Bio-electrochemical conversion of carbon dioxide to methane in geological storage reservoirs

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Abstract

Geological storage of carbon dioxide (CO2) as currently conceived is not commercially viable. To promote deployment of CO2 capture and storage (CCS), substantial value must be added to CCS operations. We have proposed a subterranean carbon plantation that involves storing CO2 in a geological reservoir, biologically converting the stored CO2 to methane in situ, and harvesting the biogenic methane as a recycled energy source. To examine the durability of methanogenic metabolism under storage reservoir conditions, the methanogenic activity of *Methanthermobacter thermautotrophicus* (a representative subsurface methanogen) was assessed under nutrient-limited and reduced-pH conditions in actual formation-water-based media. Moreover, to examine the possibility of electrochemically supplying the source of reducing power into the reservoir, methanogen was also incubated in absence of exogenously supplied molecular hydrogen with applied voltage. Applied-voltage-dependent methanogenesis was observed, suggesting that methanogen can utilize electrons and protons as a reducing-power source to reduce CO2 to methane. Towards practical deployment of the electromethanogenic system to utilize CCS reservoirs as energy-reserving tanks, further studies are required to enhance the bio-electromethanogenic activity and optimize well configurations.

1. Introduction

Geological storage of carbon dioxide (CO2) is a promising technology to mitigate greenhouse gas (GHG) emissions from large-scale fossil fuel use. For instance, in a scenario of reducing GHG emissions by 50% by 2050 (the IEA BLUE Map scenario), it is estimated that a hundred CO2 capture and storage (CCS) projects need to be globally deployed by 2020 and over 3000 projects by 2050 [1]. Other options for CO2 storage such as mineral carbonation and chemical industrial uses of CO2 have also been proposed [2]. However, in terms of cost effectiveness, storage potential, and technological maturity, geological CO2 storage is technologically superior to those alternatives (which remain largely underdeveloped) and is at the stage of large-scale demonstration or precommercialization. Nonetheless, deployment of CCS over the world, at present, is limited to only eight fully integrated operations, namely, the Sleipner, Snøhvit, In Salah, Weyburn, Shute Creek, Val Verde, Enid Fertilizer, and Century projects [3]. Such sluggish deployment is attributed to several factors, including, but not limited to, legal and regulatory aspects, public acceptance, and financial issues.

With regard to costs for employing CCS systems with fossil-fired power plant and various industrial processes, although a fairly wide range of expenses has been reported [3], it is certain that CCS is a capital-intensive technology. The BLUE Map scenario through 2050 requires an additional investment of over 30% more than equivalent non-CCS plants [1]. Financing mechanisms such as GHG reduction incentives and tax rebates need to be established to incentivise commercialization of CCS.

Because CCS alone would not be commercially viable and requires financial support to outweigh the cost of deployment, value-added options such as enhanced oil recovery (EOR), enhanced gas recovery (EGR), and enhanced coal-bed methane (ECBM) recovery have been suggested for partially offsetting the costs of CCS operations [2,4–6]. Various geological settings in sedimentary basins are suited for geological storage. Hydrocarbon pools, coal beds, and saline formations are all possible candidates, among which the value-added options are applicable to oil fields, gas fields, and coal beds, which, however, have limited storage capacity and geographic distribution [7]. In contrast, saline aquifers are believed to have by far the largest storage capacity and exist all over the globe [2], but value-added options have not yet been proposed for them. Therefore, it is desirable to develop a means to add substantial value to CO2 storage in saline aquifers.

As an economic incentive for saline aquifer storage, conversion of CO2 to a handy energy source, methane, is considered in this
study by virtue of microbial metabolism. Although the impacts of CO₂ on subterranean and near-surface microbial ecosystems have attracted considerable attention [8–10], active utilization of microbial organisms in CCS operations is rarely discussed in the literature. A few exceptions include the utility of biofilms as a means of reducing permeability of cap rocks [11] and the utility of hydro- genotrophic methanogen for converting CO₂ and hydrogen to methane [12]. The current study considers the possibility of microbial conversion of CO₂ and electrical current to methane in storage reservoirs—the core technology of a subterranean carbon plantation that could utilize the storage reservoirs as energy-reserving tanks.

