Chapter 7
Hydrogen Production and Contaminants Removal Using Microbial Electrochemical Cells

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7.1 Introduction

Microbial electrochemical cells (MEC) constitute an emerging technology between electrochemistry and microbiology. MEC have been designed for various product recovery and reduction of oxidized contaminants. They are based on the bacterial interaction with insoluble electron acceptors, relying on the exchange of metabolic electron removed e-donor or supplied to the electrode. In this chapter, we will discuss the cathodic H_2 production and the removal of oxidized contaminates in MEC.

7.2 H_2 Production on Biocathode

An alternative to precious metal catalysts for H_2 production in MEC is the use of biocathodes. It came with the development of MEC from microbial fuel cell (MFC) and bioelectrochemical system (Kim et al. 2004). However, biocathodes are still in the early stages and require a deep understanding of the bioelectrochemical mechanisms involved.
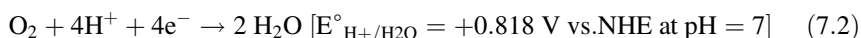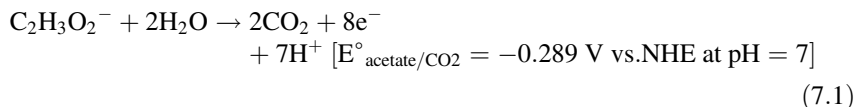
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A bioelectrochemical degradation is represented in Eq. (7.1), the simple substrate like acetate metabolize by living microorganisms. This releases H^+ and CO_2 into the anolyte and e^- to the anode as an oxidation half reaction of two-chambered MFC (Hamelers et al. 2010). Electrons then flow to the cathode through the external circuit. H^+ diffuses across the proton or cation exchange membrane and reacts with e^- and terminal electron acceptor like O_2 to form H_2O and complete reduction half reaction as in Eq. (7.2) (Oh et al. 2004). This reaction is thermodynamically favorable and spontaneous, so it produces energy.

$$C_2H_3O_2^- + 2H_2O \rightarrow 2CO_2 + 8e^- \\ + 7H^+ \ [E^\circ_{acetate/CO2} = -0.289 \text{ V vs.NHE at pH} = 7]$$
$$(7.1)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2\,H_2O \ [E^\circ_{H+/H2O} = +0.818 \text{ V vs.NHE at pH} = 7] \quad (7.2)$$

This simple system was further modified by eliminating O_2 and supporting H^+ with an extra applied voltage to reduce it to H_2 in a MEC reactor with oxidation half reaction as in Eq. (7.3) (Liu et al. 2005; Rabaey and Rozendal 2010). Such voltage turns this thermodynamically unfavorable, non-spontaneous reaction into a thermodynamically favorable and spontaneous reaction.

$$H^+ + 2e^- \rightarrow H_2 \ [E^\circ_{H+/H2} = -0.412 \text{ V vs.NHE}] \qquad (7.3)$$
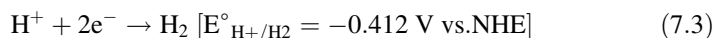
MEC provides the energy (–0.412 V) required for H^+ to H_2 reduction via microbial electron supply of 0.289 V, along with external applied voltage. Theoretically, the external applied voltage is around 0.14 V and more than 0.2 V in practice, considering electrode overpotential and Ohmic losses (Call et al. 2009). However, this applied potential is still less than the one required in water electrolysis for hydrogen production. MEC have an advantage over fermentation for producing pure H_2 due to the CO_2 and H_2 gases produced separately in anodic and cathodic chambers separated by a membrane (Rabaey and Rozendal 2010). Additionally, there are no propitious conditions for methanogens to consume H_2 gas.

Overpotential is a major issue in MEC operation. The use of platinum electrode showed promising results own to its low activation overpotential. However, it is expensive, non-renewable, imperiled to be disillusioned by carbon monoxide and certain pollutants like sulfur, and has negative effects on the environment (Chae et al. 2009). Since this electrode contributes to 47% of the total cost of MEC reactor, it definitely does not favor economic operation (Logan 2010; Rozendal et al. 2008a). A promising alternative to this catalyst is to improve the functionality of biocathode in terms of overpotential, H_2 productivity, and start-up time, while cathodic H_2 production has led to ecofriendly electrode discovery.

