Can fossil fuel energy be recovered and used without any CO₂ emissions to the atmosphere?

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Abstract

The world's energy system is still dominated by fossil fuels. While there is a rapid reduction in the cost of renewable energy and the environmental costs of continued carbon dioxide emissions from fossil fuel recovery and use are well understood, current economic, infrastructure and political constraints sustain the fossil fuel enterprise as a dominant component of the energy system. Though routes to decarbonizing fossil fuel use, such as carbon capture and storage, have been proposed and have been demonstrated at commercial scale, current CCS CO₂ storage quantities are very small and no large-scale practical route to providing fossil fuel energy, without the CO₂ emissions attendant with fuel production and use has been proposed. Here we look at some of the boundary conditions and possible routes to production of emissions free energy from fossil fuels, and specifically petroleum reservoirs. Focusing on the production of electrical power we look at possible applications of microbially mediated hydrocarbon oxidation, coupled to a range of energy harvesting strategies, to the provision of electrical power at surface at a range of scales suitable for grid power provision, powering upstream oilfield facilities or for powering *in situ* sensing and exploration systems. We also ask the question, even if practical, would direct production of electrical power from oil and gas fields be a politically and economically sensible strategy as part of the energy transition away from traditional fossil fuel use.

1. Introduction

The current climate challenge may be viewed as the consequence of three events in the energy conversion and storage domain. Firstly, living things on Earth evolved the ability to use photosynthesis to convert the energy of photons into the chemical energy in biomass. Second, Earth as a geologically active, water-rich planet enabled long-term accumulation, conversion and storage of some of this biomass as kerogen and ultimately the fossil fuels coal, oil and natural gas. This happened on timescales of millions to tens of millions of years (Tissot and Welte, 1984). The third event occurred more recently, when humans developed industrial applications for the rapid conversion of a large fraction of the chemical energy of fossil fuels into thermal energy via combustion, on timescales of decades and centuries, producing abundant CO₂ as a byproduct. Fossil fuels are versatile, convenient and abundant sources of chemical energy for these applications, as the extraordinary growth in anthropogenic CO₂ emissions and atmospheric CO₂ concentration over the last 75 years attests. The trilemma facing society today couples the benefits of fossil fuels as a high-density energy source and human development driver, with the

demonstrated hazard and risk associated with fossil fuel related air pollution and emissions driven, accelerated climate change and ocean acidification.

In this paper we examine alternate routes to energy recovery from fossil fuels and ask the question, “*Is zero emission energy from fossil fuels feasible at any useful scale*”? Even if possible, would development of such possibilities have a positive or adverse impact on a timely transition to a net zero-carbon emission energy system of the future. Are there moral hazard issues, related to prolonging conventional fossil fuel usage through such otherwise well-intentioned strategies, by considering or attempting technology developments in this direction? This perspective focuses on technical feasibility and examines at a high level, possible methods for converting the chemical energy in fossil fuels directly to other carbon-free energy carriers, such as electrons or hydrogen, without atmospheric CO₂ emission. This would enable society, in principle, to address several major challenges in the transition to a low-carbon energy system. For example, carrying out such conversions *in situ*, could allow energy production, while leaving oxidized carbon in the reservoir. This would circumvent the need to capture, transport and store CO₂ emitted when the energy conversion happens at the surface. Because the chemical energy in fossil fuel reservoirs is already concentrated in large quantities, this mode of conversion would also avoid the problem of intermittency associated with some low-carbon energy sources. The reservoirs are buried far below the surface, so this mode of producing low- or no-carbon emission energy, could also require a much smaller surface footprint than wind, solar and hydroelectric installations. Finally, the economic impact of supplying energy to world markets is large. Making the transition to a low-carbon energy system with current technologies will strand many assets of companies and countries with large fossil fuel reserves and investments, promoting incumbent legacy and political resistance to these otherwise sensible transitions. The proposed modes of energy conversion, if feasible at scale, could in principle, better align the economic interests of these players with the environmental interests of the broader community, thus facilitating a clean and politically expedient rapid energy transition. Alternatively, they might just serve as a distraction to serious attempts to quickly remove fossil fuels from the energy system!

2. How much energy and power might be extracted from typical petroleum reservoirs?

The power equivalence of oil production and combustion can be estimated from the heat of combustion of the fuel produced in a typical oil well. Oil production rates from individual wells range widely depending on oil viscosity and reservoir properties such as permeability, but well production rates range from a few, to thousands of cubic meters per day at the extreme (BOEM, 2016). Using a typical Alberta (Canada) heavy oil well production rate of 20 m³ per day of oil as a reference flow rate and a heating value of 43 GJ/ m³ for a very heavy oil -bitumen (Gates and Larter, 2014), ignoring conversion efficiencies, this corresponds to approximately 10 MW of power production per well as a reference level. The feasibility of alternatives to surface combustion for harnessing the chemical energy in hydrocarbon molecules is analyzed below. The status quo (internal combustion engines and gas-fired electricity generation) makes use of 25% to 50% of the thermal energy obtained from the chemical energy of the fuel for useful power generation. Fuel cells provide a benchmark for direct conversion of chemical energy to electrical energy, with fuel cells oxidizing small molecules such as H₂ or CH₃OH, having typical operational conversion electrical efficiencies of about 50%. Higher efficiencies are possible when cells are operated at low current densities, but this translates into larger cell/stack size and consequently into higher capital cost. Combined electrical and thermal efficiencies of as much as 90 % are possible as with high temperature solid oxide fuel cells (USEIA, 2019). Fuel cells that directly operate with larger hydrocarbons at lower operating temperature, are not yet technologically feasible. Microbial communities on the other hand routinely carry out reactions involving both small and large molecules, and enzymatic oxidation of organic molecules, including hydrocarbons, is routine in natural environments under aerobic and anaerobic conditions. However, in contrast to fuel cells, a fraction of the electrons produced in these biological reactions go to biomass, gases (H₂, CH₄) and other sinks, and this fraction typically is larger for processing of more complex molecules.

Microbial fuel cells combine the ability to oxidize complex molecules with the harvesting of electricity. The efficiency of microbial fuel cells is between ~1% and 50%, the latter obtained with molecules such as acetate (see summary in the section 4 below). Fuel cell substrate (“fuel”), to energy conversion efficiencies can exceed those of power production from oil or gas combustion, so our feasibility question becomes whether such conversions can be achieved *in situ*, mediated by microorganisms, with carbon dioxide retention in the subsurface, so that CO₂ emissions are prevented. We suggest that microbially mediated substrate (petroleum) conversion is, a priori, a plausible means of examination for conversion of hydrocarbons to carbon free energy vectors within a reservoir, as microbial communities are pervasive in the Earth’s crust, including in petroleum reservoirs (Head et al., 2014, Head et al., 2003). Moreover, communities of sulfate reducers and anaerobic methane oxidizers in shallow ocean sediments provide a proof-of-concept, having already evolved a type of microbial fuel cell that relies on extracellular electron transport (Nielsen et al., 2010). Thus, examination of the feasibility of microbially mediated electrical power production from petroleum reservoirs seems a plausible exercise.

Microbially mediated energy conversions are slow relative to familiar industrial process rates. Aerobic microbial processes are more rapid than anaerobic processes but are still much slower than combustion. Subsurface anaerobic hydrocarbon degradation rates in petroleum reservoirs under natural conditions, are very low (10^{-4} kg hydrocarbons/m²/day of oil water contact area (Larter et al., 2006, Larter et al., 2003), and would require significant engineering to produce any useful net conversion rates. Consequently, the power production per unit mass of petroleum from an *in situ* mediated microbial process, will always be much smaller than from direct combustion of any produced petroleum. However, the large volumes of petroleum reservoirs mean that low conversion rates can be scaled up volumetrically through production processes as discussed below, taking advantage of the very large volumes and surface areas for reactions possible in petroleum reservoirs with high water and oil saturations. Here, microbially mediated energy conversion has an advantage: many microbial processes involving an oil phase occur at the interface between oil and water, and the oil/water interfacial area in reservoirs is large. Oil/ water interfacial area is typically of the order of 1/10th the smooth grain surface area of a porous medium (Narter and Brusseau, 2010), thus a modest reservoir containing 10⁷ m³ of oil can easily have over 10⁴ km² of oil-water interfacial area.

In this paper, we firstly examine general routes to emissions free energy recovery from fossil fuel reservoirs as hydrogen or electricity (section 3). We then examine microbial fuel cell relevance to power generation (section 4) and explore an alternate route, involving a circulating electron shuttle system linking microbial reservoir processes with a surface fuel cell to produce electricity (section 5). Key to these routes is understanding how microorganisms can use metal oxides as electron acceptors for hydrocarbon oxidation (section 6) and the design limitations for any surface fuel cell systems necessary to accommodate “dirty” reservoir derived fluids (section 7).

3. Potential zero emission energy routes from fossil fuels. Zero emission energy from fossil fuels requires that any carbon in the fossil fuel remains in the reservoir during energy recovery and use, or that the waste carbon is returned to the subsurface as part of the process. Such processes need to be thermodynamically feasible, generate power at rates comparable to that obtainable from alternative energy recovery approaches and be feasible on a life cycle basis, avoiding adverse environmental perturbation. Processes would have to be inexpensive to engineer and politically acceptable to society. Power generation linked to classical carbon capture and storage (CCS) approaches, that simply cycle carbon bearing species (oil or gas or coal), through the power generator at the surface and return waste CO₂ to the subsurface, are technically mature and are being demonstrated in commercial pilots worldwide (Rock et al., 2017) , though there are political and economic challenges to overcome. It is estimated that perhaps 12% of our CO₂ emissions could be stored in this way (Rogelj et al., 2018) . An alternative general route could retain all carbon in the subsurface reservoir and transfer energy to the surface via alternate energy vectors, generated by biogeochemical or thermal processing of the resource

in the reservoir. Figure 1 graphically summarises four conceptual routes to zero emission energy routes from fossil fuels:

Figure 1 | . Proposed routes for electricity production from oil reservoirs without CO₂ emissions. (A) Conventional fossil fuel production combined with direct power generation and carbon capture and storage. (B) Microbial conversion of hydrocarbons to alternative energy vectors such as hydrogen. Similar processes can be designed using thermal oxidation of hydrocarbons with water. (C) Electron transporter mediated processes, using in-reservoir oil or gas shuttle redox and CO₂ retention (D) Direct power generation using macroscopic electrodes emplaced in the microbially active zone of a hydrocarbon reservoir.