2. Subterranean carbon plantation

2.1. Geological storage reservoirs as natural bioreactors for methane production

The concept of the subterranean carbon plantation proposed herein has the geological storage of CO₂, in situ biological conversion of the stored CO₂ to methane, and harvest of the biogenic methane as a recycled energy source as its sequence (Fig. 1). Geological storage reservoirs provide huge volumes of water-filled pore space maintained at geothermal temperatures. When supplied with CO₂ through CCS operations, such reservoirs could function as natural bioreactors that prompt methanogens to convert CO₂ to methane.

As is the case with the formation of petroleum reservoirs [13], migration and trapping are the key mechanisms that form methane accumulation worth developing. Primary migration is the expulsion of converted methane from a water phase into a permeable carrier bed. Expulsion can be achieved by virtue of the less-soluble nature of methane in groundwater. Under usual pressure and temperature conditions for geological storage, methane solubility in groundwater is an order of magnitude lower than that of CO₂. For higher values of salinity, often encountered in saline aquifers or petroleum reservoirs, solubility is further reduced [14]. Thus, methane converted from CO₂ tends to be transferred to a gas phase that can easily flow through a carrier bed.

Once methane is expelled from a water phase, subsequent movement, that is, secondary migration, is driven by buoyancy. Gaseous methane is much lighter and more mobile than groundwater; thus, methane can displace groundwater downward and moving itself upward. Buoyant force is proportional to the product of the height of the methane column and the density difference between the groundwater and methane [13]. Coalescence of the methane globules after expulsion increases their ability to move upward through water-filled pore space.

Upward buoyant force is opposed by capillary pressure, which is the resistance to entry of the methane gas globule into pore throats. When buoyant force is greater than capillary pressure, the globule squeezes into the pore throat and continues moving upward. Capillary pressure increases as the pore throat reduces. If the methane gas globule encounters a tight bed with tiny pore throats, capillary pressure may exceed buoyant force, and secondary migration eventually ceases. Such an impermeable bed is called a cap rock, beneath which gaseous methane is trapped. In the site selection process for geological CO₂ storage, cap rocks are essential for preventing CO₂ leakage from storage reservoirs into overlying beds, which also provide an efficient trapping mechanism for biogenic methane converted from CO₂.

2.2. Subterranean methanogenesis

Carbon atoms exhibit oxidation states ranging from +4 to −4, occurring mostly in the +4 (oxidized) state in CO₂ and carbonates. The most reduced form of carbon is methane, with an oxidation number of −4 [15]. Methane is generated by two main processes: biogenic and abiogenic. The former is microbial methanogenesis, and the latter includes thermal cracking of kerogen and pyrolysis or inorganic reaction of water with hot ultramafic rocks and metals [16]. Biogenic methane has been found all over the world [17], and at least 20% of the known natural gas resources are estimated to have been generated by microbes [18].

The Earth crust is inhabited from the surface down to more than 3000 m below ground by microorganisms [19]. Active microbial populations are recognized in various sedimentary environments such as gas hydrate sediments, sedimentary rocks, unconsolidated sediments, petroleum-contaminated aquifers, and petroleum reservoirs. Many subterranean environments are anoxic and appropriate for anaerobic microorganisms. Methanogens are a phylogenetically diverse group of obligate anaerobic microorganisms belonging to the Euryarchaeota phylum of the Archaea domain. Pore space in sedimentary environments is sufficient for methanogens, which have an average size of 1 μm, to thrive. In comparison with their surface relatives, subterranean methanogens are smaller, tolerate higher salt concentrations, and grow at a wider range of temperatures [16].

Methanogens generally compete with three other major anaerobic metabolic groups for their substrates in natural habitats: sulfate-reducing bacteria, acetogens, and ferric iron reducers. In habitats where the electron donor is limiting, there is a hierarchy for competition for electron donor in which ferric iron reducers outcompete other organisms if their electron acceptor is present, followed by sulfate-reducing bacteria, methanogens, and acetogens [20]. When only CO₂ is available as an electron acceptor, however, methanogens and acetogens dominate habitats. At low H₂ concentrations, a pH of less than 7, and high temperatures, aceto- genic bacteria channel acetic acid into H₂ and CO₂ formation. Methanogens then finally convert acetate, H₂, and CO₂ into methane [21].

