



(51) International Patent Classification:

C02F 3/28 (2006.01) *B01D 61/44* (2006.01)
C02F 1/469 (2006.01) *H01M 8/10* (2016.01)

(21) International Application Number:

PCT/IB2017/053741

(22) International Filing Date:

22 June 2017 (22.06.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/353,137 22 June 2016 (22.06.2016) US

(71) Applicant: **THE HONG KONG POLYTECHNIC UNIVERSITY** [CN/CN]; Hung Hom, Kowloon, Hong Kong (CN).

(72) Inventors: **LEE, Po-Heng**; Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong (CN). **NI, Meng**;

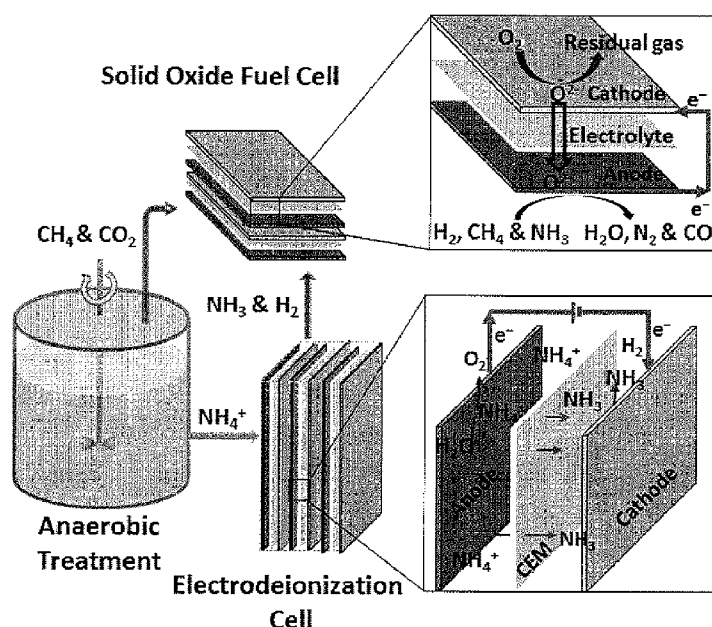
Department of Building and Real Estate, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong (CN). **XU, Linji**; Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong (CN). **DONG, Feifei**; Department of Building and Real Estate, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong (CN).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH,

(54) Title: ENERGY GENERATION FROM POLLUTANTS

Figure 1A



(57) Abstract: The present invention relates to a system of Electrodeionization (EDI)-Solid Oxide Fuel Cells (SOFC) and anaerobic treatment for energy recovery for the treatment of carbonaceous and nitrogenous pollutants. Anaerobic microorganism community metabolizes complicated carbonaceous and nitrogenous pollutants to biogas and digestate. Biogas is directly collected, and NH_4^+ is concentrated and converted to NH_3 gas accompanied with by-product H_2 in the cathode of EDI. Then, biogas, hydrogen and ammonia generated are fed into SOFC to generate power with high energy efficiency.

GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to the identity of the inventor (Rule 4.17(i))*
- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

ENERGY GENERATION FROM POLLUTANTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/353,137, filed June 22, 2016. The entire contents and disclosures of the preceding application are hereby
5 incorporated by reference into this application.

[0002] Throughout this application, various publications are cited. The disclosures of these publications in their entireties are hereby incorporated by reference into this application to more fully describe the state of the art to which this invention pertains.

FIELD OF THE INVENTION

10 [0003] This invention relates to energy generation from carbonaceous and nitrogenous pollutants via ammonium, methane, and carbon dioxide reformation.

BACKGROUND OF THE INVENTION

[0004] Reactive form of organics and nitrogen is the primary culprit causing hypoxia and eutrophication of water bodies. Increasingly strict discharge regulation is, thus, driving the
15 developments of efficient wastewater treatment processes. As the global energy crisis intensifies, reducing costs of wastewater treatment and increasing recoverable energy from waste are worldwide headlines. Energy recovery from carbon waste as methane (CH₄) has been well studied while energy potential from waste nitrogen has not yet been widely noted, let alone taking CH₄, CO₂, NH₃, and H₂ into gather. Additionally, the conventional combustion only gains 30%
20 electricity generation efficiency and methods and systems for improving the efficiency of fuels have always been reported. This work introduces an unprecedented Electrodeionization-Solid Oxide Fuel Cells (EDI-SOFC) integrated system for energy capture from carbonaceous (10.0 g L⁻¹ COD) and nitrogenous pollutants (0.5 mol L⁻¹ NH₄⁺-N) in waste(waters). Such a lab-scale system readily upgrades the net energy balance ratio from 1.11 to 1.75 in a local HK landfill
25 facilities. If successfully scaled-up, this process has the potential to lower two significant operational costs of aeration and sludge yield, increase about 60% energy recovery from “feed”

organic matter and reduce the treatment costs of concentrated $\text{NH}_4^+\text{-N}$ waste(water) treatment.

[0005] The most adopted energy recovery process from wastewater is the anaerobic treatment that converts carbonaceous and nitrogenous pollutants into biogas and digestate, respectively.

[0006] Energy extraction from waste(waters) has gained increasing interest as a route to
5 eliminate the environmental threat and offset fossil fuel consumption simultaneously^{1, 2}. Toward this end, the most readily adaptable approach is through anaerobic treatment, e.g., anaerobic digestion or landfill, converting waste(waters) into biogas with approximate 60% CH_4 and 40% carbon dioxide (CO_2) and digestate/leachate with 400~8000 mg L^{-1} $\text{NH}_4^+\text{-N}$ ³⁻⁶. Biogas is a well-established fuel for electricity generation via combined heat and power (CHP) or cogeneration
10 with gas engines^{7, 8}. However, the electricity generation efficiency is limited to around 30%^{9, 10}, and thus, further improvement is needed to reduce the environmental impact of the system¹¹⁻¹⁴.

[0007] Ammonium concentration in digestate varies between 400 and 8000 mg L^{-1} $\text{NH}_4^+\text{-N}$ ¹⁻⁴, where $\text{NH}_4^+\text{-N}$ refers to ammonium nitrogen. It is regulated to be removed preventing from hypoxia and eutrophication. The present removal or energy-producing processes of ammonium
15 includes biological nitrification-denitrification, Partial nitrification-Anammox (anaerobic ammonium oxidation), coupled aerobic-anoxic nitrous decomposition operation (CANDO) and air stripping.

[0008] The process of biological nitrification-denitrification requires intensive energy demand for aeration converting ammonium into nitrate followed by anoxic denitrification. It requires
20 KJ mol^{-1} $\text{NH}_4^+\text{-N}$ removed and produces 52 g sludge/g $\text{NH}_4^+\text{-N}$ removed⁷⁰.