A) Conventional fossil fuel production combined directly with power generation and **Carbon Capture and Storage**. These are established approaches being technically demonstrated at scale currently (Rock et al., 2017) and are not further discussed here.

B) *In situ* conversion style processes for power generation or direct fuel use. *In situ* conversion style processes, might in principle convert oil/gas thermally or biologically, to hydrogen, ammonia, or other carbon free energy vector for power generation or for direct fuel use, CO₂ being retained in the reservoir. Ammonia does not seem a plausible energy vector given the very low nitrogen to carbon ratios in fossil fuels. Hydrogen might be plausible, as it is an abundant intermediate in anaerobic, biologically mediated hydrocarbon oxidation. Methane is quantitatively produced from biodegradation of hydrocarbons in many petroleum reservoirs, utilizing water as a co-reactant, with molecular hydrogen gas being the principal intermediate (Jones et al., 2008). If the process could be engineered to inhibit methanogenesis and promote hydrogen generation and recovery *in situ*, in principle there is the basis for an energy recovery process (Larter et al., 2007). However, given the need for removal of hydrogen at low net concentrations to maintain syntrophic microbial activity, in the absence of active methanogenesis (Dolfing et al., 2008), hydrogen production, even at small scale from oil fields using petroleum biotechnology, seems unlikely, unless electrochemical or other means for energy harvesting, are coupled to active biomes (Head et al., 2014). Thermal production of hydrogen using partial combustion of petroleum *in situ* in the presence of water, may be a route to significant hydrogen production from fossil fuels, though the large amounts of carbon

dioxide produced would be difficult to control and maintain in-reservoir, if the benefits of hydrogen generation are to be maximised (Kapadia et al., 2011). Such processes are currently being field tested in Canada.

C) Electron transporter mediated processes using in-reservoir oil or gas oxidation and CO₂ retention, coupled to bulk mass transport of electron-rich shuttle species to surface power generating elements such as a fuel cell. For example, in one configuration, metal ions such as Fe(III) or Mn(IV), injected via a water flood into the reservoir, are microbially reduced using hydrocarbons and then transported to the surface and oxidized with atmospheric oxygen, generating power. The oxidized shuttles are recycled to the reservoir. The CO₂ produced by the hydrocarbon oxidation is retained in the reservoir. Other possible shuttles include the sulfide-sulfate ion pair and organic molecules such as quinone-like compounds, common in some flow batteries (Park et al., 2016). Challenges for such processes include power generation limits related to maximum shuttle flux through the reservoir to the surface fuel cell. Flux limits are related to flow rate restrictions and shuttle loss in the reservoirs, solubility limited maximum viable shuttle concentrations in the circulating fluids and possible reservoir damage issues related to precipitation of minerals such as carbonates in the reservoir. Biodegradation of organic shuttles is also a risk factor. Maintaining low pH in the reservoir would be necessary to promote a CO₂ gas phase and maximize retention of carbon dioxide *in situ*.

D) Direct power generation recovered from macroscopic electrodes emplaced or produced *in situ*. Microbial oxidation of petroleum components *in situ* via microbial fuel cells (MFCs), to generate electricity, could involve anode-reduction, with the anode connected to some form of air cathode, either in the subsurface or at the surface (Head and Gray, 2016, Head et al., 2014). This could potentially generate electrical energy while leaving CO₂ in the reservoir. However, there are many barriers that would need to be overcome to achieve this, such as large internal resistance in such cells, the low current densities commonly seen with microbial fuel cells, costs of manufacture and emplacement of large number of these devices in a reservoir media. Further complications include, maintaining electrical and proton connectivity to the reservoir, control of adverse geochemical reactions (e.g. mineral precipitation) and CO₂ leakage and escape to the surface via any O₂ distribution channels. Emplacement of large numbers of small MFCs could, in principle, provide energy-generating networks, conceptually similar to the wave energy gathering networks proposed using triboelectric generators (Wang, 2017). Such fanciful development would need a revolution in subsurface engineering, but this may happen as novel low power technologies suitable for subsurface exploration develop (Sadeghi et al., 2013) or if complex device emplacement via proppant injection approaches is developed. Currently, such proposals are very speculative. We examine limitations on MFC capabilities below.

4. In-situ microbial fuel cells in petroleum reservoirs

One obvious route to electrical power generation direct from petroleum reservoirs would be the use of in-situ microbial fuel cells (MFCs), to oxidise crude oil anaerobically, leaving produced CO₂ within the host reservoir (c.f. Figure 2). The ability of bacteria to produce electricity from organic materials has developed interest in MFCs (Logan et al., 2015). MFCs operate like any other chemical fuel cells, where the anode is supplied with an organic material such as crude oils. During anaerobic hydrocarbon degradation, microbes first activate the substrates with addition of functional groups to enhance reactivity. Many activation routes are known, including fumarate addition for activation of alkylated benzenes and acyclic alkanes, hydroxylation, carboxylation and methylation (Boll et al., 2018, Head et al., 2014, Zengler et al., 1999). Once activated, the functionalized species can be further degraded by a variety of pathways, yielding energy and generating electrons and protons. The protons pass through a proton exchange membrane (PEM), and electrons travel through the external circuit to the cathode, where terminal electron acceptors are reduced. MFCs have been built in different sizes and configurations, ranging

from microliter to several hundred liters in volume and in combination with different substrates, microbes, and operating conditions.

Figure 2 | (A) shows overall process occurring within an air breathing fuel cell. While power generation is possible, the low power densities make such approaches infeasible for large scale power generation. (B) The left panel shows possible enhancement techniques for microbial electron transfer where (1) shows direct electron transfer through nanowires and outer membrane proteins (OMP) and metal oxides serve as electron acceptor (2) shows indirect electron transfer using metal oxides as shuttles (3) shows indirect electron transfer through metabolic by-products or extracellular polymeric substances.

Figure 2A shows a conceptual schematic of a possible *in situ* MFC with an air breathing cathode, bringing oxygen from the surface and returning current to the surface, while oxidizing hydrocarbons in the reservoir anaerobically. Figure 2B shows possible enhancement techniques for microbial electron transfer where (1) shows direct electron transfer through nanowires and outer membrane proteins (OMP) and where metal oxides serve as electron acceptors (2) shows indirect electron transfer using metal oxides as shuttles (3) shows indirect electron transfer through metabolic by-products or extracellular polymeric substances.

The mechanism of electron transfer by bacteria to electrodes mainly involves two process: (i) direct electron transfer (DET) by conductive bacterial nanowires (Reguera et al., 2005) and bacterial cell surface proteins such as c type cytochromes (Myers and Myers, 1992) and flavins (Von Canstein et al., 2008) and (ii) mediated transfer by indigenous mediators like pyocyanin (Rabaey et al., 2004) or chemical compounds like neutral red (Park and Zeikus, 2000). Methylene blue, AQDS, resazurin (Sund et al., 2007), can be added externally to promote more efficient electron transfer processes. Furthermore, transition metal oxides may also promote electron transfer processes. The power output and power density (PD) of MFC is related to total anode area and has increased over time (Logan et al., 2015). Most of the highest PD values reported are from laboratory scale anaerobic MFCs using high concentrations of reactive substrate (e.g. acetate/glucose) and highly conductive electrolytes (Logan et al.,

2015). Some of the highest PD reported to date are 6.4 W m^{-2} of electrode surface area using synthetic medium and compost leachate as microbial inoculum (Rabaey et al., 2003) and 2.15 kW m^{-3} total power, with an optimized anode using a pure culture of *Geobacter sulfurreducens* and acetate as the electron donor (Nevin et al., 2008). These are significant achievements but would still present challenges for any large scaling of power generation using MFC.

It is now well established that saturated and aromatic hydrocarbons and associated aromatic hetero-compounds can be anaerobically degraded by microorganisms in MFC (VenkataMohan and Chandrasekhar, 2011, Zhang et al., 2010), but natural biodegradation rates in MFC are low (Kronenberg et al., 2017). Addition of nutrients, co-substrates and electron acceptors can stimulate degradation and additional carbon sources such as methanol, acetate, (Zhang and Lo, 2015), fumarate (Bian et al., 2015), improves the degradation of crude oil components, though viable commercial processes at scale, are unlikely to be achieved through this route. Apart from single aromatic hydrocarbons, contaminants from petroleum polluted sites containing crude oil, engine or diesel oil have also been treated using MFC with different volume of reactors ranging from 100 ml to 50 L (Kronenberg et al., 2017). The highest power density reported however, from hydrocarbon processing wastewater MFC was 21 mW m^{-2} (Chandrasekhar and VenkataMohan, 2012), while Zhou et al reported a PD of 220 mW m^{-2} with a petroleum hydrocarbon degrading soil MFC (Zhou et al., 2016). Development of MFC has enabled practical technology for real world applications with MFC volumes up to 1000 L (Logan, 2010) and applications in the mW to W range. The practical power outputs from MFC are thus however low, but for environmental remediation applications or for powering *in situ* sensors or other oilfield tools, high power output may not be the goal and applications such as biosensors, are not constrained by the amount of power generated. It is such applications that are likely more feasible for anaerobic MFC than any significant scale power generation associated with petroleum reservoirs.

The main challenge of microbial fuel cells is the low power density during operation. The feasibility of MFCs has been enhanced by demonstrating that higher power densities can be achieved by removing the Proton Exchange Membrane-PEM (Cheng et al., 2006, Liu and Logan, 2004) and through the development of air cathode systems, allowing higher power output (Logan et al., 2015). The primary issue of using an air cathode system is the mobility of oxygen into the anode chamber disrupting the anaerobic community and limiting power output. A reduced coulombic efficiency can also be observed in air cathode systems (with and without membranes), compared to dual chamber liquid phase cathodes (Liu et al., 2004). With the development of membrane-less MFCs, (Liu et al., 2004) low cost carbon electrodes, alternative fabric based separators (Fan et al., 2012) and non-platinum based catalysts, (Ben Liew et al., 2014) construction of more viable MFCs with an air breathing cathodes, for low power applications seem to be possible.