7.2.1 Biocathode MEC Categories

According to Jafary et al. (2015), Biocathode MEC can be developed and categorized as follows: (1). Half biological two-chambered biocathode MEC; (2). Full biological two-chambered biocathode MEC; (3). Full biological single-chambered biocathode MEC.

Half biological two-chambered biocathode MEC (MEC-I) was first developed from bioanode using acetate-fed bioanode with electrochemically active mixed culture, accompanied by flushing the headspace with H_2. Later, it was followed by acetate replacement with sodium bicarbonate, persistent hydrogen flushing, and reversing the polarity of the electrodes. Concerning the biological element/treatment, initially microorganisms were allowed to grow in batch mode for 50 h and then switch to continuous flow using a nutrient medium. After 250 h of inoculation and polarity reversal, the biocathode achieve a current density of -1.1 A/m^2 and a potential of -0.7 V. This current density was four times higher than the one obtained by using a titanium electrode coated with platinum (Rozendal et al. 2006). For the same value of current density (-0.47 A/m^2), the comparison of the applied potential for platinum-coated (with -0.7 V) and biocathode (with -0.65 V) MECs is encouraging. Measurements demonstrated a hydrogen yield of 0.63 m^3 H$_2$/m^3/day; however, there was a 67–94% of hydrogen loss, mostly due to its diffusion through the membrane. This approved the application of microorganisms as the cathode catalyst and still functions under half biological conditions (bioanode and abiotic cathode during the first two steps, and biocathode and abiotic anode after polarity reversal in the third step).

Jeremiasse et al. (2010) studied the first full biological electrolysis cell (MEC-II) in which both oxidation and reduction reactions were biocatalyzed with electrochemically active microorganisms (biocathode and anode). In a study by Tartakovsky et al. (2009), a current density of 3.3 A/m^2 was achieved at a cathode potential of -0.7 V and an applied voltage of 0.8 V. This result were comparable with a continuous membrane-less MEC at 3.2 A/m^2 catalyzed with 5 g/m^2 of platinum-load electrode (Tartakovsky et al. 2009). Low hydrogen rate of 0.04 N m^3/m^3/day and cathodic hydrogen recovery of 21% were reported, which were lower than those obtained in the same experimental setup for the first MEC-I (0.63 m^3 H$_2$/Volume/day and 49%, respectively) (Rozendal et al. 2008b).

In the third category, full biological single-chambered biocathode MEC (MEC-III) the highest hydrogen production rate of about 24 mmol/h was reported at a cathode potential of -1.0 V with 56% cathodic hydrogen recovery in the biocathode MEC, and with ferricyanide in the anode. The results for membrane-less MEC at a similar cathode potential of -1.0 V (0.7 V applied voltage) were 10.8 mmol/h of hydrogen production rate and 36% of cathodic hydrogen recovery. However, it was unclear whether any biocatalytic (biocathode) activity by microorganisms in one compartment of MEC was present in this research (Liu et al. 2005).

7.2.2 Substrate

MEC recorded lower product yield when compared to chemical methods but it still remains as a promising technology due to the use of renewable resources, wastewater as a feedstock, and less susceptibility to poisonous components present in real wastewater. To develop a biocathode MEC, a carbon source is necessary to supply cathodic biocatalyst growth; furthermore, they have shown an effective impact on main/side product formation (Jafary et al. 2015).

In an initial MEC experiment, while reversing the polarity, sodium acetate in anode was replaced by sodium bicarbonate and converted to the cathode. It resulted in methane as product and no H_2 production was observed. In this case, bicarbonate served as a carbon source for hydrogenotrophic methanogens to consume hydrogen and produce CH_4 (Eq. (7.4)). Methane has been also reported in MEC-II fed with sodium bicarbonate in cathode and sodium acetate in the anode. It has been hypothesized that CH_4 may have been produced in bioanode and then diffuse across the membrane to the cathode or, that there exist methanogens in the biocathode and they utilize the CO_2 from the anode and H_2 from the cathode chamber to produce methane (Eq. (7.5)):