[0009] Partial nitrification-Anammox (anaerobic ammonium oxidation) process has less aeration demand since it only necessitates 50% ammonium for partial nitrification to nitrite for anammox. However, it requires 177 KJ mol^{-1} $\text{NH}_4^+\text{-N}$ removed and produced 42 g sludge/g $\text{NH}_4^+\text{-N}$ removed⁷¹.

[0010] CANDO involves three steps: (1) oxidation of ammonium to nitrite, (2) reduction of nitrite to nitrous oxide, (3) decomposition/combustion of nitrous oxide to nitrogen and oxygen

gas with energy recovery⁷²⁻⁷³. It requires 177 KJ mol⁻¹ NH₄⁺-N removed and produces 42 g sludge/g NH₄⁺-N removed. Although CANDO can recover energy from the treatment of ammonium (44 KJ mol⁻¹ NH₄⁺-N removed), it is not easily adopted due to its complex operation requirement needed.

5 [0011] NH₄⁺-N in digestate/leachate is conventionally removed by adding chemical alkaline for raising pH level over its pK_a (9.25) followed by physicochemical methods (such as microwave radiation, air stripping, and heating with the intensive energy consumption of 1.6-2.8 kWh kg⁻¹-NH₃¹⁵⁻¹⁸. In fact, NH₃ can be served as a fuel alternative to hydrogen (H₂)¹⁹. As decomposition to nitrogen (N₂) and H₂, a thermodynamic energy of 320 kJ mol⁻¹ can be harvested²⁰⁻²², increasing
10 by approximate 10% than 285 kJ mol⁻¹ of H₂. However, the energy potential of ammonia (NH₃)/ammonium (NH₄⁺) has not yet been highly noted for some reasons. For example, feasible engines that can directly use NH₃ as a fuel under usual conditions have not been well-developed yet due to its special properties (e.g., incombustible, incomplete decomposition, toxicity, or solubility). Some other bottlenecks, such as low recovery efficiency of NH₄⁺ to NH₃, high cost,
15 and NO_x emission, restrict the exploring motivation of recovering energy from NH₃ or NH₄⁺ in waste(waters)^{23, 24}.

[0012] Solid oxide fuel cell (SOFC) is a promising electrochemical device capable of converting not only H₂, but also NH₃, CH₄, and other hydrocarbon fuels into electricity with energy conversion efficiency as high as over 50%^{25, 26}. As SOFC generates electrical power
20 through electrochemical reactions in a straightforward way and does not go through thermodynamic cycles, its power generation efficiency is not limited by the Carnot efficiency²⁷. Whereas carbon deposition could be an issue for SOFC fed with pure CH₄, it is usually not a concern if CH₄ is reformed by H₂O or CO₂. Since biogas contains both CH₄ and CO₂, it could be an ideal fuel for power generation using SOFC²⁸. When NH₃ as the fuel of SOFC, the processes
25 include NH₃ thermal decomposition for N₂ and H₂ generation, followed by H₂ oxidation for power generation²⁹. In a previous experimental study, it is found that the carbon deposition can be

prevented by adding NH_3 into the CH_4 fuel for SOFC^{25, 30}.

[0013] Use of biogas in SOFC is straightforward^{18,28}. Concerning the aqueous NH_4^+ in digitate/leachate for SOFC, it needs an additional step turning into gaseous NH_3 . Traditionally, it can be done by adding chemical alkaline for raising pH level over its pK_a (9.25) into $\text{NH}_{3(\text{aq})}$ followed by volatilization and recovery by heating to form $\text{NH}_{3(\text{g})}$ ³¹⁻³³. As alkaline is not economically and environmentally friendly, EDI is a better alternative option since ion migration is driven by the electrically potential gradients instead of physical pressure^{34, 35}. Mondor et al. used EDI to produce fertilizers with $1.0 \text{ kWh kg}^{-1}\text{-NH}_3$ energy input from a swine manure³⁶, which saved $1.8 \text{ kWh kg}^{-1}\text{-NH}_3$ compared to air stripping for $2.8 \text{ kWh kg}^{-1}\text{-NH}_3$. Phillip et al. disclosed that an applied current in EDI created an alkaline condition that increased transformation of NH_4^+ into NH_3 ³⁵, so the dosage of alkaline was reduced. Moreover, the potential reductive cathode product (H_2) in EDI can be served as an additional fuel for SOFC³⁷.

[0014] Although CHP-AS is considered an attractive process of generating electricity involving biogas, CHP has low electricity conversion efficiency of only 30-40%. In addition, ammonia used in CHP-AS system is considered an unfeasible fuel, which cannot be easily used in existing Otto cycle engines because of its very narrow flammability range and there are also other barriers to widespread automobile usage. Moreover, cost ineffective ammonia recovery is also a concern. Ammonium concentration in wastewater is highly diluted that cannot be easily recovered. The existing approaches such as air stripping, alkalization, and heating require either intensive energy or a large amount of chemical dosage. Furthermore, ammonia oxidation usually produces NO_x species as secondary pollutants which has been known to bring adverse effects on the environment.

[0015] In the present technology, intensive energy consumption is observed for wastewater treatment. Also there is negative net energy benefit of wastewater treatment plants (WWTPs) which caused big footprint. Large amount of excess sludge is generated from conventional wastewater treatment processes. Hypoxia and eutrophication of water bodies are caused by excess

discharge of nitrogen compounds. Greenhouse gas (N_2O) is produced in the process of the conventional nitrification-denitrification and partial nitrification-anammox.

[0016] The present invention involves a novel system towards a high fuel-to-electricity conversion efficiency by integrating EDI, SOFC and anaerobic digestion and landfill facility to convert NH_3 and biogas into electrical power for simultaneous waste(waters) treatment and energy generation.

SUMMARY OF THE INVENTION

[0017] The present invention discloses a system of EDI-SOFC by integration with anaerobic treatment to recover energy from carbonaceous and nitrogenous pollutants. In this system, anaerobic microorganism community metabolizes complicated carbonaceous and nitrogenous pollutants to biogas and digestate. Biogas is directly collected, and NH_4^+ is concentrated and converted to NH_3 gas accompanied with by-product H_2 in the cathode of EDI. Then, biogas, hydrogen and ammonia generated are fed into SOFC to generate power with high energy efficiency.

[0018] In one embodiment, the present invention discloses a system for generating energy from pollutants, comprising: (a) one or more chambers containing microorganisms for digestion of the pollutants into products comprising one or more hydrocarbons and ammonium; (b) one or more devices for converting ammonium into ammonia gas and hydrogen gas; (c) a first electric cell for converting one or more hydrocarbons into carbon dioxide, H_2O and electrons; (d) a second electric cell for converting ammonia gas and hydrogen gas into nitrogen gas, H_2O , and energy; and (e) one or more current collectors in electrical connection with the first electric cell to capture electrons for energy generation.