Energy harvesting from MFC is challenging, not only because of the low power densities commonly associated with these devices, but also because of the difficulty of stable operation of large devices or of connecting several reactors in series or parallel because of issues such as voltage reversal (Aelterman et al., 2006, Wang et al., 2015). Table 1 shows a summary of some MFCs with highest reported maximum power densities, current densities, and coulombic efficiencies for pure or mixed culture-based fuel cells. *In situ* devices would also require additional costly emplacement and engineering plus issues related to the challenges of electrical/proton connection to the reservoir, electrolyte/oxygen and produced water flow through the device, low electrode areal power density as well as scaling up the reactor configuration.

It seems most unlikely that MFC routes to generating multiple megawatts of power from individual oil wells are likely to be feasible and economically viable. MFC undoubtedly have applications in near surface environmental cleanup activities associated with minor power generation and, as we discuss below, MFC may prove viable as

onboard power sources for a new generation of subsurface sensors and exploration tools but in terms of significant *in situ* power generation they do not seem a viable option. Section 5 looks at biogeochemical energy harvesting strategies beyond microbial fuel cells.

Table 1. Summary of higher reported power densities, current densities, and coulombic efficiencies for pure or mixed culture based microbial fuel cells (MFC).

Reactor design	Anode substrate	Inoculum source	Anode	Cathode	Separator	Power density/ current density	CE (%)	Reference
Electrochemical half cell	Deaerated artificial wastewater with Na-Acetate as electron donor	Wastewater	Layered corrugated carbon electrode	-	-	400 A/m ²	NR.	(Chen et al., 2012)
Single chamber air cathode	Na-Acetate as substrate in synthetic medium	Wastewater	Carbon cloth J cloth was sandwiched between anode and cathode to form Cloth Electrode Assembly (CEA)	Carbon cloth/pt/PTFE cathode	None	1,550 W/m ³	NR.	(Fan et al., 2007)
Single chamber	Synthetic nutrient medium amended with Na-Acetate	Wastewater	Toray carbon paper (non-wet proof)	Carbon cloth with platinum loading of 0.5 mg/cm ²	None	6,860 mW/m ²	NR.	(Fan et al., 2008)
Dual chamber stacked cell	Synthetic medium with Na-Acetate as electron donor	<i>Geobacter sulfurreducens</i>	Carbon fibre	Carbon cloth	Nafion 117	2.15 kW/m ³ 4.6 A/m ²	100	(Nevin et al., 2008)
Dual chamber	Na-Acetate as electron donor in synthetic medium	<i>Thermincola ferriacetica</i>	Graphite rod	Graphite carbon fibre	AEM (AMI 7001)	12 A/m ²	93	(Parameswaran et al., 2013)
Dual chamber	Synthetic medium	<i>Shewanella oneidensis</i> MR-1	3D-Nitrogen doped graphene aerogel	Plain carbon cloth	CEM	225 W/m ³	NR	(Yang et al., 2016)
Ministack fuel cell	Fresh water medium with Na-acetate	<i>Geobacter sulfurreducens</i> KN400	Unpolished graphite stick electrode	Graphite cloth	Nafion 117	3.9 W/m ² 7.6 A/m ²	85	(Yi et al., 2009)
Stacked	Synthetic wastewater amended with Na-Acetate	Pre-enriched inoculum from previously operating cell	Activated carbon granules	Activated carbon granules	CEM	50.9 W/m ³	NR	(Wu et al., 2016)

Single chamber	Domestic wastewater with PBS and Na-Acetate	Wastewater	Graphite fiber brush	Fe–N–C co-catalyst on activated carbon	None	4.7 W/m ²	NR	(Yang and Logan, 2016)
Dual chamber	Synthetic wastewater amended with Na-Acetate	Pre-enriched inoculum from previously operating cell	Carbon felt as anode	Metallic copper plates as cathode	AEM	23 A/m ² 5.5 W/m ²	Recovery of copper	(Rodenas Motos et al., 2015)
Miniature	Na-Acetate medium	<i>Geobacter</i> enriched bacterial community from anaerobic sludge reactor	3D macroporous graphene scaffold anode	Glass slide coated with a layer of Cr/Au or Ti/Pt	CEM	5.61 W/m ² 11,220 W/m ³	NR	(Ren et al., 2016)
Single chamber	Synthetic medium with Na-Acetate and PBS	Pre-enriched inoculum from previously operating cell	Graphite fiber brush	Activated carbon with different conductive particles	AEM	1,900 mW/m ²	NR	(Zhang et al., 2017)
Single chamber	Synthetic medium with Na-Acetate	Compost leachate	Carbon cloth used in 3D pattern	Carbon cloth with 0.5 mg/cm ² pt loading	Different separators (plastic grid, J cloth, baking paper)	6.4 W/m ²	NR	(Oliot et al., 2017)

AEM: Anion exchange membrane, CEM: Cation exchange membrane, PEM: Proton exchange membrane, CE: Coulombic Efficiency (defined as the ratio of total coulombs actually generated by substrate utilization, to maximum possible coulombs if entire substrate converted to current) *NR: Not reported

5. Routes to *in-situ/ex-situ* production of electricity beyond the limits of MFCs

One alternate potential technological route to zero emission energy recovery from oil reservoirs that we have examined in more detail, involves microbially mediated, in-reservoir oil or gas oxidation and CO₂ retention, coupled to bulk mass transport of reduced electron-rich shuttle species to a surface, power generating fuel cell (Figure 3). This has the advantage, compared to *in situ* MFC, where diffusive supply of reactants to the cell will be limiting, of using large fractions of the reservoir volume for the anaerobic microbial hydrocarbon oxidation step, followed by advective transport of large quantities of a reduced electron shuttle to a surface fuel cell for aerobic oxidation. Such an approach could in principle, to some extent circumvent issues relating to slow conversion kinetics and avoids construction of *in situ* devices as all fuel cell hardware is on the surface. For example, in one configuration, metal ions such as Fe(III) or Mn(IV), are circulated, likely as oxides, through a reservoir via a water flood, and are microbially reduced in the reservoir using hydrocarbons. The reduced species are then transported to the surface by water flow and re-oxidized with atmospheric oxygen, generating power in a fuel cell, before

being recirculated again to the reservoir. The ideal reservoir would be one that is biologically active, with a significant water content in the porosity, enabling a large water-oil surface area for biome development, and permitting high water flow rates and minimal oil production. Such “watered out wells”, are common in many oilfields after extended oil production periods, or where incomplete charging of the reservoir happened on geological timescales. Challenges for such processes, include power generation limits related to maximum shuttle flux through the reservoir to the surface fuel cell (related to flow rate restrictions, shuttle loss in a complex porous medium and maximum viable circulating shuttle concentrations), plus possible reservoir damage issues related to precipitation of minerals such as carbonates in the reservoir itself. While the diagram below shows a very traditional vertical well water flood configuration, to maintain high shuttle flow rates through the reservoir and retain CO₂ in the reservoir, more complex well configurations, including horizontal wells, would likely be needed. CO₂ retention in the reservoir would likely not be straightforward, as to maintain a dominant gas phase CO₂ component, low pH conditions will be required.

Figure 3|. An example of an energy harvesting mode using circulating electron shuttles (e.g. Mn IV, FeIII, quinones), microbially oxidizing oil in the reservoir, the reduced shuttles being circulated to a fuel cell at the surface for re-oxidation and electricity generation. CO₂ produced in the reservoir remains trapped *in situ*.

An active microbiota in petroleum reservoirs cooler than 80°C is common (Head et al., 2014). The microbial oxidation of organic matter using metal oxides as electron acceptors is common in metal and organic matter contaminated environments and is discussed in detail below in section 6. Redox sensitive minerals such as iron (Fe(III)) and manganese (Mn(III, IV)) oxides support microbial growth in various ways including as I.) electron acceptors for heterotrophic bacterial growth, II.) electron donors for autotrophic bacterial growth, III.) as electron storage vectors and IV.) as electron conducting materials that enable electron transport between microorganisms. This process is discussed in detail below. Table 2 shows three plausible reaction systems for an in-reservoir microbially mediated hydrocarbon oxidation step. Oxidation by sulfate ions is a well-known reservoir scale

process, known as reservoir souring, which occurs during sea water injection into offshore oil reservoirs to maintain reservoir pressure (Hubert, 2010). This would not be a desirable route given the production of toxic hydrogen sulfide, which could be engineered effectively but which would terminate microbial activity at low concentrations of sulphide (c.f. 30 mM) (Peters and Fowler, 2002). The routes using manganese or iron, probably as nano particulate metal oxides migrated through the reservoir, or other, soluble transition metal ions or degradation resistant organic shuttles seem much more plausible. Nano particulate slurries at up to 19 weight percent can be percolated through reservoir media (Rodriguez Pin et al., 2009).