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (7.4)$$

$$CH_3\,COOH \rightarrow CH_4 + CO_2 \qquad (7.5)$$
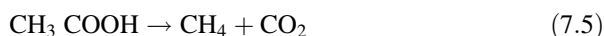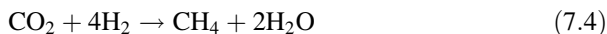
Besides, the replacement of bicarbonate (autotrophic) with acetate (heterotrophic) as carbon source helps improving the start-up time and H_2 production rate up to seven times, about 2.2 m^3 H_2/m^3 reactor/day (Jeremiasse et al. 2012; Rozendal et al. 2008a). In another biocathode study performed by Marshal et al., carbon dioxide presented a capability as the sole carbon to produce hydrogen at a rate of 11.8 mM/day at cathode potential of –1590 mV; aside from acetate and methane as two other coproducts in an electrosynthetic system (Marshall et al. 2012). The results improved to around 100 mM/day at the same cathode potential of –590 mV in a similar experimental setup operated in a semi-batch mode over 150 days in a later study (Marshall et al. 2013).

7.2.3 Challenges

Hydrogen loss across the membrane is a considerable fact that maintains both membrane-less and two-chambered configurations as an appealing research focus. Using a membrane in an abiotic cathode MEC was preferred due to the prevention of methanogens to consume H_2 in the product chamber. Concerning membrane-less setups, they resulted in low cathodic H_2 recovery which was probably due to the utilization of H_2 products by exoelectrogens to produce electricity on the anode.

Other challenges include a long adaption and start-up time of the biocathode, along with a low production rate in comparison to metal catalysts.

7.3 Perchlorate Removal

Perchlorate is a kind of persistent chemical included in the US EPA candidate list as an emerging surface and groundwater contaminant (Yang et al. 2019). The main concern is its mobility in the environment and its inhibitory effect on thyroid function (Butler et al. 2010). Among the various process developed for its treatment, the biological option is highly effective and economical (Hatzinger 2005). Most of the biological processes rely on the ability of perchlorate-reducing bacteria (PCRB) which are ubiquitous in the environment and are mainly facultative anaerobes and denitrifies (Shea et al. 2008). They are used as terminal electron acceptor and an organic carbon as electron donor; however, the use of this donor creates the issue of secondary pollutants (Logan 1998). Among the biological processes, perchlorate reduction using biocathodic microbial fuel cell (MFC) setups have the distinct advantage of decoupling oxidative (anodic) reactions from reductive (cathodic) reactions across a proton exchange membrane (PEM), thereby minimizing any secondary water quality effects.

A study done by Shea et al. (2008) investigates a functioning MFC with a denitrifying biocathode for perchlorate reduction, as a means to confirm the existence of biocathode-utilizing PCRB and the possibility of perchlorate remediation. The maximum perchlorate removal was 12 mg/L-d, contributing 64% to the 0.28 mA produced by the cell. This result suggests that PCRB are utilizing the cathode as an electron donor without exogenous electron shuttles. Butler et al. did a similar study by increasing the concentration of perchlorate and decreasing the nitrate concentration at a fixed potential. They achieved a maximum perchlorate removal of 24 mg/L-d and a cathodic conversion efficiency of 84% (Butler et al. 2010). When the concentration of sole perchlorate and sole nitrate was 0.40 mmol/L and 0.32 mmol/L respectively, both MFCs showed excellent performance on removal efficiency and current stability. As the influent molar ratio of NO_3^-/ClO_4 was 1:1, the holistic substrate reduction (40.97% for perchlorate, 86.03% for nitrate) and electricity generation performance ($3.10 A/m^3$) reached the optimum (Jiang et al. 2017).

7.3.1 Kind of Electrode

Yang et al. also studied the effect of electrode material on the perchlorate removal without external energy supply of perchlorate-reducing microbial pre-enrichment in MESs. They analyzed dual-chambers MESs with four kinds of cathode materials including Fe/C particles (Fe/C), zero valent iron particles (ZVI), blank carbon felt

(CF), and active carbon (AC). The highest perchlorate ClO_4^- removal rates in these reactors were 18.96 (Fe/C), 15.84 (ZVI), 14.37 (CF), and 19.78 mg/L/day (AC) at 100 Ω. A previous research about the electrochemical characteristics of perchlorate and iron group metals reported that ClO_4^- was adsorbed on the surface of iron material and then reduced to nontoxic Cl^- (Lang et al. 2005). However, since in the MES electrons of anode could be transferred to the cathode and ClO_4^- reduced directly by it, the removal of ClO_4^- was not only an adsorption process, but also a redox reaction process (Yang et al. 2019).