[0019] In one embodiment, the present invention discloses a system for generating energy from pollutants, comprising: (a) one or more chambers containing anaerobic microorganisms for anaerobic digestion of the pollutants into products comprising methane and ammonium; (b) one or more electrodeionization cells for converting ammonium into ammonia gas and hydrogen gas;

(c) a first solid oxide fuel cell for converting one or more hydrocarbons into carbon dioxide, H_2O and electrons; (d) a second solid oxide fuel cell for converting ammonia gas and hydrogen gas into nitrogen gas, H_2O , and energy; and (e) one or more current collectors in electrical connection with the first solid oxide fuel cell to capture electrons for energy generation.

5

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Figure 1A shows a schematic graph of the EDI-SOFC system integrated with anaerobic treatment. Figure 1B shows deionization efficiency of EDI with 0.5-4.0 V applied voltage. Figure 1C shows deionization efficiency at 7.5 mm to 60.0 mm internal electrode distance. Figure 1D shows deionization efficiency and rate changes within 2.0 h.

10 [0021] Figure 2A shows total nitrogen mass balance in forms of ammonium, ammonia and other nitrogen species. Figure 2B shows CV curve of EDI at 0 to 1.5 V vs. Ag/AgCl under 0.5-10 $mV s^{-1}$.

[0022] Figure 3A shows voltage-current (V-I) and power density-current (P-I) polarization curves of SOFC fed with 100% H_2 at 550-750 °C. Figure 3B shows V-I and P-I polarization curves
15 of SOFC fed with 0-60% NH_3 concentration in H_2-NH_3 mixture. Figure 3C shows V-I and P-I polarization curves of SOFC fed with 20-80% CO_2 concentration in CO_2-CH_4 mixture.

[0023] Figure 4 shows comparisons of mass and energy flow between air stripping- combined heat and power (AS-CHP) and EDI-SOFC. (AD: anaerobic digestion, CHP: combined heat and power, AS: air stripping, BNR: biological nitrogen removal, SOFC: solid oxide fuel cell, EDI:
20 electrodeionization, COD: chemical oxygen demand.

[0024] Figure 5A shows drift velocity of NH_4^+ varying with applied voltages. Figure 5B shows drift velocity of NH_4^+ varying with internal electrode distance.

[0025] Figure 6A shows the SEM image of cation exchange membrane before EDI cell operation. Figure 6B shows the SEM image of cation exchange membrane after EDI cell operation.

25 [0026] Figure 7A shows current efficiency of waster splitting and migration varying within 0.5 to 4.0 V. Figure 7B shows hydrogen yield and the yield ratios of ammonia to hydrogen varying

within 2.0 h.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The present invention discloses an EDI-SOFC integrated system for energy capture from carbonaceous and nitrogenous pollutants in waste (waters). Such an energy producing system demonstrates higher net energy output over the conventional system.

[0028] The present invention involves a system of EDI-SOFC by integration with anaerobic treatment to recovery energy from the treatment of carbonaceous and nitrogenous pollutants.

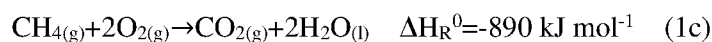
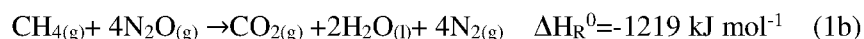
[0029] The present invention involves development of a wastewater-derived energy system (EDI-SOFC) and its feasibility. The present invention also optimizes of the system and its net energy balance assessment with different strength of wastewaters. As the unique device of energy consumption in EDI-SOFC, EDI's performances are affected by the architectural structure, initial NH_4^+ concentration, and energy input. So obtaining the optimal operating parameters for EDI cell is the second significant aspect. In addition, the performances of SOFC fed with mixed fuels are influenced by the compositions of mixed fuels, operating temperature, and cell stability. Therefore, another essential aspect is to find the optimal operating conditions such as the best ratio of mixed fuels, an adaptable temperature range, and stability measurement.

[0030] Firstly, anaerobic microorganism community metabolizes complicated carbonaceous and nitrogenous pollutants to biogas and digestate (Fig. 1A, left panel). Then, biogas is directly collected, and NH_4^+ is concentrated and converted to NH_3 gas accompanied with by-product H_2 in the cathode of EDI (Fig. 1A, lower right panel). Furthermore, biogas, hydrogen and ammonia generated are fed into SOFC to generate power with an energy efficiency of around 50% (Fig. 1A, upper right panel).

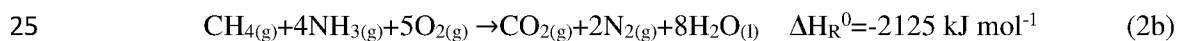
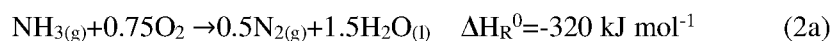
[0031] EDI is used to convert aqueous NH_4^+ in digitate/leachate into gaseous NH_3 with ion migration driven by the electrical potential gradients. As displayed in the lower right panel of Fig. 1A, the directed movement leads to the accumulation and concentration of target ion so that the concentrated ion could be harvested with low energy consumption.

[0032] SOFC is a promising electrochemical device converting biogas, including H₂, NH₃, CH₄, and other hydrocarbon fuels, into electricity with energy conversion efficiency as high as over 50%. The upper right panel of Fig. 1A exhibits the mechanism of power generation in SOFC. At the anode, CH₄, when serving as the fuel, can be reformed by H₂O or CO₂ to produce H₂ and CO, which are oxidized by oxygen ions (O²⁻) to produce CO₂, H₂O and electrons (e⁻). The released electrons are collected by the current collector, flow through the external circuit to produce useful electrical power, and then reach the cathode to react with O₂ molecules to produce O²⁻. Subsequently, oxygen ions are transported from the cathode to the anode through the dense electrolyte to complete the cycle. In these processes, O₂ and the fuel are consumed for electricity generation.

[0033] Recently, Scherson et al. provided a demonstration that the principle of NH₄⁺ containing in wastewaters was applicable by CANDO for obtaining a more powerful oxidant (N₂O) over O₂ owing to an additional energy release of 82 kJ mol⁻¹ from N₂O to N₂ (Eq. 1a)³⁸. Thus, one mole of CH₄ combustion with 4 moles of N₂O (Eq. 1b) lifts approximate 30% more stoichiometric energy over that with 2 moles of O₂ (Eq. 1c)³⁹.



[0034] The present invention discloses a system to capture higher energy from CH₄ and NH₃. As for SOFC, NH₃ (Eq. 2a) releases four times more energy than N₂O dissociation (Eq 1a). On the basis of one mole of CH₄, 4 moles of NH₃ as an additional fuel (Eq. 2b) generate 915 kJ mol⁻¹ more energy than that as an oxidant (Eq. 1b), inferring that NH₃ as an additional fuel is encouraging. Additionally, H₂ generated in EDI releases an extra 285 kJ mol⁻¹ (Eq. 2c).