Table 2. Three microbially mediated potential reaction systems for in-reservoir microbial oxidation of hydrocarbons to produce a reduced electron rich shuttle

reaction	ΔG_r (kJ/mol hexadecane)	
	pH = 7	pH = 0
$C_{16}H_{34} + 98 Fe^{3+} + 32 H_2O \rightarrow 16 CO_2 + 98 Fe^{2+} + 98 H^+$	-9953.3	-6049.96
$C_{16}H_{34} + 49 MnO_2 + 98 H^+ \rightarrow 16 CO_2 + 49 Mn^{2+} + 66 H_2O$	-6487.53	-10390.9
$C_{16}H_{34} + 12.25 SO_4^{2-} + 12.25 H^+ \rightarrow 16 CO_2 + 12.25 HS^- + 17 H_2O$	-632.52	-1120.44

Given a fuel cell operating voltage of 0.5 V, a fuel cell efficiency of 50% and a circulating shuttle concentration of 1.5 molar (a 13% by weight oxide slurry for example), with a two-electron oxidation step in the fuel cell (e.g. $Mn^{II} \rightarrow Mn^{IV}$), then with a flow rate of fluid of 1600 m³ per day through the reservoir to the fuel cell, then at steady-state, reservoir simulations suggest that over 1 MW of continuous power is theoretically possible. This incurs a pumping power cost of around 150 kW. This assumes of course, that microbially mediated redox kinetics in the reservoir can reduce this quantity of shuttle at an appropriate rate and the reaction kinetics and shuttle conformance and loss in the reservoir are not rate limiting. It also assumes that metal oxide reduction is the only process driving hydrocarbon oxidation which is unlikely and recently, Novotnik et al. (2019b) have shown, for example, that metal reduction did not outcompete fermentation processes during manganese mediated lactate degradation, thus 1 MW is likely a very optimistic upper bound for power generation levels. There are in addition, many key properties of the system which are currently poorly estimated or unknown. Given typical wind turbine power outputs of a few MW (Bilgili et al., 2011), a 1 MW power output from a single well would not be an outstanding achievement, but does suggest that such technologies are worthy of some examination to see, if they are capable of more than just being able to power conventional oil production facilities from a few power-generating wells. One consideration is that such technologies could in principle, access in a relatively clean manner, the energy stored in the vast reserve of oil left in a reservoir after conventional and enhanced oil recovery processes have taken place. The average oil recovery for a conventional light oil reservoir is around 35% globally, with heavy oil production in Alberta, for example, averaging less than 15% of the in-place crude oil being recovered by conventional methods. Clearly there are many other considerations as well, not the least of which are any life cycle impacts related to injection of large quantities of metal ions into the subsurface and the economic aspects of any process. Generally, as the surface infrastructure needs of such processes would be not very different from typical oilfield activities today, with the exception of a fuel cell installation of course, this area seemed worthy of

laboratory and small-scale pilot testing to assess if it is truly a feasible, scalable and useful technology for zero emission energy recovery from oil fields. Improved understanding of microbially mediated metal oxide-organic matter oxidations through such studies, may also have collateral benefits in terms of environmental and sensor applications beyond energy recovery aspirations, and these are reviewed below.

6. Insights on metal reducing organisms and microbiology, solid phase electron acceptors and electrogenic microbes

Redox sensitive minerals such as iron (Fe(III)) and manganese (Mn(III, IV)) oxides support microbial growth in various ways including as I.) electron acceptors for heterotrophic bacterial growth, II.) electron donors for autotrophic bacterial growth, III.) as electron storage vectors and IV.) as electron conducting materials that enable electron transport between microorganisms. The most well known microorganisms that can respire Fe(III) and Mn(III,IV) oxides are *Geobacter sp.* (Lovley and Phillips, 1988) and *Shewanella sp.* (Myers and Nealson, 1988). On the other side of the spectrum are microorganisms such as *Rhodopseudomonas sp.* and *Sideroxydans sp.* that can oxidise insoluble minerals (e. g. FeS and FeCO₃) with reduction of O₂, CO₂, and NO₃⁻ (Liu et al., 2012, Xing et al., 2008). Although certain species can only oxidise or reduce iron and manganese, there are some species that can perform both, such as *G. metallireducens* (Finneran et al., 2002). It has been inferred that metal reduction can be linked to hydrocarbon oxidation in contaminated aquifer and soil settings (Kleinstaub and Schleinitz, 2012), and studies in our laboratory show that microbial consortia, containing oxide utilizing microorganisms, can biodegrade a wide range of hydrocarbons in bulk phase whole crude oils under anaerobic conditions, producing reduced metal ions in solution (Novotnik et al., 2019a).

Metal respiring bacteria use Mn(III, IV) and Fe(III) oxides as electron acceptors for respiration. Iron is an abundant element in Earth's crust and the reducible iron in soils and sediments are in the form of poorly soluble iron oxides such as hematite (α -Fe₂O₃), goethite (α -FeOOH), or ferrihydrite. The presence of low solubility electron acceptors in the environment selects for bacteria that can preferentially utilize extracellular electron transport. The redox potentials of various Fe(III) oxides are around - 0.3 V (Ilbert and Bonnefoy, 2013). Manganese oxides such as birnessite [(Mn⁴⁺, Mn³⁺)₂O₄ · 1.5H₂O] and pyrolusite (MnO₂) are far less abundant than iron, but are still relevant electron acceptors in the environment (Richter et al., 2012).

The low redox potentials of these metal oxides together with their poor solubility, makes them at first sight, an unfavourable substrate for bacterial utilisation. Since the bacterial cell wall is impermeable to particulate metal oxides, several mechanisms have been developed that enable extracellular electron transport (Cao et al., 2011, Sacco et al., 2017). For both *Shewanella* and *Geobacter* strains, c-type cytochromes are essential electron transfer proteins (Shi et al., 2016). *Shewanella* and *Geobacter* developed slightly different ways of transferring electrons. In either case, the electrons travel from the cytoplasm via a series of multiheme cytochromes to the cell surface. From the cell surface the electrons can be donated to the minerals in several ways. Firstly, direct electron transfer from the cytochrome when there is either direct contact between the cell and the mineral, via pili (Walker et al., 2016) or nanowires (Myers and Myers, 1992, Pirbadian et al., 2014, Roden et al., 2010). Secondly, electrons are donated indirectly via endogenous or exogenous shuttles or bacterial by-products (Choi and Sang, 2016, Marsili et al., 2008, Shi et al., 2012). The shuttles must be chemically stable, not easily biodegraded and must easily pass the cell membrane, trapping and transporting electrons. Examples of endogenous shuttles are quinones (Glasser et al., 2017) and flavin derivatives (Marsili et al., 2008). One of the most commonly used exogenous electron shuttles are AQDS (anthraquinone disulfonate), and humic substances (Finneran et al., 2002, Paquette et al., 2014). A third way is via extracellular polymeric substances in biofilms (Cao et al., 2011, Sacco et al., 2017) that can contain extracellular DNA, RNA, cytochromes and other redox sensitive molecules that aid in electron transfer (Liu et al., 2014).

Minerals with iron centers can also act as conductors for electrons between species such as from metal reducing bacteria to methanogens (Pan et al., 2017). Special interest has been shown for mixed redox minerals such as magnetite ($\text{Fe(II)Fe(III)}_3\text{O}_4$), where iron can undergo oxidation-reduction cycles without any significant Fe(II) dissolution (Zhao et al., 2015a). Namely, Fe(III) serves as electron acceptor for a metal reducing bacteria that generates biogenic Fe(II) which can then be re-oxidised by a different syntrophic bacteria (Zhao et al., 2015a). Hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite can act as conductors (Kato, 2015) between Fe(III) reducing *Geobacter sulfurreducens* and *Thiobacillus denitrificans* that uses the electrons to reduce NO_3^- (Shi et al., 2016). Similar cycling is observed when Fe(II) is oxidised photo autotrophically by *Rhodopseudomonas palustris* TIE-1, then the biogenic Fe(III) is reduced in a co-culture by the anaerobic, Fe(III)-reducing bacterium *Geobacter sulfurreducens* (Byrne et al., 2015). In both cases iron minerals can act as electron sinks and electron sources, depending on the environmental parameters, hence making iron oxides natural batteries (Shi et al., 2016).

Another phenomenon of interspecies electron transfer is the filamentous or so called “cable” bacteria of the family *Desulfobulbaceae*. These filamentous bacteria control both the anodic and the cathodic reactions and can couple oxidation of sulfide in the anaerobic sediment zone with O_2 reduction at the sediment-water interface (Müller et al., 2016, Risgaard-Petersen et al., 2015). It seems the outer membrane acts as an insulator that prevents electrons from leaking out of the cell and enables electron transfer (Shi et al., 2016), although the exact mechanism of intercellular transport is not yet understood. An electric field is created by promoting a charge imbalance by separating anodic and cathodic reactions and ionic transport in the pore water completes the overall electric circuit. This example is relevant as cable bacteria can conduct electrons over much larger distances than via nanowires and may be important in the context of *in situ* or *ex situ* microbial fuel cells as it could lead to larger effective electrode surface areas and hence power densities.

Microorganisms capable of extracellular electron transport are also known to exchange electrons with electrodes, which leads to their application in electricity generation (Bond and Lovley, 2003, Gregory et al., 2004, Joo Kim et al., 2002). Microorganisms can transfer electrons to the anode either via direct electron transfer, via electron shuttles or pili mediated routes (Semenec and Franks, 2015). For example, *Geobacter* spp. and *S. oneidensis* can utilize anodes or cathodes as electron donors or acceptors for respiration (Bond and Lovley, 2003, Gregory et al., 2004, Joo Kim et al., 2002). When microbes receive electrons from cathodes, these processes are generally used for electrosynthesis purposes where cathodes serve as electron donors to, for example, reduce CO_2 into utilizable organic compounds for the organism to make a living (Choi and Sang, 2016). As discussed above, anaerobic oxidation of crude oil in the presence of metal oxides, coupled to an air breathing cathode, can generate power within a microbial fuel cell, albeit at low power densities, demonstrating electron transfer to electrodes. The common association of anaerobic microbial consortia with shallow, cool petroleum reservoirs suggests that further ideation and investigation of microbial routes to carbon free power generation from petroleum containing reservoirs is worthwhile, though our current studies suggest only low power level recovery will be possible with the propositions made in this paper.

7. Transporter routes to power generation: shuttles and surface redox flow cells

Though there are many critical challenges, the concept of using a circulating electron shuttle, moving between reservoir and surface fuel cell, coupling in-reservoir microbial anaerobic hydrocarbon oxidation with surface re-oxidation of the shuttle in air-breathing fuel cell can be used in principle, to directly harvest energy from petroleum reservoirs, potentially leaving all carbon in the reservoir (Fig 4). Effectively, such a system would be equivalent to a redox flow cell (RFC) or redox flow battery (RFB), with reduced reactants in the reservoir (oil), and oxygen in the atmosphere (oxygen). Technically, a fuel cell is a type of redox cell where oxygen is reduced and

hydrogen is oxidized, but for practical purposes and to distinguish the application from more familiar battery applications, we use the term redox flow cell (RFC) instead of 'redox flow battery (RFB)'. Though, as discussed above, the challenges are many and complex to such an approach, examining the specific challenges of an RFC dealing with dirty electrolytes, as with an oilfield application, may provide insights to other applications.