In the Fe/C and ZVI MES reactors, iron materials were used as the cathode materials, where ClO_4^- could be adsorbed and then transformed into other products under the reduction of iron materials (Yang et al. 2019). In these systems, ClO_4^- is reduced to Cl^- by Fe^0 under anoxic conditions as in Eq. (7.6) (Im et al. 2011). Fe^0 was oxidized to Fe^{2+} and then further oxidized into Fe^{3+}, therefore, cathodes were consumable.

$$ClO_4^- + 4Fe^0 + 8H^+ \rightarrow 4Fe^{2+} + Cl^- + 4H_2O \qquad (7.6)$$
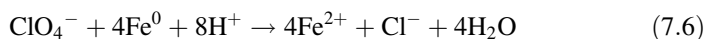
7.3.2 Effect of pH

Perchlorate reduction in the biocathode of MFC depends on both: cathode potential and pH. The maximum perchlorate reduction was observed at a cathode potential of −375 mV vs. Ag/AgCl and pH of 8.5. With an increase in pH from 6.2 to 8.1, the perchlorate reduction nearly tripled, increasing from 19% to 57%. When the pH of the influent was slightly raised to 8.5, complete perchlorate removal was achieved (Butler et al. 2010). While using the Fe/C ZVI, electrodes are consumable. The generation of hydroxides (e.g., ferrihydrite with high surface sites) when basic pH excursion occurs in the cathode chamber likely induces the adsorption and/or co-precipitation of ClO_4^- in the Fe/C and ZVI reactors.

7.3.3 Microbial Community

The perchlorate-reducing biocathode bacterial community, which contained putative denitrifying Betaproteobacteria, shared little overlap with a purely denitrifying biocathode community, and was composed primarily of putative iron-oxidizing genera.

The bacterial community presents in the perchlorate-reducing biocathode contains putative denitrifying Betaproteobacteria. However, it shared little overlap with the purely denitrifying biocathode community and was composed primarily of putative iron-oxidizing genera. On comparing the microbial community in the

chambers of perchlorate-reducing MFC and denitrifying MFC, the anode communities are similar to each other but highly distinct in their biocathode communities (Butler et al. 2010). At a broad phylogenetic scale, the biocathode communities in denitrifying MFC were dominated by Betaproteobacteria, including established denitrifying lineages and predominantly composed of sequences affiliated with iron-oxidizing bacteria (FeOB) from the Betaproteobacteria genera *Ferritrophicum* and *Sideroxydans.* In perchlorate-reducing MFC, the microbial community within the perchlorate-fed biocathode was significantly more diverse than its denitrifying counterpart and was primarily composed of bacterial sequences more similar to a clone from a dioxin-dechlorinating microcosm (Yoshida et al. 2005) and to sequences from bacteria of the genera *Chryseobacterium* and *Kaistella* (phylum Bacteroidetes). *Proteobacteria* and *Chloroflexi* were dominant in biocathode of perchlorate-reducing MFC. Among Proteobacteria, phylum, b-Proteobacteria, and a-Proteobacteria were identified as the most significant classes in biocathodes (Jiang et al. 2017).

7.4 Chromate Reduction

Chromium is a metallic species widely used in industrial applications including metal plating, leather tanning, and dye manufacturing. Its two most common species found in the environment are hexavalent, Cr^{VI}, and trivalent, Cr^{III} (Fonseca et al. 2012). The former is highly mobile and soluble which results in contamination of soils, surface waters, and groundwater; while the latter is generally considered harmless to the environment due to its lack of mobility as an insoluble species (Dong et al. 2013; Hsu et al. 2012). Thus, the reduction of Cr^{VI} to Cr^{III} has been proposed as an effective mechanism for limiting exposure and movement in the natural environment.