[0035] In one embodiment, the extraction of energy and contaminants removal can be simultaneously executed in the same system. In another embodiment, there is no sludge yields from the developed EDI-SOFC system. In a further embodiment, the EDI-SOFC system integrates with anaerobic treatment.

5 [0036] In one embodiment, the EDI-SOFC system can readily be implemented in all of existing anaerobic treatment wastewater facilities and landfill plants. In some embodiments, EDI are operated under the conditions of ambient temperature and pressure. In another embodiment, the equipment and materials for EDI and SOFC module are market available. In a further embodiment, the operations of this invention can be conducted by an automatic process control system.

10 [0037] In one embodiment, membrane-less capacitive deionization (CDI) replacing the present two-compartment EDI can be used to reduce energy consumption as this invention scaled up. In one embodiment, Pt-Ti is used as electrode materials. In another embodiment, cheaper pore electrode materials (e.g. graphite, carbon, and graphene) can be used. In some embodiments, online detection of mixed gas can be used to analyze the compositions. Based on the detected
15 results, artificial adjustment of the gas composition can be conducted to guarantee the high performances of SOFC.

[0038] In one embodiment, the system of present invention can output 60% more electricity from the Hong Kong West New Territories (WENT) Landfill. In some embodiments, the applied voltage can be lower than 4.0 V, the internal electrode distance can be controlled within 7.5mm,
20 and NH_4^+ concentration can be higher than 0.1 mol L^{-1} . In another embodiment, the total mass of nitrogen indicates NH_4^+ , NH_3 and N_2 are main nitrogen species in the system.

[0039] In one embodiment, the deionization efficiency of EDI has to be increased while energy consumption rises with the increase in the number of membranes. For SOFC, energy output varies with the compositions of biogas and $\text{NH}_3\text{-H}_2$ mixed gas. In another embodiment, the EDI-SOFC
25 system has to be adaptable for net energy recovery from the dilute waste(water). In a further embodiment, this invention can be applied to concentrated wastewaters.

[0040] The present invention is a pioneering model that can extract energy potential both in carbonaceous and nitrogenous pollutants. It is an approach to the double energy converting efficiency (from 35% to 50-60%) compared to the present technologies. The present invention also significantly reduced the sludge yield due to no biomass yield in the EDI-SOFC system, therefore it has high efficiency and small footprint.

[0041] The EDI-SOFC system integrates with anaerobic treatment of the present invention provide the following advantages:

- (a) Positively net energy output can be achieved by this invention.
- (b) Efficient pollution control with a small footprint can be obtained through this invention.
- (c) No sludge yield in this invention so that there is no need for sludge handling that is an issue for the present technologies
- (d) NH_3 stripping does not require extra alkaline addition.
- (e) The effluent of EDI cathode recycles to anaerobic digestion and neutralizes H^+ , which can prevent the activity of methanogens from the inhibition of over acid so as to increase the production of CH_4 .
- (f) Conservative 50% electricity conversion efficiency can be obtained by SOFC fed with a mixed gas of biogas and $\text{NH}_3\text{-H}_2$, which makes that SOFC has around 20% higher electricity conversion efficiency than 30% of gas fired turbine.
- (g) The reformation of CH_4 with $\text{H}_2\text{O}/\text{CO}_2$ and decomposition of NH_3 to H_2 and N_2 can not only eliminate carbon deposition, but also increase the pressure of H_2 .

[0042] The system of the present invention is expected to be useful as: (a) electricity generation and NH_4^+ removal from domestic WWTPs; (b) treatment of landfill leachate with concentrated NH_4^+ ; and (c) NH_4^+ removal from wastewater of fertilizer plant.

[0043] In one embodiment, the present invention discloses a system for generating energy from pollutants, comprising: (a) one or more chambers containing microorganisms for digestion of the pollutants into products comprising one or more hydrocarbons and ammonium; (b) one or more

devices for converting ammonium into ammonia gas and hydrogen gas; (c) a first electric cell for converting one or more hydrocarbons into carbon dioxide, H₂O and electrons; (d) a second electric cell for converting ammonia gas and hydrogen gas into nitrogen gas, H₂O, and energy; and (e) one or more current collectors in electrical connection with the first electric cell to capture
 5 electrons for energy generation. Electricity can be stored in batteries or used to drive the outside loads.

[0044] In one embodiment, one or more microorganisms comprise anaerobic microorganisms. The digestion comprises anaerobic digestion. In one embodiment, one or more anaerobic microorganisms comprise secondary activated sludge with 3% VS (volatile solid).

10 **[0045]** In another embodiment, the pollutants are carbonaceous or nitrogenous pollutants or a combination thereof. In one embodiment, the carbonaceous pollutants has concentration ranging from 8 to 12 g L⁻¹ COD, 9 to 11 g L⁻¹ COD, 9.5 to 10.5 g L⁻¹ COD, or 9.9-10.1 g L⁻¹ COD. In one embodiment, the nitrogenous pollutants has concentration ranging from 0.4 to 0.6 mol L⁻¹ NH₄⁺-N, 0.45 to 0.55 mol L⁻¹ NH₄⁺-N, or 0.48 to 0.52 mol L⁻¹ NH₄⁺-N.

15 **[0046]** In another embodiment, one or more hydrocarbons comprise methane, methanol and ethanol.

[0047] In one embodiment, one or more devices comprise electrodeionization cells. In some embodiments, one or more devices comprise one or more titanium bat coated mixed metal oxide iridium-ruthenium (MMO Ir-Ru), MMO Ir-Ru-Ti, La_{0.8}Sr_{0.2}MnO_{3-δ} (LSM), La_{1-x}Sr_xCoO₃ (LSC),
 20 La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF), Sm_{0.5}Sr_{0.5}CoO_{3-δ} (SSC), PrBaCo₂O_{5+δ} (PBC), La_{0.7}Sr_{0.3}FeO₃ (LSF) cathodes. In one embodiment, one or more devices comprise electrolytes, supporting electrolyte, cation exchange membrane and one or more anodes. In one embodiment, one or more electrolytes comprises (NH₄)₂SO₄, SDC, LSGM, BZCY, ZrO₂, KOH, YSZ. In one embodiment, the anode comprises Ti coated Pt anodes. In one embodiment, the electrolyte is (NH₄)₂SO₄ and
 25 the supporting electrolyte is Na₂SO₄.

[0048] In one embodiment, one or more devices comprise one or more current collectors. The

cathode current collector is made of Pt wire and the anode current collector is made of a graphite rod or a Ni rod. In another embodiment, platinum and gold pastes can be painted onto the sides of the cathode and anode, which were then sintered to form current collectors.

[0049] In one embodiment, ammonium feed to the device has concentration 400, 600, 800, 1000, 2000, 4000, 6000 or 8000 mg L⁻¹ NH₄⁺-N.