Though many excellent review articles on RFB science and technology address the fundamental and applied aspects of design, material components and redox couples (Park et al., 2016, Soloveichik, 2015, Wang et al., 2013, Wei et al., 2017) for RFB, this section focuses on the challenges and opportunities a surface RFB or RFC might offer when adapted to a petroleum reservoir application. Typically, renewable energy sources are coupled with flow batteries for energy storage in a grid parallel design permitting release of energy on demand, due to the scalable energy storage capacity, and long energy storage and discharge times of flow batteries (Alotto et al., 2014) (Fig. 4a). RFBs provide deep charging/discharging cycles with long lifecycles up to and beyond the MW power range. Different combinations of redox metal, metal complex and organic redox couples have been demonstrated in both aqueous and non-aqueous electrolyte systems in recent RFB designs (Fig. 4b). Conventional RFB environmental impacts are considered minimal and recent innovations in this direction, demonstrate a low capital cost per kWh stored, with costs as low as \$100 kWh (Gong et al., 2015). Redox active materials enabling higher cell voltage than that bounded by water splitting reactions (>1.5 V) use non-aqueous redox electrolytes, such as ferrocene, cobaltocene, and its combination (Jia et al., 2015, Zhao et al., 2015b) to achieve high energy density. Redox couples composed of earth abundant metals, metal complexes, or organic species (Fig. 4b), tolerant to impurities and possessing fast electrode kinetics, high electrolyte solubility and high open circuit voltage have also been demonstrated (Colli et al., 2016, Lin et al., 2016). The electron shuttle circulation system being evaluated here would form part of the electrolyte delivery system for a fuel cell that is effectively functioning as a RFC linking an electron donor-crude oil in the reservoir, with electron acceptor atmospheric oxygen, via a circulating electron shuttle. A further constraint on electrolyte composition is that the shuttle can be reduced by microbial hydrocarbon oxidation, directly or indirectly, so many current RFB electrolytes would not be appropriate, or cost effective.

Figure 4 | . Electrochemical energy storage systems. (a) Comparison of key system descriptors for generation and storage of electrical energy using different technologies (after Alotto et al., 2014) and (b) various flow battery types and redox species combinations currently available using aqueous and non-aqueous electrolytes.

The energy density, E , (Wh/L) of a RFC is related to the concentrations of the redox active species in the anode (C_a) and cathode (C_c) compartments, the operating voltage (V), and the number of electrons involved in the redox reaction at the anode (n_a) and cathode (n_c) (Soloveichik, 2015). For a system with equal concentration of anolyte and catholyte, the energy density is expressed as;

$$E = \frac{nCFV}{2} (1)$$

Figure 5 | Reduction potentials of redox couple elements and potential auxiliary electrode couples (AEs) under acidic and alkaline media that may be employed in an energy recovery system. The estimated theoretical energy storage density is 14 Wh/L for a 0.5 M $ZnCl_2$ -0.5 M AQS (anthraquinone sulphonate) system, while for a molar concentration of $Fe^{3+/2+}$ and $SO_4^{2-}/S_2O_6^{2-}$ an RFC might exhibit storage capacities of 67 and 70 Wh/L, respectively (Soloveichik, 2015). Many of these redox couples would not be practical for a reservoir linked system.

Energy densities of a redox flow battery depends primarily on the effective shuttle concentration and redox potential difference of the redox couples used. The redox potentials of a variety of redox elements are presented in Fig. 5 with the estimated theoretical energy density from the literature (Soloveichik, 2015). Apart from the

shuttle's electrochemical compatibility to extract high power from the power source, there are a few more conditions to be satisfied such as energy conversion rates and compatibility of the flow battery with fluids arriving from the reservoir, the affordability and availability of the shuttle material and materials issues for corrosive species. For a reservoir scale flow cell system, there are several key constraints, such as the primary redox shuttle species compatibility with the microbial colony and its ability to be reduced by the microbes and be subsequently re-oxidized, directly or indirectly, at the surface in the power generating cell. The availability of large quantities of inexpensive shuttle (Mn^{4+} , Fe^{3+} or sulphate ion), mainly in the form of nanoparticles of MnO_2 or Fe_2O_3 to circulate into the reservoir volume is also crucial. While, Mn^{7+} and Mn^{6+} were recently demonstrated to represent high energy density RFC components (Colli et al., 2016), cost, abiotic reactivity and corrosivity render them impractical options as circulating shuttles.

Increasing the flux and concentration of circulating redox shuttles would lead to an increased current density but could also negatively affect the microbial community in the reservoir which could attenuate microbial action. For example, the biodegradation of hydrocarbons by sulfate reducing bacteria was found to be affected at hydrogen sulfide concentrations higher than 30 mM (Peters and Fowler, 2002). Such effects put a constraint on the maximum concentration of the shuttle for the working microbial communities. This problem can be alleviated by solid nanoparticles dispersed in a carrier fluid such as water. An advantage of using nano-particulate solid phase shuttles is that high net abundances of shuttles, such as iron or manganese oxides could be circulated, while maintaining low intracellular metal concentrations to enable a high selectivity of organic matter oxidation by a variety of anaerobic microorganisms (Lovley, 1991). Migration of nano-particulate species through porous media at concentrations of up to 19 weight percent has been demonstrated (Rodriguez Pin et al., 2009). Conversely, use of solid phase shuttles or production of insoluble reduced mineral phases (e.g. metal carbonates), could potentially result in formation damage and reservoir plugging, which would adversely affect the process through loss of shuttle material in the reservoir and reduction in circulation flow rate due to formation permeability reduction. The mild operating temperature range favorable for biological activity in the reservoir (ca 30-80°C), is favorable for direct connection of fluids arriving, at near reservoir temperature, to an RFC. However, the produced fluids from the reservoir will not be "clean", and may contain various additional solutes and particulate material, as well as water and oil, thus a sensible separation system and novel fuel-cell design would be needed. A cell design including separation of electrode compartments is likely desirable. Reservoir fluids can be re-oxidised in a membrane free configuration, via auxiliary electrodes connecting the anode compartment of a RFC with clean and optimized electrolytes in a (air breathing) cathode compartment (Figure 6.) (Thangadurai et al., 2019). Further complications will likely also arise, if transition metal-based shuttles were used, as it is likely that the re-oxidized shuttle might precipitate on electrochemical cell components as insoluble phases. Such designs will require much engineering innovation. In the general context of flow cells and flow batteries, alkaline electrolytes are preferred over acidic electrolytes since, alkaline electrolyte based RFB alleviate costs, corrosion and safety concerns over acidic RFB. However, as the circulating redox shuttle approach described here, has a primary objective of securely storing produced carbon dioxide in the reservoir, a low pH operating fluid is desirable to maintain CO_2 predominantly in the gas phase where it could migrate to the reservoir crest for safe storage. Low pH circulating fluids would also tend to minimize carbonate precipitation in the reservoir and consequent formation damage.

The energy density of the system depends on the voltage of operation of the RFB, which is bounded by the water splitting region in the case of an aqueous redox flow battery. Non-aqueous electrolytes could mitigate the energy density issue by providing higher cell voltages >1.5V, but these systems commonly suffer from lower Faradaic efficiency and higher electrolyte resistance than aqueous electrolyte based RFBs (Soloveichik, 2015). Additionally, with the reservoir portion of the cycle operating with water-based fluids, at least part of the system would likely

have to use water-based electrolytes in at least one compartment. With the requirement that the shuttles are inexpensive and are elements that can mediate microbial redox processes then iron, manganese or vanadium are logical design choices with the main challenge being the coupling of a dirty reservoir fluid to a viable surface RFC. There are thus, many design challenges for such a system.

Figure 6 | A hybrid redox flow cell designs where the reservoir fluid is in direct contact with the anode chamber for energy harvesting. Auxiliary electrodes (red and blue electrodes linked by green wire) link the anode compartment to an air breathing cathode chamber.

A possible conceptual design for a practical cell is shown in Fig 6. This consists of two separate compartments processing the electrolytes for redox reactions and generating power in a fuel cell utilizing auxiliary electrodes. Auxiliary electrode (AE) based electrolyzers have been proposed (Landman et al., 2017), and while a flow battery is a fundamentally different entity, some of the same concepts can be further extended to such an application. The main advantage of such a design is that it permits coupling of complex reservoir fluids and electrodes in one cell, to a separately optimized air breathing cathode in another. Such devices have been tested in our lab at both high and low pH conditions (Venkatesan et al., 2019). These AE-designed RFCs devices may exhibit low efficiency due to the increased polarization loss related to additional auxiliary electrode reactions and redox couples in anolyte and catholyte chambers. Such an RFC system can potentially harvest energy by coupling the in-reservoir microbial oxidation of heavy oil and electrochemical reduction of oxygen mediated via a circulating electron shuttle in two separate compartments. With shuttle circulation, continuous power generation is in principle possible, though as described above, there are many challenges both within the reservoir and in the design of the redox flow cell to achieving significant power levels.

8. A summary perspective and outlook on the possibilities for zero emission energy recovery from oil and gas fields

The world's energy system is still dominated by fossil fuels and though routes to decarbonizing fossil fuel use, such as carbon capture and storage, have been proposed and have been demonstrated at commercial scale, current

CCS CO₂ storage quantities are very small (ca 40MT CO₂/year). Until recently, no other large-scale practical route to providing fossil fuel energy, without the CO₂ emissions attendant with fuel production and end-user combustion has been proposed but a corporate alliance of Carbon Engineering and oil and gas companies, recently have begun a project to link large scale direct air capture of CO₂, to CO₂ driven enhanced oil recovery (Carbon Engineering, 2019), with net storage of enough CO₂ to produce a reduced or even negative net carbon emission barrel of oil. A pilot project is underway. Examining routes to energy recovery from reservoirs using carbon free energy vectors such as hydrogen or electricity, we have focused on microbially mediated approaches. While hydrogen is produced during anaerobic hydrocarbon biodegradation in petroleum reservoirs, scaling recovery of the biologically produced hydrogen to practical levels seems infeasible given current understandings. Recovery of electrical power from petroleum reservoirs using microbial fuel cells is possible, but practical routes to megawatt levels of power generation are not evident through this route, which is also complicated by the cost and complexity of subsurface engineering and the need for numerous linked devices to achieve any significant power. Microbial fuel cells will have practical application in environmental remediation applications near the surface and, we speculate, are potentially a route to providing internal power for subsurface sensing and exploration probes if practical devices can be engineered. Standard subsurface exploration protocols involve relatively rapid drilling (days or weeks), at costs in the range of millions of dollars. Slower, less expensive exploration is potentially possible using low penetration rate devices over much longer time scales, not inconsistent with the overall multi-year timescales of subsurface exploration and resource production strategies (De la Fuente et al., 2019). Such approaches, conceptually analogous to low cost, long timeline exploration with space probes, could be an alternative paradigm to conventional drilling-based investigation of subsurface reservoirs but remain speculative at this time. On board microbial fuel cells may be possible power sources for such systems.