A study was done by Hsu et al. using *Shewanella* strains as biocatalysts for chromate reducing in a microbial fuel cell shows a maximum power generation of between 10.2 and 59.4 nW cm^{-2}. *Shewanella* acting as the sole biocatalysts at the cathode are capable of achieving the reduction of chromium concentrations to less than 5 ppb, well within acceptable guidelines established by regulatory agencies (Hsu et al. 2012). The chromate reduction takes place as per the following reaction:

$$HCrO_4^- + 7H^+ \, 3e^- \rightarrow Cr^{3+} + 4H_2O \; [E° = +0.382 \text{ V vs.SHE at pH} = 7]$$
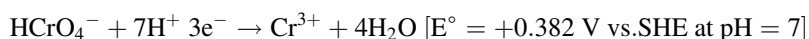
A facultative electroactive bacterium (*Bacillus*-accession number MH782060) was aerobically isolated from the biocathode of a Cr^{VI} reducing MFC. This strain showed efficient reducing ability in both heterotrophic (aerobic LB broth) and autotrophic (anaerobic MFC cathode) environments. Cr^{VI} removal reached 50.6% after 20 h in LB broth supplemented with Cr^{VI} (40 mg/L).
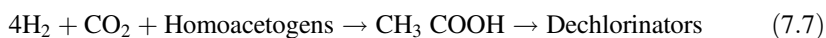
7.5 Dechlorination

MEC are progressively considered for bioremediation applications like the reductive transformation of chlorinated hydrocarbons, where a polarized solid-state cathode serves as an electron donor for reductive dechlorination catalyzed by microbes (Di Battista et al. 2012; Strycharz et al. 2008). The dichlorination of these chlorinated hydrocarbons can be achieved via two different electron transfer mechanisms. The first one is in situ electrolytic generation of molecular hydrogen, which in turn serves as an electron donor for the reductive dichlorination. The second one is the direct exchange of electrons between the electrode and the dechlorinating bacterial growth attached to the cathode surface in form of an electroactive biofilm (Aulenta et al. 2010). However, some non-organohalide respiration microorganisms, such as methanogens and denitrifying bacteria will also participate in electron competition, reducing the efficiency of electron utilization for organohalide respiration (Aulenta et al. 2011). The relative amount of electron transfer towards the dichlorination mainly depends on the set cathode potential in the MEC reactor (Rosenbaum et al. 2011).

7.5.1 Effect of Applied Potential

A study was done by Aulenta et al., proven that the set cathode potential effect the rate of dichlorination of TCE, competition for available e^- and spectrum of lower chlorinated by-products. According to them, when cathode potential was maintaining at -250 mV no abiotic H_2 production was detected, and TCE dichlorination progress slowly. Methanogenesis was almost completely suppressed and dechlorination accounted for nearly all the electric current flowing in the system. However, at the lower electrode potential of -450 mV and below higher rate of TCE dechlorination was achieved that result in the formation of vinyl chloride and ethane. At this potential, very active methanogenesis occurred that accounting for over 60% of the electric current (Aulenta et al. 2011).

A continuous study was done by the same group of authors also concluded that cathode potential maintained at -250 a negligible amount of CH_4 produce and as the potential was maintained further low the electric current of -750 mV gradually increased and higher rates of TCE dechlorination were achieved, along with the presence of very active methanogenesis due to abiotically produced H_2. The dominance of dechlorinators also at the cathode in MEC is also affected by the applied potential. All known dechlorinating bacteria are heterotrophic in nature and require organic compounds. Study done by Di Battista et al. (2012) shows that acetate concentration in the cathode effluent was always below the analytical detection limit, it cannot be excluded that some acetate was still being produced by homoacetogens by using H_2 and CO_2 and then rapidly absorbed up by dechlorinators (Di Battista

et al. 2012). This reaction occurs at the lower applied potential from −550 mV to 750 mV where H_2 production is possible (Eq. (7.7)).

$$4H_2 + CO_2 + Homoacetogens \rightarrow CH_3COOH \rightarrow Dechlorinators \quad (7.7)$$

In case of higher applied potential of −250, no H_2 was available and growth of dechlorinators are slow and their slow growth maintained by organic carbon released from the decay of the biofilm, grown during previous runs at more reducing cathode potentials. Under open circuit conditions (no current flowing in the circuit), during which a slow dechlorination was observed, clearly indicating that biofilm decay supplied the reducing power needed to drive the reductive dechlorination process (Aulenta et al. 2011).