[0050] In one embodiment, one or more electric cells comprise solid oxide fuel cells and proton exchange membrane (PEM) fuel cell. In another embodiment, the first electric cell has an increased conversion efficiency in the presence of carbon dioxide. In one embodiment, the second electric cell has an increased conversion efficiency in the presence of hydrogen gas. In some embodiments, one or more electric cells further comprise one or more NiO+(ZrO₂)_{0.92}(Y₂O₃)_{0.08} (YSZ, NiO:YSZ=6:4 by weight), Sr₂MgMoO_{6-δ} (SMM), Sr₂Mg_{1-δ}Mn_δMoO_{6-δ} (SMMO) anodes. In one embodiment, electric cell comprises yttria-stabilized zirconia (YSZ) electrolyte, Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) interlayer and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) cathode.

[0051] In one embodiment, the volume ratio of one or more hydrocarbons and carbon dioxide feed to the first electric cell is 20:80, 40:60, 45:55, 50:50, 55:45, 60:40, 65:35, 70:30, 75:25 or 80:20.

[0052] In one embodiment, the volume ratio of the ammonia gas and the hydrogen gas used in the second electric cell is 0:100, 10:90, 20:80, 30:70 or 60:40.

[0053] In one embodiment, the present invention discloses a system for generating energy from pollutants, comprising: (a) one or more chambers containing anaerobic microorganisms for anaerobic digestion of the pollutants into products comprising methane and ammonium; (b) one or more electrodeionization cells for converting ammonium into ammonia gas and hydrogen gas; (c) a first solid oxide fuel cell for converting one or more hydrocarbons into carbon dioxide, H₂O and electrons; (d) a second solid oxide fuel cell for converting ammonia gas and hydrogen gas into nitrogen gas, H₂O, and energy; and (e) one or more current collectors in electrical connection with the first solid oxide fuel cell to capture electrons for energy generation.

[0054] In one embodiment, the present invention discloses a process for generating energy from pollutants, comprising the steps of: (a) digesting the pollutants with microorganisms to form products comprising one or more hydrocarbon, and ammonium; (b) converting ammonium to ammonia gas and hydrogen gas; (c) feeding one or more hydrocarbon from step (a) to an anode of a first electric cell to produce carbon dioxide, H₂O and electrons; (d) feeding ammonia gas and hydrogen gas from step (b) to an anode of a second electric cell to produce nitrogen gas, H₂O and energy; and (e) capturing the electrons from step (c) with one or more current collectors to generate energy.

[0055] In one embodiment, ammonium is converted to ammonia and hydrogen by one or more electrodeionization cells operated at an applied voltage ranging from 0.5-4.0 V.

[0056] In one embodiment, anode is fed at a flow rate ranging from 50-150 ml min⁻¹, optionally at 1 atm and 273K (0 °C).

[0057] In one embodiment, first solid oxide fuel cell and said second solid oxide fuel cell are operated at temperatures ranging from 550, 600, 700, or 750 °C.

[0058] In one embodiment, the total energy potential is 0.5, 5, 10, 20, 30, 50, 80, 100, 150 or 200 × 10⁵ MW h year⁻¹, depending on the industrial scale of landfill.

[0059] In one embodiment, the net energy captured is 0.5, 1, 5, 10, 20, 50, 80, 90 or 100 × 10⁵ MWh year⁻¹.

[0060] In one embodiment, the energy conversion efficiency is 50%, 60%, 70%, or 80%.

In one embodiment, the net energy balance ratio is 0.4, 0.7, 0.9, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.75, 2, 2.15, 2.25 or 2.45.

In one embodiment, the present invention discloses a process for generating energy from pollutants, comprising the steps of: (a) anaerobic digesting the pollutants with anaerobic microorganisms to form products comprising methane and ammonium; (b) converting ammonium to ammonia gas and hydrogen gas with electrodeionization cells; (c) feeding methane from step (a) to an anode of a first solid oxide fuel cell to produce carbon dioxide, H₂O and electrons; (d)

feeding ammonia gas and hydrogen gas from step (b) to an anode of a second solid oxide fuel cell to produce nitrogen gas, H₂O and energy; and (e) capturing the electrons from step (c) with one or more current collectors to generate energy.

[0061] The invention will be better understood by reference to the Experimental Details which follow, but those skilled in the art will readily appreciate that the specific experiments are provided only for illustrative purpose, and are not meant to limit the invention scope as described herein, which is defined by the claims following thereafter.

[0062] It is to be noted that the transitional term “comprising”, which is synonymous with “including”, “containing” or “characterized by”, is inclusive or open-ended, and does not exclude additional, un-recited elements or method steps.

EXAMPLE 1

Electrodeionization (EDI)

(1) Experimental Setup

[0063] EDI: EDI's anode and cathode were made of two square Perspex frames with internal dimensions of 10 × 10 × 0.5 cm³ and 2 cm wall thickness, separated by a cation exchange membrane (IONSEP® AM-C, Hangzhou Iontech Environmental Technology CO., Ltd, China). The materials of anode and cathode were Titanium coated Platinum with dimensions of 4 × 4 cm; 0.4 mm thickness (Shenzhen 3N Industrial Equipment CO., Ltd., China), and titanium bat coated mixed metal oxide iridium-ruthenium (MMO Ir-Ru) having the same dimensions, respectively.

EDI cell was sealed by two pieces of silicon shim and locked by screws.

[0064] Synthetic wastewater in EDI's anode contained 0.25 mol L⁻¹ (NH₄)₂SO₄ as electrolyte. The same concentration of Na₂SO₄ was the supporting electrolyte in EDI's cathode. All static batch experiments were carried out at room temperature (25 ± 2 °C). Each set was operated under 0.5, 1.0, 2.0, 3.0, and 4.0 V within 0.5, 1.0, 1.5 and 2.0 h per cycle, respectively. After obtaining the highest deionization efficiency, EDI was operated at 7.5, 15.0, 30.0 and 60.0 mm internal electrode distance within 0.5, 1.0, 1.5 and 2.0 h per cycle, respectively. The real-time current and

voltage were recorded by Keithley 2700 (Tektronix, Inc., USA). The ammonia electrochemical oxidation was analyzed by an electrochemical working station (CorrWare®, Scribner Associates Inc., USA).