Alternative routes to direct electrical power generation from oil (or natural gas), reservoirs can as we have suggested, in principle, involve circulation of an electron shuttle which is reduced in the reservoir through anaerobic microbial activity and becomes re-oxidized at the surface with atmospheric oxygen in a redox flow cell to produce electricity. Though energetically possible, the research and technology design challenges are many and power levels possible are related ultimately to reduced shuttle circulation fluxes. While we do not have a complete picture of the mechanisms and kinetics of microbial metal ion reduction, it is not efficient, so actual power outputs would be severely limited and below practical limits (<<1 MW per well). At this time, we doubt such approaches would be scalable to significant-scale commercial power generation technology. While viable microbiological routes to zero emission energy recovery and use, as discussed here, seem to us unlikely, further ideation in this space may yet provide novel insights to such a goal. Abiotic routes to hydrogen production and recovery from oilfields, are being field tested and such routes may have more utility.

Authors' contribution

Breda Novotnik, Arpita Nandy, Senthil Velan Venkatesan, and Jagoš R. Radović carried out the major part of review work related to project definition in the areas of microbiology, electrochemistry and geochemistry and wrote major portions of the text. **These authors contributed in equal part.** Juan De La Fuente, Siavash Nejadi, Renzo C. Silva, Angela Kouris contributed to the paper in the areas of subsurface engineering, reservoir simulation, carbon storage geochemistry and microbiology. Venkataraman Thangadurai, Steven Bryant, Kunal Karan, Roman Shor, Marc Strous, and Stephen R. Larter directed and designed the project. All authors contributed to the text.

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Competing interests

The authors declare no competing interests.

References

- AELTERMAN, P., RABAEY, K., PHAM, H. T., BOON, N. & VERSTRAETE, W. 2006. Continuous electricity generation at high voltages and currents using stacked microbial fuel cells. *Environmental Science and Technology*, 40, 3388-3394.
- ALOTTO, P., GUARNIERI, M. & MORO, F. 2014. Redox flow batteries for the storage of renewable energy: A review. *Renewable and Sustainable Energy Reviews*, 29, 325-335.
- BEN LIEW, K., DAUD, W. R. W., GHASEMI, M., LEONG, J. X., SU LIM, S. & ISMAIL, M. 2014. Non-Pt catalyst as oxygen reduction reaction in microbial fuel cells: A review. *International Journal of Hydrogen Energy*, 39, 4870-4883.
- BIAN, X. Y., MBADINGA, S. M., LIU, Y. F., YANG, S. Z., LIU, J. F., YE, R. Q., GU, J. D. & MU, B. Z. 2015. Insights into the anaerobic biodegradation pathway of n-Alkanes in oil reservoirs by detection of signature metabolites. *Scientific Reports*, 5, 1-12.
- BILGILI, M., YASAR, A. & SIMSEK, E. 2011. Offshore wind power development in Europe and its comparison with onshore counterpart. *Renewable and Sustainable Energy Reviews*, 15, 905-915.
- BOEM 2016. Deepwater Gulf of Mexico December 31, 2014. New Orleans: US Dept. of the Interior, Bureau of Ocean Energy Management.
- BOLL, M., ESTELMANN, S. & HEIDER, J. 2018. Anaerobic Degradation of Hydrocarbons: Mechanisms of Hydrocarbon Activation in the Absence of Oxygen. In: BOLL, M. (ed.) *Anaerobic Utilization of Hydrocarbons, Oils, and Lipids*. Cham: Springer International Publishing.
- BOND, D. R. & LOVLEY, D. R. 2003. Electricity production by *Geobacter sulfurreducens* attached to electrodes. *Applied and Environmental Microbiology*, 69, 1548-1555.
- BYRNE, J. M., KLUEGLEIN, N., PEARCE, C., ROSSO, K. M., APPEL, E. & KAPPLER, A. 2015. Redox cycling of Fe(II) and Fe(III) in magnetite by Fe-metabolizing bacteria. *Science*, 347.
- CAO, B., AHMED, B., KENNEDY, D. W., WANG, Z., SHI, L., MARSHALL, M. J., FREDRICKSON, J. K., ISERN, N. G., MAJORS, P. D. & BEYENAL, H. 2011. Contribution of extracellular polymeric substances from *Shewanella* sp. HRCR-1 biofilms to U(VI) immobilization. *Environmental Science and Technology*, 45, 5483-5490.
- CARBON ENGINEERING. 2019. *Oxy Low Carbon Ventures and Carbon Engineering begin engineering of the world's largest Direct Air Capture and sequestration plant* [Online]. Available: <https://carbonengineering.com/worlds-largest-direct-air-capture-and-sequestration-plant/>.
- CHANDRASEKHAR, K. & VENKATAMOHAN, S. 2012. Bio-electrochemical remediation of real field petroleum sludge as an electron donor with simultaneous power generation facilitates biotransformation of PAH: Effect of substrate concentration. *Bioresource Technology*, 110, 517-525.
- CHEN, S., HE, G., LIU, Q., HARNISCH, F., ZHOU, Y., CHEN, Y., HANIF, M., WANG, S., PENG, X., HOU, H. & SCHRÖDER, U. 2012. Layered corrugated electrode macrostructures boost microbial bioelectrocatalysis. *Energy and Environmental Science*, 5, 9769-9772.
- CHENG, S., LIU, H. & LOGAN, B. E. 2006. Increased performance of single-chamber microbial fuel cells using an improved cathode structure. *Electrochemistry Communications*, 8, 489-494.
- CHOI, O. & SANG, B. I. 2016. Extracellular electron transfer from cathode to microbes: Application for biofuel production. *Biotechnology for Biofuels*, 9.
- COLLI, A. N., PELJO, P. & GIRAULT, H. H. 2016. High energy density MnO₄⁻/MnO₄²⁻ redox couple for alkaline redox flow batteries. *Chem. Commun.*, 52, 14039-14042.
- DE LA FUENTE, J., SHOR, R. & LARTER, S. R. 2019. Single Actuator Peristaltic Robot for Subsurface Exploration and Device Emplacement. *IEEE*, submitted.

- DOLFING, J., LARTER, S. R. & HEAD, I. M. 2008. Thermodynamic constraints on methanogenic crude oil biodegradation. *The ISME journal*, 2, 442.
- FAN, Y., HAN, S. K. & LIU, H. 2012. Improved performance of CEA microbial fuel cells with increased reactor size. *Energy and Environmental Science*, 5, 8273-8280.
- FAN, Y., HU, H. & LIU, H. 2007. Sustainable power generation in microbial fuel cells using bicarbonate buffer and proton transfer mechanisms. *Environmental Science and Technology*, 41, 8154-8158.
- FAN, Y., SHARBROUGH, E. & LIU, H. 2008. Quantification of the internal resistance distribution of microbial fuel cells. *Environmental Science and Technology*, 42, 8101-8107.
- FINNERAN, K. T., ANDERSON, R. T., NEVIN, K. P. & LOVLEY, D. R. 2002. Potential for bioremediation of uranium-contaminated aquifers with microbial U(VI) reduction. *Soil and Sediment Contamination: An International Journal*, 11, 339-357.
- GATES, I. D. & LARTER, S. R. 2014. Energy efficiency and emissions intensity of SAGD. *Fuel*, 115, 706-713.
- GLASSER, N. R., SAUNDERS, S. H. & NEWMAN, D. K. 2017. The Colorful World of Extracellular Electron Shuttles. *Annual Review of Microbiology Annu. Rev. Microbiol.*, 71, 731-51.
- GONG, K., MA, X., CONFORTI, K. M., KUTTLER, K. J., GRUNEWALD, J. B., YEAGER, K. L., BAZANT, M. Z., GU, S. & YAN, Y. 2015. A zinc-iron redox-flow battery under \$100 per kW h of system capital cost. *Energy and Environmental Science*.
- GREGORY, K. B., BOND, D. R. & LOVLEY, D. R. 2004. Graphite electrodes as electron donors for anaerobic respiration. *Environmental Microbiology*, 6, 596-604.
- HEAD, I. M. & GRAY, N. D. 2016. Microbial Biotechnology 2020; microbiology of fossil fuel resources. *Microbial biotechnology*, 9, 626-634.
- HEAD, I. M., GRAY, N. D. & LARTER, S. R. 2014. Life in the slow lane; biogeochemistry of biodegraded petroleum containing reservoirs and implications for energy recovery and carbon management. *Frontiers in microbiology*, 5, 566.
- HEAD, I. M., MARTIN JONES, D. & LARTER, S. R. 2003. Biological activity in the deep subsurface and the origin of heavy oil. *Nature*.
- HUBERT, C. 2010. Microbial ecology of oil reservoir souring and its control by nitrate injection. *Handbook of Hydrocarbon and Lipid Microbiology*, 2753-2766.
- ILBERT, M. & BONNEFOY, V. 2013. Insight into the evolution of the iron oxidation pathways. *Biochimica et Biophysica Acta - Bioenergetics*.
- JIA, C., PAN, F., ZHU, Y. G., HUANG, Q., LU, L. & WANG, Q. 2015. High-energy density nonaqueous all redox flow lithium battery enabled with a polymeric membrane. *Science advances*, 1, e1500886.
- JONES, D. M., HEAD, I. M., GRAY, N. D., ADAMS, J. J., ROWAN, A. K., AITKEN, C. M., BENNETT, B., HUANG, H., BROWN, A., BOWLER, B. F. J., OLDENBURG, T., ERDMANN, M. & LARTER, S. R. 2008. Crude-oil biodegradation via methanogenesis in subsurface petroleum reservoirs. *Nature*, 451, 176-180.
- JOO KIM, H., SOO PARK, H., SIK HYUN, M., SEOP CHANG, I., KIM, M. & HONG KIM, B. A mediator-less microbial fuel cell using a metal reducing bacterium, *Shewanella putrefaciens*. 2002.
- KAPADIA, P. R., KALLOS, M. S. & GATES, I. D. 2011. Potential for hydrogen generation from in situ combustion of Athabasca bitumen. *Fuel*, 90, 2254-2265.
- KATO, S. 2015. Biotechnological Aspects of Microbial Extracellular Electron Transfer. *Microbes and environments* *Microbes and Environments*, 30, 133-139.
- KLEINSTEUBER, S. & SCHLEINITZ, K. M. 2012. Key players and team play : anaerobic microbial communities in hydrocarbon-contaminated aquifers. *Applied Microbiology and Biotechnology*, 94, 851-873.
- KRONENBERG, M., TRABLY, E., BERNET, N. & PATUREAU, D. 2017. Biodegradation of polycyclic aromatic hydrocarbons: Using microbial bioelectrochemical systems to overcome an impasse. *Environmental Pollution*, 231, 509-523.