Energy metabolism of methanogens has been considered to be restricted to the formation of methane from CO₂/H₂, formate, methanol, methylamines, and/or acetate [21]. Among these limited metabolic reactions, the two main methanogenic pathways are CO₂ reduction and acetate fermentation, as shown below, respectively:

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \]  
(1)

\[ \text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2 \]  
(2)

![Fig. 1. Concept of carbon plantation using electromethanogenesis. CO₂ is captured from large point sources (such as fossil-fuel power plants) and stored in geological reservoirs. The stored CO₂ is then reduced to methane by electromethanogenic microorganisms within the reservoir. Electrical current generated by renewable energy sources is used as a reducing-power source in electromethanogenic reduction of CO₂ and thereby stored as methane. The resulting methane can be recovered from the reservoir in a manner similar to that for natural-gas production.](image-url)
Although both CO$_2$ reduction and acetate fermentation operate in near-surface sediments, CO$_2$ reduction is the dominant pathway for deeply buried formations [18].

To promote CO$_2$ reduction (Eq. (1)), molecular hydrogen needs to be sustainably supplied. As an abiotic process, hydrogen can be generated by hydrolysis of formation water resulting from weathering of ferrous minerals in mafic and ultramafic rocks [22,23]. However, although hydrogen is a ubiquitous compound in anaerobic environments, it usually exists at very low concentration [24]. In deep subsurface sediments, the proportion of CO$_2$ converted to methane depends upon hydrogen flux [8].

Another methanogenic pathway has recently been reported [25], in which methanogenic microorganism(s) reduce CO$_2$ by using electrical current as a reducing power source.

\[
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad (3)
\]

It must be noted, however, that the mechanism of this reaction is yet to be elucidated. Although several observations have supported the hypothesis that methanogenic microorganisms can directly utilize protons and electrons (as in Eq. (3)), there is still a formal possibility that the process involves de novo formation of molecular hydrogen (Eq. (4)), which is then immediately utilized by hydrogenotrophic methanogen for CO$_2$ reduction (Eq. (1)):

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (4)
\]

The electrochemical pathway is of interest in this study, Eq. (3) (or Eq. (1) coupled with Eq. (4)), which is hereafter referred to as electromethanogenesis. An electromethanogenic biocathode yields methane from electrical current (via Eq. (3) and/or Eq. (4) + (1)), which would be provided by renewable energy sources in a sustainable system. In other words, intermittent electric energy provided by, for instance, wind turbines and photovoltaic cells can be stored in a stable form as methane. As an innovating step towards realization of a carbon plantation system, durability of methanogenic metabolism against some aspects of storage reservoir conditions and technical feasibility of electromethanogenesis applied in storage reservoirs are examined.

3. Materials and methods

3.1. Methanogenic activity under reservoir conditions

To assess methanogenic activity under reservoir conditions, a thermophilic hydrogenotrophic methanogen, Methanothermobacter thermautotrophicus (hereafter M. thermautotrophicus) strain ΔH (the type strain of the methanogen species) [27], was used as the representative species of subsurface methanogens because species closely related to the methanogen have almost ubiquitously been detected in many subsurface environments [26]. For methane production, M. thermautotrophicus strain ΔH was grown in either formation water A or B, both of which were taken directly from distinct production wellheads of the Yabase oil field, Japan, along with a mineral salt (MS) medium [12]. To prepare formation waters as growth media, the water samples were aseptically filtered and anaerobically prepared with a N$_2$ purge, and Na$_2$S was subsequently added prior to use. The MS medium for M. thermautotrophicus strain ΔH was prepared as a threefold concentrated solution and diluted with either sterilized water or buffer as appropriate. The pH of the MS medium was adjusted to pH 7.4 with HCl unless otherwise described.

For methane production from CO$_2$ and H$_2$, M. thermautotrophicus strain ΔH was anaerobically precultured in 50 mL of the MS medium at 65 °C with constant agitation (200 rpm). After 24 h of precultivation, the culture (approximately 2.0 × 10$^8$ cells mL$^{-1}$) was harvested by centrifugation (15,000g, 25 °C, 10 min). The cell pellet was washed with Tris–HCl buffer (pH 7.4), resuspended in the same buffer, and subsequently inoculated into 5 mL of either MS medium or formation waters in 30-mL screw-capped vials containing a gas mixture of 80% H$_2$:20% CO$_2$ at 0.2 MPa, unless otherwise described. Initial cell densities of the cultures were adjusted to 3.0 × 10$^6$ cells mL$^{-1}$.

