biomethanation (Equation (3)). Figure 1 illustrates a possible reactor setup for MES integration with an AD unit.

$$8NH_4^+ + 3CO_2 \rightarrow 4N_2 + 3CH_4 + 6H_2O + 8H^+ \quad (3)$$

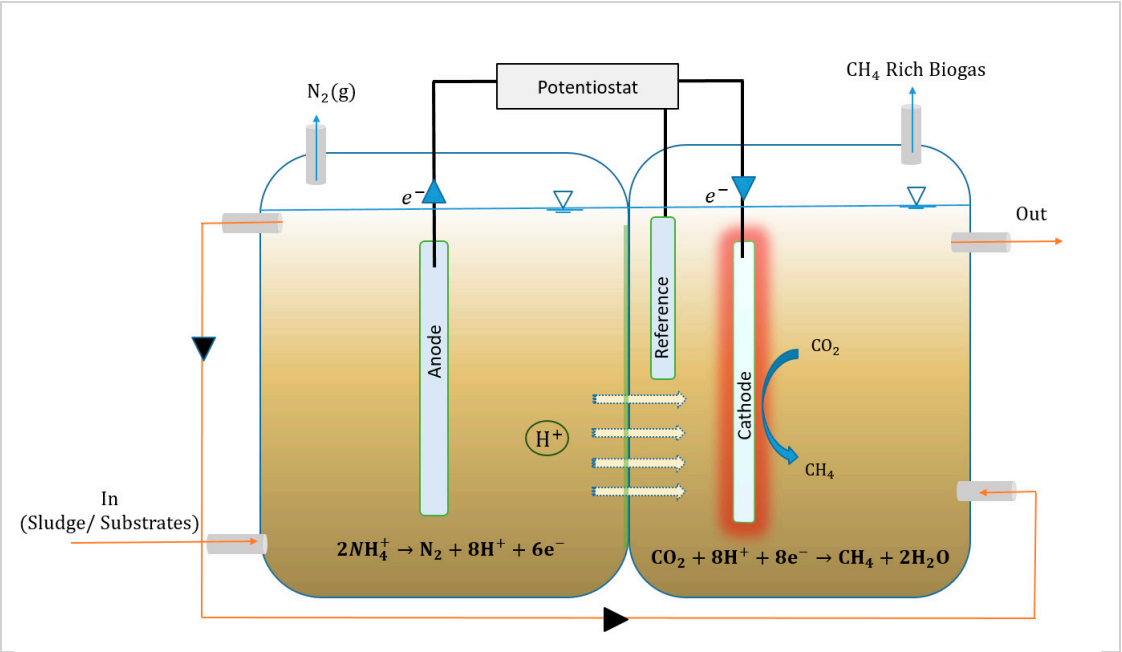


**Figure 1.** Microbial electrosynthesis (MES) reactor setup with two chambers: Anode chamber is fed any anaerobic digestion (AD) feed for biogas production (i.e., wastewater treatment plant sludge) for ammonium oxidation, and the liquid is cycled through the cathode chamber for biomethane production.

## 2. Processes

### *2.1. Anode:Electrochemical Process*

Oxidation of water and organics are the best-known anode reactions used in MES [7–9], while using ammonium as anode p&e source has, to the best of our knowledge, not yet been investigated. Ammonium can be completely oxidized at −0.273 V vs. Standard Hydrogen Electrode (SHE). This electrochemical oxidation process generates nitrogen gas p&e (Equation (4)) [17]. The possible oxidation of ammonium by a biofilm attached to the anode, such to require lower energy consumption, should also be addressed in future research.

$$2NH_4^+ \rightarrow N_2 + 8H^+ + 6e^- \quad (4)$$

Municipal wastewater and reject water from most AD are rich in ammonium. Hence, this ammonium can provide the p&e for the $CO_2$ reduction to methane and, at the same time, remove ammonium as nitrogen gas (Equation (3)) [14] from processes where it represents a problem.

Here we limit our deduction to abiotic oxidation of ammonium, where the produced electrons directly pass through the anode via conductive wires to the cathode. A potentiostat drives the electrons from anode to cathode. However, electro-active biofilm may grow on the anode surface and may catalyze oxidation reactions [18,19]. Whether this reduces the potential requirement of ammonium oxidation has not yet been investigated. A proton-permeable membrane between the anode and cathode chambers may be applied to allow transfer of the anode-generated protons to the cathode chamber.

### *2.2. Cathode:Bioelectrochemical Process*

The $CO_2$ in biogas can be reduced to methane (Equation (1)) by p&e generated from ammonium oxidation. The reduction process at the cathode is catalyzed by cathodic biofilm. Both direct and indirect electron transfers from the cathode to the biofilms facilitate the reduction process [18]. The electroactive methanogens receive electrons directly from the cathode, referred to as direct electron transfer [18]. Indirect electron transfer implies that hydrogen gas is produced as an intermediate at the cathode, either electrochemically or by electro-active $H_2$-producing organisms (Equation (5)) [2,15]. Hydrogenotrophic organisms can utilize the produced hydrogen to form methane (Equation (6)). Direct electron transfer is probably a more sustainable pathway because it requires lower cathodic potential (−0.24 V vs. SHE) than that of the indirect electron transfer pathway (−0.41 V vs. SHE) [18].

$$2H^+ + 2e^- \rightarrow H_2 \quad (5)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (6)$$

In our laboratories, we have observed the removal of ammonium in a long-term BES-methanation experiment on reject water from a food waste biogas plant. It led us to a conservative estimation of 2% increase in the methane content and 3–4% in the total biogas production. The experiment that lasted 1 year was not designed or focused on ammonium removal, but it motivated this short communication [20]. The extraction and use of ammonium as a fertilizer instead of as p&e sources for MES is not considered here, but it should be when choosing practical solutions for real cases. Ammonium recovery technologies to make consumable products, such as mineral fertilizers, consume considerable amounts of energy [14]. Ammonium as a p&e source for $CO_2$ reduction to methane, on the contrary, contributes to renewable fuel production while also preventing ammonium inhibition of acetoclastic methane production. Such MES can use the ammonium as is, without any purification, available as ions in the aqueous phase so that it can diffuse to the electrode (anode) to be oxidized. This suggests that utilization of ammonium for biomethane production by MES can often be a sustainable option in fertilizer production.

## 3. Conclusions

Anode-generated protons and electrons (p&e) in MES are used in bio-catalytic $CO_2$ reduction to methane at the cathode. Water and organic substrates are source of p&e. Ammonium is proposed as an additional and favorable p&e source. A theoretical foundation for this option is presented here, including descriptions of environmental and energetic advantages. A conservative estimation of the effect ammonium oxidation at the anode and $CO_2$ methanation was made.

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