[0065] $\text{NH}_4^+\text{-N}$ was measured through the Berthelot method; and NH_3 was absorbed by 1 mol L^{-1} H_2SO_4 and then determined with the same method as $\text{NH}_4^+\text{-N}$. Total nitrogen (TN) was analyzed with 720 °C catalytic thermal decomposition/chemiluminescence methods of TOC-L analyzers (TOC-LCSH/CPH, Shimadzu). Due to water splitting caused by a certain applied voltage, O_2 was produced so that the pH value gradually dropped in the anode while H_2 was generated so that the corresponding pH value was up to 10 in the cathode. The composition of $\text{NH}_3\text{-H}_2$ mixed gas was detected by gas chromatography (Agilent 4890D; J&W Scientific, USA) equipped with a column, HP-MoleSieve (30 m × 0.53 mm × 50 m); He served as the carrier gas and injected at a rate of 6 mL min⁻¹. The temperatures of the injection port, column, and thermal conductivity detector (TCD) were 200°C, 35°C, and 200 °C, respectively. The 200 microliters gas were injected by GC micro-syringe (Shanghai Anting Scientific., China). The composition of biogas was detected using the same method as H_2 detection.

[0066] Fuel cell: Single cells with an anode-supported, thin-film dual-layer electrolyte configuration were prepared via a tape casting process, spray deposition and subsequent high-temperature sintering. The fuel cells tested in this study consisted of $\text{NiO}+(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ (yttria-stabilized zirconia (YSZ), $\text{NiO:YSZ}=6:4$ by weight) anode, YSZ electrolyte, $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) interlayer and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) cathode. BSCF and SDC powder were synthesized using a combined EDTA-citrate complexing sol-gel process. NiO and YSZ are commercial products obtained from suitable suppliers (Chengdu Shudu Nano-Science Co., Ltd. and Tosoh, respectively). The details for preparing anode substrates NiO+YSZ through the tape casting process are available in the literature. The YSZ/SDC double electrolyte layers were prepared by a wet powder spraying technique. The YSZ suspension was firstly sprayed onto the anode substrate using a spraying gun (HD-130 A) followed by calcination at 1400 °C for 5 h,

with the subsequent repeated procedure for the SDC suspension (buffering layer) deposited onto the dense YSZ surface. The resulting three-layered pellets were then calcined at 1350 °C for 5 h in air. Finally, BSCF slurry was sprayed onto the central surface of the SDC interlayer and fired at 1000 °C for 2 h in air to function as the cathode layer. The current-voltage curves of the coin-shaped fuel cells operated at 550-750 °C were obtained using a Keithley 2420 source meter based on a four-probe configuration. During the test, H₂, NH₃-H₂ or CH₄-CO₂ gas mixtures were fed into the anode chamber at a flow rate of 100 ml min⁻¹ [STP] while ambient air was served as the oxidant gas in the cathode chamber. (STP refers to Standard Temperature and Pressure at 1 atm and 273K (0 °C)).

[0067] Chemical Analysis: NH₄⁺-N was measured through the Berthelot method while NH₃ was absorbed by 1 mol L⁻¹ H₂SO₄ and then determined with the same method. Total nitrogen (TN) was analyzed with 720 °C catalytic thermal decomposition/chemiluminescence methods of TOC-L analyzers (TOC-LCSH/CPH, Shimadzu). H₂ were determined by a gas chromatography (Agilent 4890D; J&W Scientific, USA) equipped with a column, HP-MoleSieve (30 m × 0.53 mm × 50 m); He served as the carrier gas and injected at a rate of 6 mL min⁻¹. The temperatures of the injection port, column, and TCD were 200°C, 35°C, and 200 °C, respectively. The 200 microlitres was injected by microsyringe (Shanghai Anting Scientific., China).

(2) Deionization and current efficiencies

[0068] The deionization efficiency (E_p) was expressed:

$$E_p = \frac{C_i^0 - C_i^t}{C_i^0} \times 100\% \quad (\text{Eq. 3})$$

where C_i is the concentration of i and the superscripts 0 and t are the time of the beginning and end of the trial, respectively.⁷⁴

[0069] Current efficiency (E_c)⁷⁵ is defined as:

$$E_c = F \times (V_0 \times C_0 - V_f \times C_f) / n \times I \times \Delta t \quad (\text{Eq. 4})$$

where F refers to the Faraday constant; V_0 and V_f are the initial and final volumes of diluted

solution, respectively; C_0 and C_f are the initial and final concentration of the electrolyte. n is the number of membrane pairs, and I is the current during the time interval Δt .

(3) Ion migration

[0070] The drift velocity is the flow velocity of a particle defined as⁷⁶:

$$u = \frac{m \sigma \Delta E}{\rho e f l} \quad (\text{Eq. 5})$$

where u is the drift velocity of the electrons, in m s^{-1} ; m is the molecular mass of the solution, in kg; $\Delta \phi_{ap}$ is the voltage applied to the conductor, in V; ρ is the density (mass per unit volume) of the conductor, in kg m^{-3} ; e is the elementary charge, in C; f is the number of free electrons per ion; l is the length of the conductor, in m; σ is the electric conductivity of the medium at the temperature considered, in S m^{-1} . Since other parameters were constants in this test, the drift velocity was only associated to the ratio of $\Delta \phi_{ap} / L$ which stands for the strength of the electric field⁴. Thus, the drift velocity linearly increases with applied voltage increasing but reciprocally decreases as L expanding. Fig. 5A and 5B shows the relationships between applied voltage, internal electrode distance, and drift velocity. The drift velocity can be enhanced through increasing applied voltage and narrowing internal electrode distance.

(4) Mass balance analysis of total nitrogen

[0071] Fig. 6A and Fig. 6B are the SEM images of cation exchange membrane (CEM) before and after EDI cell operation. Table 1 is the element contents of CEM before and after EDI cell operation. The images illustrate that the properties of CEM are not significantly changed during the operations. The element analysis demonstrates that the contents of Na and S increased from 1.17 and 8.84 before to 1.38 and 10.43 after. The increase in elemental Na and S were transformed from Na^+ and SO_4^{2-} in the solution.

Table 1 Elemental analysis of CEM by SEM before and after EDI cell operation

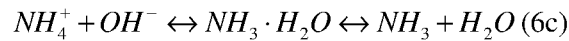
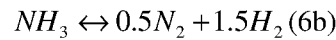
Elements*	Before (%)	After (%)
C	89.99	88.19

Na	1.17	1.38
S	8.84	10.43
Totals	100.00	100
*The content of element in CEM		

(5) Ammonium reduction mechanism

[0072] As reported by Simons et al., the formation of N_2 is a two-step process, given as Eq. 6a and 6b. N_2 production is restricted by the concentration of $NH_{3(aq)}$ ⁷⁸ in this process. At the cathode, however, the concentration of $NH_{3(aq)}$ depends on its equilibrium determined by OH^- (Eq. 6c).

5



[0073] Initially, the electrolytes were neutral, and the cathode NH_4^+ concentration was quite low. So N_2 did not produce. With H_2O splitting, the NH_4^+ and increasingly concentrated OH^- promoted the equilibrium reaction (Eq. 6c) proceeding NH_3 production. As $NH_{3(aq)}$ existing might surround the electrode reaching a certain concentration, the reduction of NH_3 to N_2 and H_2 occurred.