The concentrations of H$_2$ and methane in the headspace were measured at appropriate intervals by using a GC-2014 gas chromatograph (Shimadzu, Kyoto, Japan) with a Shincarbon ST column (6 m × 3 mm ID, Shimadzu). Volumetric production rates of methane in formation-water-based media were compared to that under standard conditions in the MS medium at pH 7.4 with a gas mixture of 80% H$_2$:20% CO$_2$. All experiments were performed in triplicate, unless otherwise described.

3.2. Electromethanogenesis

Single-chamber electrochemical reactors were constructed from 10-mL serum bottles (Fig. 2). Anode electrodes were made of plain carbon paper (3 cm$^2$; Tsukuba Materials Information Laboratory, Tsukuba, Japan), and cathode electrodes were made of carbon paper (3 cm$^2$) coated with a carbon layer (2.5 mg/cm$^2$; Vulcan XC-72R, Cabot, Billerica, MA, USA), using Nafion (Sigma–Aldrich, St. Louis, MO, USA) as binder) on one side. A nylon filter (NY6H; Millipore, Billerica, MA, USA) was inserted between the cathode and anode to prevent direct contact between the electrodes. Titanium wires (0.5-mm diameter, Alfa Aesar, Ward Hill, MA, USA) were used to connect the electrodes to the circuit. M. thermautotrophicus strain ΔH was precultured anaerobically with a gas mixture of 80% H$_2$:20% CO$_2$ in the Methanobacterium medium (NBRC medium No. 1067; http://www.nbrc.nite.go.jp/NBRC2/NBRCMediumDetailServlet?NO=1067) in 200-mL serum bottles with thick butyl rubber stoppers. Cultivated cells were harvested by centrifugation and resuspended in fresh Methanobacterium medium. 8 mL of cell suspension was inoculated into each reactor. The reactors were sealed with butyl rubber stoppers and incubated anaerobically with a gas mixture of 80% N$_2$:20% CO$_2$ at 60 °C without agitation. Constant voltage was applied to the reactors, with the positive pole connected to the anode and the negative pole to the cathode, using a digital power supply (Array 3645A; Array Electronics, Nanjing, China). Production of methane from the samples was monitored by gas chromatography, as described above.

![Fig. 2. Schematic configuration of a single-chamber electrochemical reactor.](Image)
4. Results

4.1. Methane production in formation-water-based media

To estimate microbial methane productivity under nutrient-limiting conditions specific to geological storage reservoirs, two formation waters A and B were used as growth media for \( M. \) \textit{thermautotrophicus} strain \( \Delta H \). The yield of methane produced in formation water A-based medium was comparable to that in the MS medium at theoretical maximum (0.42 mmol of methane in headspace), whereas the yield in formation water B-based medium was reduced by 40% compared to that in the MS medium (Fig. 3). The production rates of methane in formation water A- and B-based media were 0.5-fold and 0.25-fold lower than that in the MS medium, respectively. In formation-water-based media, methane production continued after the growth arrest. These results suggested that at least one-quarter of the methanogenic activity is retained under nutrient-limiting conditions expected in geological reservoirs.

4.2. Limitation factors on methane production in the formation-water-based media

To confirm that the lower production rate of methane in the formation-water-based media was due to nutrient limitations in the media, nutrients such as nitrogen (as ammonium chloride), phosphate, and trace minerals were individually added to formation water A-based media. Methane production rates in formation-water-based media amended with nitrogen or phosphate were both 1.5-fold higher than that without the nutrients although production rates were still lower than that in the MS medium (Fig. 4). In formation-water-based media amended with trace minerals, a relatively high production rate of methane was also observed compared to that without trace minerals, suggesting that nutrient limitations of nitrogen, phosphate, and trace minerals can result in reduced production rates of methane by \( M. \) \textit{thermautotrophicus} strain \( \Delta H \) in formation-water-based media.