So, dichlorination is good at lower potential but it also results in the production of CH_4 and bacterial biomass which consume the redox equivalent. Study was done by Chen et al., reveal the electron fluxes in biocathode BES performing dichlorination of chlorinated aliphatic hydrocarbon (CAHs), 1,1,2,2-tetrachloroethene (PCE), 1,1,2-trichloroethene (TCE), and 1,2-dichloroethane (1,2-DCA) with a constant cathode potential of −0.26 V, open circuit and abiotic cathode. The biocathode (99%) had significantly higher dichlorination efficiency than the opened circuit (17.2%) and abiotic cathode (5.5–10.8%), respectively, indicating the improved CAHs dichlorination capacities. The dichlorination pathway in biocathode systems was consistent with the pure microbial system, that with cis-1,2-dichloroethene and ethene as the primary products for PCE/TCE and 1,2-DCA, respectively. Besides, methane was the main by-product of heterotrophic biocathode, and methane production was enhanced to some (Chen et al. 2018).

Apart from chlorinated aliphatic hydrocarbon, complex chlorinated nitroaromatic antibiotic chloramphenicol (CAP) is also a priority pollutant in wastewaters (Liang et al. 2013). A fed-batch bioelectrochemical system (BES) with biocathode with an applied voltage of 0.5 V (served as extracellular electron donor) and glucose as an intracellular electron donor was applied to reduce CAP to amine product ($AMCl_2$). The biocathode BES converted $87.1 \pm 4.2\%$ of 32 mg/L CAP in 4 h, and the removal efficiency reached $96.0 \pm 0.9\%$ within 24 h. Conversely, the removal efficiency of CAP in BES with an abiotic cathode was only $73.0 \pm 3.2\%$ after 24 h. One intermediate, CAP-acetyl, was found in biocathode BES, indicating that it was produced from bioactivity since CAP acetyltransferase catalyzes acetylation of 3-hydroxyl of CAP while 3-hydroxyl acetylated CAP can also be transformed reversibly to 1-hydroxyl acetylated CAP (Shaw and Leslie 1991).

When the biocathode was disconnected (no electrochemical reaction but in the presence of microbial activities), the CAP removal rate was dropped to 62.0% of that with biocathode BES. Acetylation of one hydroxyl of CAP was noted exclusively in the biocatalyzed process, while toxic intermediates, hydroxylamino (HOAM), and nitroso (NO), from CAP reduction, were observed only in the abiotic cathode BES. Electrochemical hydrodechlorination and dehalogenase were responsible for the dechlorination of $AMCl_2$ to AMCl in abiotic and microbial cathode BES, respectively (Liang et al. 2013).

7.5.2 Microbial Population Responsible for Dechlorination

CARD-FISH analysis done by Battista et al. shows the presence of *Chloroflexi* in the whole range of explored cathode potentials. Notably, they accounted for a major share (from 65% to 100%) of total Bacteria and most probably played a key role in the bioelectrochemical dechlorination process (Di Battista et al. 2012). *Chloroflexi* phylum is capable of growth-linked reductive dechlorination of aliphatic and aromatic compounds (Krzmarzick et al. 2012).

Among them, *Dehalococcoides* sp. is the only one capable of dechlorinating toxic chloroethenes all the way to harmless ethene. For such a unique metabolic feature, the presence of Dehalococcoides is often regarded as a prerequisite of successful bioremediation systems based on reductive dechlorination processes. Dehalococcoides a well-known TCE to ethene dechlorinating microorganism was the predominant dechlorinating bacterium when TCE dechlorination was supported by abiotically produced H_2 gas. Interestingly, *Chloroflexi* phylum seemed to play a key role in the reductive dechlorination of TCE, at cathode potentials in the range from -250 mV to -450 mV, when the reaction was most probably driven by direct extracellular electron transfer from the cathode to the microorganisms (Di Battista et al. 2012).

7.6 Conclusion

MEC constitute a relatively recent innovation approach for wastewater treatment. Laboratory scale MEC operation shows remarkable results in terms of removal of organic matter and oxidized contaminates of interest. However, there are still several challenges that must be overcome for scaling up the technology. This effort should be focus on detail molecular understanding, development of new electrode material, inoculum, and MEC configuration.

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