10

Discussion

[0074] The EDI performances (The experimental setup and Deionization and current efficiencies) were investigated through adjustments of applied voltage (0.5 to 4.0 V) and the internal electrode distance (7.5 to 60 mm). Results of deionization efficiencies and deionization kinetics are shown in Fig. 1B, 1C, and 1D. The deionization efficiency linearly increased with applied voltage enhanced and reached the highest value of 75% at 4.0 V (Fig. 1B). At this applied voltage, the efficiency reciprocally declined from 80% at 7.5 mm to 30% at 60 mm along with the increase of the internal electrode distance (Fig. 1C). This trend of NH_4^+ deionization efficiency

20

signifies that the internal electrode length is much more substantial than the applied voltage as can be verified by Stock's model^{40, 41}. For the effects of ions, the drift velocity has a positive correlation with applied voltage but a negative relationship with the electrode distance. More details are available in the Ion migration study (Eq. 4 and Fig. 5A and Fig. 5B). The deionization rate climbed to 80 mmol L⁻¹ d⁻¹ within 0.5 h but dropped to 20 mmol L⁻¹ d⁻¹ at 2.0 h, indicating that the deionization efficiency does not increase anymore along with the extending of operating time (Fig. 1D). This appearance is likely related to Donnan equilibrium that ion migration is stopped along with concentration gradient narrowed^{42, 43}.

[0075] Of peculiar interest is to exploit whether NH₄⁺ occurs electrochemical reactions as voltage rising. If NH₄⁺ oxidation occurs at the anode, NH₃ recovery would be reduced at the cathode, which means less feed amount to SOFC. Thus, the mass balance of nitrogen considering NH₄⁺, NH₃, nitrite (NO₂⁻), nitrate (NO₃⁻), and N₂ was investigated. As a result, only NH₄⁺, NH₃, and N₂ are detected, but the other species were all below detection levels (10.0 mol L⁻¹) (Fig. 2A, Fig. 6A and Fig. 6B and Table 1). The formation of N₂ had our attention and was wondered whether it was related to NH₃ oxidation, and ammonium reduction mechanism was investigated. Accordingly, the cycle voltammetry (CV) was performed at a scanning rate of 0.5-10 mV s⁻¹ using Ag/AgCl as the reference electrode within 0 to 1.5 V and the curves obtained were displayed in Fig. 2B. There were not any oxidation peaks but a reduction peak at 0.3 V, exhibiting a possibly electrochemical reduction of NH₄⁺.

EXAMPLE 2

Solid Oxide Fuel Cells (SOFC)

Experimental Setup

[0076] Single cells with an anode-supported, thin-film dual-layer electrolyte configuration were prepared via a tape casting process, spray deposition and subsequent high-temperature sintering. The fuel cells tested in this study consisted of NiO+(ZrO₂)_{0.92}(Y₂O₃)_{0.08} (Yttria-stabilized zirconia(YSZ), NiO:YSZ=6:4 by weight) anode, YSZ electrolyte, Sm_{0.2}Ce_{0.8}O_{1.9} (SDC)

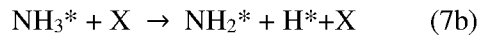
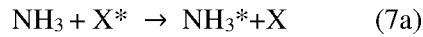
interlayer and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) cathode. BSCF and SDC powder were synthesized using a combined EDTA-citrate complexing sol-gel process. NiO and YSZ were commercial products obtained from suitable suppliers (Chengdu Shudu Nano-Science Co., Ltd. and Tosoh, respectively). The details for preparing anode substrates NiO+YSZ through the tape casting
5 process were available in the literature²². The YSZ/SDC double electrolyte layers were prepared by a wet powder spraying technique. The YSZ suspension was firstly sprayed onto the anode substrate using a spraying gun (HD-130 A) followed by calcination at 1400 °C for five hours, with the subsequently repeated procedure for the SDC suspension (buffering layer) deposited onto the dense YSZ surface. The resulting three-layered pellets were then calcined at 1350 °C for five
10 hours in the air. Finally, BSCF slurry was sprayed onto the central surface of the SDC interlayer and fired at 1000 °C for two hours in air to function as the cathode layer.

[0077] CH_4 fuel can be reformed by H_2O or CO_2 to produce H_2 and CO , which are subsequently oxidized by oxygen ions (O^{2-}) to produce CO_2 , H_2O and electrons (e^-) at the anode. The released electrons are collected by the current collector, flow through the external circuit to produce useful
15 electrical power, and then reach the cathode to react with O_2 molecules to produce O^{2-} . Subsequently, oxygen ions are transported from the cathode to the anode through the dense electrolyte to complete the cycle. In this invention, H_2 , $\text{NH}_3\text{-H}_2$ or $\text{CH}_4\text{-CO}_2$ gas mixtures are fed into the anode chamber at a flow rate of 100 ml min^{-1} [STP] while ambient air is served as the oxidant gas in the cathode chamber. The CH_4 reforming by H_2O or CO_2 produces gaseous
20 intermediates such as CO and H_2 instead of C and solves the issue of carbon deposition as feeding with pure CH_4 ¹². When $\text{NH}_3\text{-H}_2$ is used as the fuel of SOFC, the processes include NH_3 thermal decomposition for N_2 and H_2 generation, followed by H_2 oxidation for power generation¹³. Current-voltage curves of the coin-shaped fuel cells operated at 550-750 °C are obtained using a Keithley 2420 source meter based on a four-probe configuration.

25 Ammonia decomposition and methane reformation

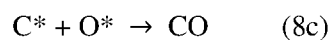
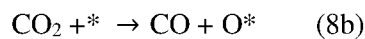
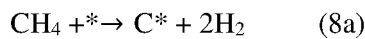
[0078] The mechanism of ammonia decomposition includes three-step reaction: 1) ammonia

adsorption onto catalyst sites, 2) N-H bond cleavage, 3) N atoms recombinative desorption, illustrated in Eqs. 7a to 7c⁷⁹⁻⁸².



where * is an active site and X is one of species adsorbed onto an active site. However, Bradford and Vitvitskii found that the released hydrogen inhibited the decomposition reaction with diluted NH₃. Later studies observed that hydrogen inhibition was eliminated as ammonia concentration increase^{83, 84}. The latest research confirmed that the recombinative desorption of nitrogen atoms determined the reaction rate with higher NH₃ pressure^{85, 86}. Collectively, suitable NH₃ pressure can acquire ideal NH₃ decomposition.

[0079] Many references reported that CH₄ reforming process consisting of many elementary paths was far more complicated than expected⁸⁷⁻⁹⁰. However, the reforming process can be approximated with the following simplified steps with sufficient accuracy⁹¹: 1) CH₄ dissociation to C* and H₂ (Eq. 8a); 2) CO₂ dissociation to form CO and O* (Eq. 8b); 3) carbon oxidation to CO (Eq. 8c).