4.3. Effects of concentrations of nitrogen and phosphate on methane production

To estimate the effect of nitrogen and phosphate concentrations in the media on methane production rate, methane production by \( M. \) \textit{thermautotrophicus} strain \( \Delta H \) was investigated in the MS medium containing ammonium chloride and phosphate in the range from 0 to 1000 mg L\(^{-1}\) and 0 to 300 mg L\(^{-1}\), respectively. As the concentration of ammonium was reduced, methane production rate was considerably attenuated by 90% in a dose-dependent manner (Fig. 5A). On the other hand, methane production rates in phosphate-limiting media were gradually reduced by 70%, whereas a statistical difference was not observed in MS media con-
taining phosphate in the range higher than 10 mg L\(^{-1}\) (Fig. 5B). These results suggest that less than 500 mg L\(^{-1}\) of nitrogen or 10 mg L\(^{-1}\) of phosphate could result in reduced production rates of methane by \(M.\) \textit{thermautotrophicus} strain \(\Delta H\).

4.4. Effect of pH on methane production

The effect of low pH, which is expected within the geological storage reservoir, on methanogenic activity was also investigated. Methane production rates were reduced by reducing the pH of MS media (Fig. 6). Methanogenic activity observed at pH 5.5 was approximately one quarter of that observed at pH 7.4, and it was still retained at pH 4.9.

4.5. Electromethanogenesis without exogenously supplied hydrogen gas

To examine whether thermophilic methanogens have electromethanogenic activity, \(M.\) \textit{thermautotrophicus} strain \(\Delta H\) was incubated in single-chamber electrochemical reactors in absence of exogenously supplied hydrogen gas. The anode and cathode of each reactor were respectively connected to the positive and negative poles of a digital power supply, which applied a negative voltage to the reactor. At an applied voltage of \(-1.0\) V, methane was actively produced at a maximum rate of 95.5 mmol CH\(_4\) day\(^{-1}\) m\(^{-2}\) (cathode geometric surface area) (Fig. 7). Low level of methane production detected in reactors without applied voltage was possible because of carryover of trace amounts of hydrogen from the preculture or the anaerobic chamber, where reactors were inoculated with the cell suspension.

4.6. Effect of applied voltage on electromethanogenesis

To further examine the effect of applied voltage on methane production, a range of voltages (from \(-0.5\) to \(-1.5\) V) were applied to the reactors. At these applied voltages, 4.5–87.2 mmol CH\(_4\) m\(^{-2}\) of methane was accumulated after 2 days of incubation (Fig. 8). With the range of applied voltages examined so far, the higher the voltage, the higher was the methane production. Thus, these results indicate that \(M.\) \textit{thermautotrophicus} strain \(\Delta H\) can electrochemically reduce CO\(_2\) to methane by using electrical current from the electrode (instead of hydrogen gas) as the reducing-power source.

5. Discussion

5.1. Durability of methanogenic CO\(_2\) reduction in storage reservoirs

In subsurface petroleum reservoirs, methane is biologically produced at a rate of 1.3–80 nmol CH\(_4\) d\(^{-1}\) L\(^{-1}\) [28], which are two orders of magnitude less than those in terrestrial environments [29]. Methanogenic activity can be severely affected by conditions specific to deep subsurface environments such as high temperature, high pressure, and nutrient limitations [30,31]. In this study, attenuated production rates of methane were observed in formation-water-based media (Fig. 3). We showed that methanogenic activity was restricted by the limited availability of phosphate and nitrogen sources (Fig. 4). Concentrations of nitrogen and phosphate in formation water A have been reported to be 75 mg L\(^{-1}\) (as ammonium chloride) and less than 1 mg L\(^{-1}\) (as potassium dihydrogenphosphate), respectively [12]. Under such a nutrient-limited condition, it is assumed that methane production rates are reduced by 60% and 30% owing to nitrogen and phosphate limitations, respectively.