- LANDMAN, A., DOTAN, H., SHTER, G. E., WULLENKORD, M., HOUAIJIA, A., MALJUSCH, A., GRADER, G. S. & ROTHSCILD, A. 2017. Photoelectrochemical water splitting in separate oxygen and hydrogen cells. *Nature Materials*, 16, 646-651.
- LARTER, S., HEAD, I., JONES, D., ERDMANN, M. & WILHELMS, A. 2007. Process for Stimulating Production of Hydrogen from Petroleum in Subterranean Formations. Google Patents.
- LARTER, S., HUANG, H., ADAMS, J., BENNETT, B., JOKANOLA, O., OLDENBURG, T., JONES, M., HEAD, I., RIEDIGER, C. & FOWLER, M. 2006. The controls on the composition of biodegraded oils in the deep subsurface: Part II—Geological controls on subsurface biodegradation fluxes and constraints on reservoir-fluid property prediction: Part I of this study was published in *Organic Chemistry* in 2003 (Larter et al., 2003). *AAPG Bulletin*, 90, 921-938.
- LARTER, S., WILHELMS, A., HEAD, I., KOOPMANS, M., APLIN, A., DI PRIMIO, R., ZWACH, C., ERDMANN, M. & TELNAES, N. 2003. The controls on the composition of biodegraded oils in the deep subsurface—part 1: biodegradation rates in petroleum reservoirs. *Organic Geochemistry*, 34, 601-613.
- LIN, K., GÓMEZ-BOMBARELLI, R., BEH, E. S., TONG, L., CHEN, Q., VALLE, A., ASPURU-GUZIK, A., AZIZ, M. J. & GORDON, R. G. 2016. A redox-flow battery with an alloxazine-based organic electrolyte. *Nature Energy*, 1, 16102.
- LIU, H. & LOGAN, B. E. 2004. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environmental Science and Technology*, 38, 4040-4046.
- LIU, H., RAMNARAYANAN, R. & LOGAN, B. E. 2004. Production of Electricity during Wastewater Treatment Using a Single Chamber Microbial Fuel Cell. *ENVIRONMENTAL SCIENCE & TECHNOLOGY*, 38, 2281-2285.
- LIU, J., WANG, Z., BELCHIK, S. M., EDWARDS, M. J., LIU, C., KENNEDY, D. W., MERKLEY, E. D., LIPTON, M. S., BUTT, J. N., RICHARDSON, D. J., ZACHARA, J. M., FREDRICKSON, J. K., ROSSO, K. M. & SHI, L. 2012. Identification and characterization of M to A: A decaheme c-type cytochrome of the neutrophilic Fe(II)-oxidizing bacterium *Sideroxydans lithotrophicus* ES-1. *Frontiers in Microbiology*, 3.
- LIU, Y., WANG, Z., LIU, J., LEVAR, C., EDWARDS, M. J., BABAUTA, J. T., KENNEDY, D. W., SHI, Z., BEYENAL, H., BOND, D. R., CLARKE, T. A., BUTT, J. N., RICHARDSON, D. J., ROSSO, K. M., ZACHARA, J. M., FREDRICKSON, J. K. & SHI, L. 2014. A trans-outer membrane porin-cytochrome protein complex for extracellular electron transfer by *Geobacter sulfurreducens* PCA. *Environmental Microbiology Reports*, 6, 776-785.
- LOGAN, B. E. 2010. Scaling up microbial fuel cells and other bioelectrochemical systems. *Applied Microbiology and Biotechnology*, 85, 1665-1671.
- LOGAN, B. E., WALLACK, M. J., KIM, K. Y., HE, W., FENG, Y. & SAIKALY, P. E. 2015. Assessment of Microbial Fuel Cell Configurations and Power Densities. *Environmental Science and Technology Letters*, 2, 206-214.
- LOVLEY, D. R. 1991. Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiological reviews*, 55, 259-287.
- LOVLEY, D. R. & PHILLIPS, E. J. P. 1988. Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. *Applied and environmental microbiology*, 54, 1472-80.
- MARSILI, E., BARON, D. B., SHIKHARE, I. D., COURSOLE, D., GRALNICK, J. A. & BOND, D. R. 2008. *Shewanella* secretes flavins that mediate extracellular electron transfer. *Proceedings of the National Academy of Sciences*, 105, 3968-3973.
- MÜLLER, H., BOSCH, J., GRIEBLER, C., DAMGAARD, L. R., NIELSEN, L. P., LUEDERS, T. & MECKENSTOCK, R. U. 2016. Long-distance electron transfer by cable bacteria in aquifer sediments. *ISME Journal*, 10, 2010-2019.
- MYERS, C. R. & MYERS, J. M. 1992. Localization of cytochromes to the outer membrane of anaerobically grown *Shewanella putrefaciens* MR-1. *Journal of Bacteriology*, 174, 3429-3438.
- MYERS, C. R. & NEALSON, K. H. 1988. Bacterial Manganese Reduction and Growth with Manganese Oxide as the Sole Electron Acceptor. *Science*, 240, 1319-1321.

- NARTER, M. & BRUSSEAU, M. L. 2010. Comparison of interfacial partitioning tracer test and high-resolution microtomography measurements of fluid-fluid interfacial areas for an ideal porous medium. *Water Resources Research*, 46.
- NEVIN, K. P., RICHTER, H., COVALLA, S. F., JOHNSON, J. P., WOODARD, T. L., ORLOFF, A. L., JIA, H., ZHANG, M. & LOVLEY, D. R. 2008. Power output and columbic efficiencies from biofilms of *Geobacter sulfurreducens* comparable to mixed community microbial fuel cells. *Environmental Microbiology*, 10, 2505-2514.
- NIELSEN, L. P., RISGAARD-PETERSEN, N., FOSSING, H., CHRISTENSEN, P. B. & SAYAMA, M. 2010. Electric currents couple spatially separated biogeochemical processes in marine sediment. *Nature*, 463, 1071.
- NOVOTNIK, B., RADOVIC, J., NANDY, A., LARTER, S. R. & STROUS, M. 2019a. Microbial metal dependent conversions of hydrocarbons for zero CO₂ emission energy extraction. *7th International Symposium on Applied Microbiology and Molecular Biology in Oil Systems (ISMOS-7)*
- NOVOTNIK, B., ZORZ, J., BRYANT, S. & STROUS, M. 2019b. The Effect of Dissimilatory Manganese Reduction on Lactate Fermentation and Microbial Community Assembly. *Frontiers in Microbiology*, 10.
- OLIOT, M., ETCHEVERRY, L., MOSDALE, R. & BERGEL, A. 2017. Microbial fuel cells connected in series in a common electrolyte underperform: Understanding why and in what context such a set-up can be applied. *Electrochimica Acta*, 246, 879-889.
- PAN, P., HONG, B., MBADINGA, S. M., WANG, L. Y., LIU, J. F., YANG, S. Z., GU, J. D. & MU, B. Z. 2017. Iron oxides alter methanogenic pathways of acetate in production water of high-temperature petroleum reservoir. *Applied Microbiology and Biotechnology*, 101, 7053-7063.
- PAQUETE, C. M., FONSECA, B. M., CRUZ, D. R., PEREIRA, T. M., PACHECO, I., SOARES, C. M. & LOURO, R. O. 2014. Exploring the molecular mechanisms of electron shuttling across the microbe/metal space. *Frontiers in Microbiology*, 5.
- PARAMESWARAN, P., BRY, T., POPAT, S. C., LUSK, B. G., RITTMANN, B. E. & TORRES, C. I. 2013. Kinetic, electrochemical, and microscopic characterization of the thermophilic, anode-respiring bacterium *Thermicola ferriacetica*. *Environmental Science and Technology*, 47, 4934-4940.
- PARK, D. H. & ZEIKUS, J. G. 2000. Electricity Generation in Microbial Fuel Cells Using Neutral Red as an Electronophore. *Applied Environmental Microbiology*, 66, 1292-1297.
- PARK, M., RYU, J., WANG, W. & CHO, J. 2016. Material design and engineering of next-generation flow-battery technologies. *Nature Reviews Materials*, 2.
- PETERS, K. E. & FOWLER, M. G. 2002. Applications of petroleum geochemistry to exploration and reservoir management. *Organic Geochemistry*, 33, 5-36.
- PIRBADIAN, S., BARCHINGER, S. E., LEUNG, K. M., BYUN, H. S., JANGIR, Y., BOUHENNI, R. A., REED, S. B., ROMINE, M. F., SAFFARINI, D. A., SHI, L., GORBY, Y. A., GOLBECK, J. H. & EL-NAGGAR, M. Y. 2014. *Shewanella oneidensis* MR-1 nanowires are outer membrane and periplasmic extensions of the extracellular electron transport components. *Proceedings of the National Academy of Sciences*, 111, 12883-12888.
- RABAEY, K., BOON, N., SICILIANO, S. D., VERHAEGE, M. & VERSTRAETE, W. 2004. Biofuel Cells Select for Microbial Consortia That Self-Mediate Electron Transfer. *APPLIED AND ENVIRONMENTAL MICROBIOLOGY*, 70, 5373-5382.
- RABAEY, K., LISSENS, G., SICILIANO, S. D. & VERSTRAETE, W. 2003. A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency. *Biotechnology Letters*, 25, 1531-1535.
- REGUERA, G., MCCARTHY, K. D., MEHTA, T., NICOLL, J. S., TUOMINEN, M. T. & LOVLEY, D. R. 2005. Extracellular electron transfer via microbial nanowires. *Nature*, 435, 1098-1101.
- REN, H., TIAN, H., GARDNER, C. L., REN, T.-L. & CHAE, J. 2016. A miniaturized microbial fuel cell with three-dimensional graphene macroporous scaffold anode demonstrating a record power density of over 10000 W m⁻². *Nanoscale*, 8, 3539-3547.
- RICHTER, K., SCHICKLBERGER, M. & GESCHER, J. 2012. Dissimilatory reduction of extracellular electron acceptors in anaerobic respiration. *Applied and Environmental Microbiology*.