Methanogenic activity under CO\(_2\) storage conditions is a critical component in establishing the carbon plantation system. A previous study on reservoir microorganisms from an oilfield showed that methanogens closely related to \(M.\) \textit{thermautotrophicus} were a main catalyst of methanogenesis at 55 \(^{\circ}\)C and a pressure of 5 MPa, thus indicating that such in situ conditions of subsurface reservoir did not severely affect the methanogenic activity of the microorganism [32]. Unlike natural formations, however, large amounts of CO\(_2\) are artificially injected into the subsurface reser-
voir for CCS operation, thereby reducing the pH of the aquifer. It is estimated that CO₂ injection into deep saline aquifers (1500–2000 m) lowers the pH from 8.25 to 5.1 [33,34]. In the present study, methanogenic activity under low pH condition, as expected in geological storage reservoirs, was investigated. It has been reported that *M. thermautotrophicus* strain ΔΗ grows at a pH range of 6.0–8.8 [35,36]. We showed that although the methane production rate of *M. thermautotrophicus* strain ΔΗ was reduced by lowering the media pH, 24% of the methanogenic activity was retained at pH 5.5 (Fig. 6). Thus, together with our previous study [12], we showed that *M. thermautotrophicus* strain ΔΗ retained the methanogenic activity (albeit attenuated) under our experimental conditions (low pH, high concentration of CO₂, and nutrient limitations), which were partly imitating the physicochemical conditions in CO₂ geological storage reservoirs.

Hydrogenotrophic methanogens related to *M. thermautotrophicus* have widely been detected in subsurface environments including oil–gas fields and deep aquifers, which have typically been suggested as CO₂ storage sites [27,37]. Our results, combined with the previous reports [12,32], suggest that CO₂ stored in such reservoirs can be reduced to methane by the reservoir-inhabiting methanogens (or related methanogens exogenously injected into the reservoir) as long as a reducing-power source is available for the microbes.

5.2. Technical feasibility of electromethanogenesis

To provide a reducing-power source for the subterranean carbon plantation, we examined the technical feasibility of electromethanogenesis. In electromethanogenesis, methanogenic microorganisms catalyze CO₂ reduction by using the electrode (cathode) of an electrochemical reactor as a direct (Eq. (3)) or indirect (Eqs. (4) + (1)) electron donor [25]. In either pathway, however, the theoretical potential for electromethanogenesis is negative (−0.24 and −0.41 V (vs. NHE) for Eqs. (3) and (4), respectively, under biologically relevant conditions). Thus, a small external voltage is required to achieve the negative potential for the cathode. In general, because of overpotential at the cathode, voltages greater than theoretical potential must be applied to the reactor to make the reaction thermodynamically feasible.

As the first proof-of-concept study, we examined the electromethanogenic activity of *M. thermautotrophicus* strain ΔΗ. In absence of exogenously supplied molecular hydrogen, *M. thermautotrophicus* strain ΔΗ can produce methane in an applied-voltage-dependent manner (Figs. 7 and 8), thus suggesting that the microbe possesses electromethanogenic activity. At an applied voltage of −0.5 V, methane production was similar to that with no applied voltage, suggesting that the level of applied voltage was not sufficient to overcome cathode overpotential. With applied voltages from −0.75 to −1.5 V, however, the methane production level was positively correlated with voltage strength. Therefore, it can be deduced that the methanogen can utilize electrons from the electrode (cathode) and protons from the media (water) as the reducing-power source in the reduction of CO₂ into methane. In a previous study [25], electromethanogenic activity of a purely cultured microorganism has only been shown with *Methanobacterium palustre*, a mesophilic methanogen. At an applied voltage of −1.0 V, *M. thermautotrophicus* produced methane at a maximum rate of 95.5 mmol-CH₄ day⁻¹m⁻², which was at least several-fold higher than that reported with *M. palustre*.

In this study, the mechanism of applied-voltage-dependent methane production still remains to be elucidated: hydrogen evolution was not detected in electrochemical cells during incubation of *M. thermautotrophicus*, possibly because of direct utilization of electron and proton by the methanogen (Eq. (3)). Alternatively, it was also possible that hydrogen gas evolved at the electrode surface (Eq. (4)) and was immediately consumed by the methanogen (Eq. (1)). Elucidating the reaction mechanism requires further studies (including detailed electrochemical and microbial analyses), which are, however, beyond the scope of this study. Yet, regardless of the actual mechanism (whether Eqs. (3), (4) + (1)), utilization of electromethanogenesis in the carbon plantation is an attractive option as the pathway does not require exogenous molecular hydrogen for CO₂ reduction. Conservation of electromethanogenic activity in thermophilic methanogen suggests a possibility to supply, instead of molecular hydrogen, electrical power as a reducing-power source to reservoir-inhabiting methanogens.

For applying electromethanogenic reaction to reduce the geologically stored CO₂, we propose a system for carbon plantation using electrical power, which is supplied to the reservoir via a specialized well (an electrode well) as an electron donor for methane production (Fig. 9). The proposed configuration of the electrode well is shown in Fig. 10. It can be constructed by using a horizontal well as the vessel for electrodes (Fig. 10A). The horizontal well is filled with graphite granules as the electrode material (Fig. 10B). Cathode and anode chambers are compartmented by a separator, which is made of electrically nonconductive materials and has high fluid (ion) permeability (e.g., cloth or felt made of plastic or glass microfiber). The casing of the well is reticulated or has slits, allowing exchange of fluids and gases between the interior (the electrodes) and exterior (the reservoir) of the well. On the surface of graphite granules in the cathode compartment, methanogens (either indigenous to the reservoir or exogenously injected) utilize electrons from the electrode and protons from the reservoir brine to reduce CO₂, which is dissolved in the brine, to methane. This carbon plantation system to bio-electromethanogenically reduce geologically stored CO₂ represents an interesting possibility that a CCS reservoir could be used as a storage tank for electrical energy. For instance, annual injection of one million tons of CO₂ for 20 years amounts to 4.55 × 10¹² moles of CO₂ stored in a reservoir. As shown in Eq. (3), eight electrons are captured to reduce one molecule of CO₂ to CH₄. It has been reported that, in electromethanogenesis, electrons can be captured in methane with an efficiency as high as 96% [25]. Thus, by converting the entire amount of CO₂, 3.79 × 10¹² moles (3.65 × 10¹² C) of electrons can be captured as methane, yielding roughly 10 billion m³ (0.35 Tcf) of in-place methane resource potential. This amounts to the storage of 9.7 × 10¹² MWh of electrical energy in the reservoir (with a constant applied voltage of 1.0 V and an electron-capture efficiency of 96%).
5.3. Practical deployment

The current limitation of the system is the relatively slow rate of electromethanogenesis, and further studies are required to improve it. In one study, the electromethanogenic activity of a mesophilic microbial consortium, which was enriched in an electrochemical cell and consisted of multiple microbial species, was at least 30-fold higher than that of the purely cultured methanogen [25]. Recruiting natural consortium (or consortia) with 0.5-fold reduction due to unfavorable environmental conditions), it would be necessary to provide a graphite surface area of 1.66 × 10^7 m^2 to convert 4.55 × 10^{11} moles of CO_2 to methane in 50 years. This amount is equivalent to a fracture bulk volume of 3950 m^3, which can be created by current fracturing technologies such as massive fracturing [40], tip screen-out fracturing [41], and multistage fracturing [42], applied to a feasible number of horizontal wells.

With current technologies, however, some technical matters remain to be settled for practical deployment of electrode wells in the carbon plantation system, including well intervention operations for electrode-material installation, maintenance, and monitoring purposes. In particular, considering that a carbon plantation takes a few decades before the product (methane) can be harvested, electrode well maintenance needs to be executed as needed without posing any difficulty for sustained electromethanogenesis.

6. Concluding remarks

Although restricted to the experimental conditions adopted in this study, the following conclusions can be drawn through a series of biological and electrochemical experiments using M. thermautotrophicus strain ΔH:

1. Methanogenic activity, albeit attenuated, was confirmed in actual formation water media.
2. Nutrient limitations of nitrogen, phosphate, and trace minerals were causally related to the reduced methane production.
3. Although acidic condition had prominent impacts on the methanogen, methanogenic activity was retained with lowered pH values, as low as 4.9.
4. Electromethanogenic reduction of CO_2 to methane, without exogenous molecular hydrogen, was confirmed with the thermophilic methanogen.
5. Electromethanogenesis was enhanced with an increase in applied voltage, which supported the assertion of electromethanogenic reduction of CO_2.

These outcomes imply the durability of methanogens and possibility of electromethanogenesis in storage reservoirs. It is obvious, however, that further studies are required on electrochemical reduction of CO_2 under more realistic conditions: at higher (hydrostatic) pressures, in presence of solid (rock) surfaces, and in microbial symbioses. In addition, to realize a subterranean carbon plantation, the activity of electromethanogenesis must be enhanced. We are currently in the process of enriching thermophilic electromethanogenic consortia from various sources and optimizing the configuration of the electrode well.

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