- RISGAARD-PETERSEN, N., KRISTIANSEN, M., FREDERIKSEN, R. B., DITTMER, A. L., BJERG, J. T., TROJAN, D., SCHREIBER, L., DAMGAARD, L. R., SCHRAMM, A. & NIELSEN, L. P. 2015. Cable Bacteria in Freshwater Sediments. *Applied and Environmental Microbiology*, 81, 6003-6011.
- ROCK, L., O'BRIEN, S., TESSAROLO, S., DUER, J., BACCI, V. O., HIRST, B., RANDELL, D., HELMY, M., BLACKMORE, J., DUONG, C., HALLADAY, A., SMITH, N., DIXIT, T., KASSAM, S. & YAYCHUK, M. 2017. The Quest CCS Project: 1st Year Review Post Start of Injection. *Energy Procedia*, 114, 5320-5328.
- RODEN, E. E., KAPPLER, A., BAUER, I., JIANG, J., PAUL, A., STOESEER, R., KONISHI, H. & XU, H. 2010. Extracellular electron transfer through microbial reduction of solid-phase humic substances. *Nature Geoscience*, 3, 417-421.
- RODENAS MOTOS, P., TER HEIJNE, A., VAN DER WEIJDEN, R., SAAKES, M., BUISMAN, C. J. N. & SLEUTELS, T. H. J. A. 2015. High rate copper and energy recovery in microbial fuel cells. *Frontiers in Microbiology*, 6.
- RODRIGUEZ PIN, E., ROBERTS, M., YU, H., HUH, C. & BRYANT, S. L. 2009. Enhanced Migration of Surface-Treated Nanoparticles in Sedimentary Rocks. *SPE Annual Technical Conference and Exhibition*. New Orleans, Louisiana: Society of Petroleum Engineers.
- ROGELJ, J., POPP, A., CALVIN, K. V., LUDERER, G., EMMERLING, J., GERNAAT, D., FUJIMORI, S., STREFLER, J., HASEGAWA, T., MARANGONI, G., KREY, V., KRIEGLER, E., RIAHI, K., VAN VUUREN, D. P., DOELMAN, J., DROUET, L., EDMONDS, J., FRICKO, O., HARMSSEN, M., HAVLÍK, P., HUMPENÖDER, F., STEHFEST, E. & TAVONI, M. 2018. Scenarios towards limiting global mean temperature increase below 1.5 °C. *Nature Climate Change*, 8, 325-332.
- SACCO, N. J., BONETTO, M. C. & CORTÓN, E. 2017. Isolation and characterization of a novel electrogenic bacterium, *Dietzia* sp. RNV-4. *PLoS ONE*, 12.
- SADEGHI, A., TONAZZINI, A., POPOVA, L. & MAZZOLAI, B. Robotic mechanism for soil penetration inspired by plant root. 2013 IEEE International Conference on Robotics and Automation, 2013. IEEE, 3457-3462.
- SEMENEC, L. & FRANKS, A. 2015. Delving through electrogenic biofilms: from anodes to cathodes to microbes. *AIMS Bioengineering*, 2, 222-248.
- SHI, L., DONG, H., REGUERA, G., BEYENAL, H., LU, A., LIU, J., YU, H. Q. & FREDRICKSON, J. K. 2016. Extracellular electron transfer mechanisms between microorganisms and minerals. *Nature Reviews Microbiology*. Nature Publishing Group.
- SHI, L., ROSSO, K. M., CLARKE, T. A., RICHARDSON, D. J., ZACHARA, J. M. & FREDRICKSON, J. K. 2012. Molecular underpinnings of Fe(III) oxide reduction by *Shewanella oneidensis* MR-1. *Frontiers in Microbiology*, 3.
- SOLOVEICHIK, G. L. 2015. Flow Batteries: Current Status and Trends. *Chemical Reviews*, 115, 11533-11558.
- SUND, C. J., MCMASTERS, S., CRITTENDEN, S. R., HARRELL, L. E. & SUMNER, J. J. 2007. Effect of electron mediators on current generation and fermentation in a microbial fuel cell. *Applied Microbiology and Biotechnology*, 76, 561-568.
- THANGADURAI ET AL. 2019. Auxiliary electrode mediated membrane-free electrochemical redox cell for energy storage. *United States Patent Application*.
- TISSOT, B. & WELTE, D. 1984. Petroleum Formation and Occurrence, 2nd edn, 699 pp. Springer, Berlin.
- USEIA 2019. Cost and Performance Characteristics of New Generating Technologies, Annual Energy Outlook 2019. US Energy Information Administration.
- VENKATAMOHAN, S. & CHANDRASEKHAR, K. 2011. Self-induced bio-potential and graphite electron accepting conditions enhances petroleum sludge degradation in bio-electrochemical system with simultaneous power generation. *Bioresource Technology*, 102, 9532-9541.
- VENKATESAN, S., KARAN, K., LARTER, S. R. & THANGADURAI, V. 2019. Auxiliary electrode mediated membrane-free electrochemical redox cell for energy storage. *Energy and Environmental Science*, submitted.
- VON CANSTEIN, H., OGAWA, J., SHIMIZU, S. & LLOYD, J. R. 2008. Secretion of flavins by *Shewanella* species and their role in extracellular electron transfer. *Applied and Environmental Microbiology*, 74, 615-623.
- WALKER, D. J. F., DANG, Y., HOLMES, D. E. & LOVLEY, D. R. 2016. The electrically conductive pili of *Geobacter* species are a recently evolved feature for extracellular electron transfer. *Microbial Genomics*, 2.

- WANG, H., PARK, J. D. & REN, Z. J. 2015. Practical energy harvesting for microbial fuel cells: A review. *Environmental Science and Technology*, 49, 3267-3277.
- WANG, W., LUO, Q., LI, B., WEI, X., LI, L. & YANG, Z. 2013. Recent progress in redox flow battery research and development. *Advanced Functional Materials*, 23, 970-986.
- WANG, Z. L. 2017. Catch wave power in floating nets. *Nature News*, 542, 159.
- WEI, X., PAN, W., DUAN, W., HOLLAS, A., YANG, Z., LI, B., NIE, Z., LIU, J., REED, D. & WANG, W. 2017. Materials and systems for organic redox flow batteries: status and challenges. *ACS Energy Letters*, 2, 2187-2204.
- WU, S., LI, H., ZHOU, X., LIANG, P., ZHANG, X., JIANG, Y. & HUANG, X. 2016. A novel pilot-scale stacked microbial fuel cell for efficient electricity generation and wastewater treatment. *Water Research*, 98, 396-403.
- XING, D., ZUO, Y., CHENG, S., REGAN, J. M. & LOGAN, B. E. 2008. Electricity generation by *Rhodospseudomonas palustris* DX-1. *Environmental Science and Technology*, 42, 4146-4151.
- YANG, W. & LOGAN, B. E. 2016. Immobilization of a Metal–Nitrogen–Carbon Catalyst on Activated Carbon with Enhanced Cathode Performance in Microbial Fuel Cells. *ChemSusChem*, 9, 2226-2232.
- YANG, Y., LIU, T., ZHU, X., ZHANG, F., YE, D., LIAO, Q. & LI, Y. 2016. Boosting Power Density of Microbial Fuel Cells with 3D Nitrogen-Doped Graphene Aerogel Electrode. *Advanced Science*, 3, 1-8.
- YI, H., NEVIN, K. P., KIM, B. C., FRANKS, A. E., KLIMES, A., TENDER, L. M. & LOVLEY, D. R. 2009. Selection of a variant of *Geobacter sulfurreducens* with enhanced capacity for current production in microbial fuel cells. *Biosensors and Bioelectronics*, 24, 3498-3503.
- ZENGLER, K., RICHNOW, H. H., ROSSELLÓ-MORA, R., MICHAELIS, W. & WIDDEL, F. 1999. Methane formation from long-chain alkanes by anaerobic microorganisms. *Nature*, 401, 266-269.
- ZHANG, T., GANNON, S. M., NEVIN, K. P., FRANKS, A. E. & LOVLEY, D. R. 2010. Stimulating the anaerobic degradation of aromatic hydrocarbons in contaminated sediments by providing an electrode as the electron acceptor. *Environmental Microbiology*, 12, 1011-1020.
- ZHANG, X., WANG, Q., XIA, X., HE, W., HUANG, X. & LOGAN, B. E. 2017. Addition of conductive particles to improve the performance of activated carbon air-cathodes in microbial fuel cells. *Environmental Science: Water Research & Technology*, 3, 806-810.
- ZHANG, Z. & LO, I. M. 2015. Biostimulation of petroleum-hydrocarbon-contaminated marine sediment with co-substrate: involved metabolic process and microbial community. *Applied Microbiology and Biotechnology*, 99, 5683-5696.
- ZHAO, L., DONG, H., KUKKADAPU, R. K., ZENG, Q., EDELMANN, R. E., PENTRÁK, M. & AGRAWAL, A. 2015a. Biological redox cycling of iron in nontronite and its potential application in nitrate removal. *Environmental Science and Technology*, 49, 5493-5501.
- ZHAO, Y., DING, Y., LI, Y., PENG, L., BYON, H. R., GOODENOUGH, J. B. & YU, G. 2015b. A chemistry and material perspective on lithium redox flow batteries towards high-density electrical energy storage. *Chemical Society Reviews*.
- ZHOU, L., DENG, D., ZHANG, D., CHEN, Q., KANG, J., FAN, N. & LIU, Y. 2016. Microbial Electricity Generation and Isolation of Exoelectrogenic Bacteria Based on Petroleum Hydrocarbon-contaminated Soil. *Electroanalysis*, 28, 1510-1516.