20 Discussion

[0080] Considering the energy output, the performances of SOFC were studied with 100% H₂ at 550~750 °C operating temperatures (Experimental set up in Example 1). SOFC's polarization curves show that an open circuit voltage value (OCV) of 1.134 V was obtained at 750 °C presented in Fig. 3A. This operation approached closest to the Nernst potential of 1.23 V, indicating the dense electrolyte and the gas-tight sealing⁴⁴. Fixed all of the undermentioned tests at 750 °C and altered H₂ with 20 to 60% by volume (v/v) of NH₃ in NH₃-H₂ stream, SOFC achieved OCV of

1.056-1.085 V that was slightly lower than that obtained from pure H₂. This phenomenon caused by lower H₂ partial pressure in NH₃-H₂ is consistent with the theoretical simulation by Meng et al.⁴⁵. Moreover, the occurrence of incomplete decomposition of NH₃ (Eq. 7a) along with increasingly concentrated NH₃ in H₂ resulted in insufficient H₂ supply. Thus, the peak power density declined from 1194 mW cm⁻² at 20% NH₃ to 1018 mW cm⁻² at 60% NH₃ (Fig. 3B). NO_x was not detected in the off-gas of the anode as could be projected by the mentioned studies^{46, 47}. This observation can be explained by the mechanism of ammonia decomposition.

[0081] Fed with 20-80% (v/v) CH₄ in CH₄-CO₂, the OCVs of 0.991, 1.171, 1.177, and 1.167 V were attained respectively (Fig. 3C). An OCV of 1.177 V and a peak power density of 1178 mW cm⁻² were obtained at 60% of CH₄ in CO₂. Carbon deposition was not observed with the fuel of CH₄-CO₂ mixture in the stability test, implying that CH₄ reforming by CO₂ is efficient⁴⁸⁻⁵⁰. Using biogas as the fuel, SOFC obtained over 50% energy conversion efficiency and even close to 80% for CHP application^{51, 52}. The high-efficiency SOFC validates the feasibility of power generation from biogas along with ammonia nitrogen extracted from digestate/leachate.

EXAMPLE 3

EDI-SOFC system

(1) Net energy balance ratio

[0082] Net energy balance ratio (R_{NEB}) is the ratio of the energy input to output as expressed by Eq. 9 to evaluate the fuel cells' efficiency.

$$R = \frac{W_{out} \times r}{W_{in}} \quad (\text{Eq. 9})$$

where W_{out} is the enthalpy of CH₄, NH₃ and H₂, respectively; r is the electricity conversion efficiency of SOFC, W_{in} is the energy consumption.

W_{in} is calculated as follows:

$$W_{in} = \sum (\Delta W) = \sum (I \times \phi_{ap} \times dt) \quad (\text{Eq. 10})$$

$$W_{in} = Q \times \phi_{ap} \quad (\text{Eq. 11})$$

$$Q = I \times t = \int i \times dt \quad (\text{Eq. 12})$$

$$W_{out} = m_j \times \Delta H \quad (\text{Eq. 13})$$

where φ_{ap} is the applied voltage, Q is electric quantity, m_j is the mass of fuel species, and ΔH is the enthalpies.

5 (2) Current efficiency and fuel production

[0083] As applied voltage adopted, NH_4^+ migration occurs with NH_3 and H_2 generation. Fig. 7A and Fig. 7B show energy utilization and gas production, respectively. NH_4^+ deionization's current efficiency almost linearly dropped from 95% at 1.0V to 10% at 4.0V while H_2 production's current efficiency climbed from 0% at 1.0V to 26% at 4.0V. The distributions of energy of EDI in table 2 show that energy loss takes up about 64% of total energy input including 40% ohmic loss caused by ion exchange membrane, electrolyte and electrodes, and 24% loss via water splitting. With this context, the ratio of NH_3/H_2 and total volume increase from 0 in the beginning to 0.38 and 80 mL at 2.0 h, respectively.

Table 2 Energy distribution of EDI at 1.0 to 4.0V

Applied Voltage (V)	E_c (NH ₄ ⁺)	E_c (H ₂ O)	Energy Loss	H ₂ Volume	NH ₃ /H ₂
	(%)			(mL)	
1.0	95±4.75	0	5±0.25	0	0
2.0	60±0.30	23±1.15	17±0.85	15±0.75	0.10±0.01
3.0	30±1.50	26±1.30	44±2.20	50±2.50	0.26±0.01
4.0	10±0.50	26±1.30	64±3.20	80±4.00	0.40±0.02

15 (3) Biogas and ammonia resources

[0084] Table 3 gives details of West New Territories (WENT) Landfill in Nim Wan, Tuen Mun, Hong Kong mainly disposing of municipal solid waste. This landfill area is 110 ha and has been operating since 1993⁹².

Table 3 Details of the Hong Kong West New Territories (WENT) Landfill*

Parameter	Value	Unit
Current waste intake	> 6,700	ton d ⁻¹
Biogas Yield	7,185±360	m ³ h ⁻¹
CH ₄ percentage	60±10	%
Raw Leachate	1,800±900	m ³ d ⁻¹
NH ₃ -N	7,000±1,500	mg L ⁻¹
NO _x -N	1.25±0.50	mg L ⁻¹
Total Inorganic Nitrogen	7,000±1,000	mg L ⁻¹
Total Nitrogen	7,500±1,800	mg L ⁻¹
pH	8±1	-
*Data are provided by the West New Territories (WENT) Landfill in Hong Kong		

(4) Techno-economic analysis

[0085] Table 4 compares the net energy balances of the AS-CHP and EDI-SOFC sytems interagtred in the West New Territories (WENT) Landfill in Hong Kong. Calculations are based on ΔH_R^0 values of Eqs. 1a, 1b, and 2a to 2c with 30% and 50% of electricity coversion

5 efficiencies by CHP and SOFC, respectively.

Table 4 Comparisons of net energy balances of the AS-CHP and EDI-SOFC sytems interagtred in the Hong Kong West New Territories (WENT) Landfill (Unit in 10⁵ MW h year⁻¹)

Processes		AS-CHP	EDI-SOFC
Energy	Heat Recovery	3.29±0.19	-
Distribution	Electricity Generation	0.17±0.01	4.02±0.20
	Non-captured Energy	0.39±0.02	4.04±0.20
Total Energy Potential		3.85±0.19	8.06±0.40
Effective Energy Captured		3.46±0.17	4.02±0.20
Energy Input Required		3.29±0.16	2.32±0.12
R _{NEB}		1.11±0.06	1.75±0.09

Discussion

[0086] The implementation potential of the EDI-SOFC system was estimated by the net energy balance ratio (R_{NEB}) (Eqs. 5 and 9-12) as an index of energy input to output. The energy requirement of this system lies in EDI's current efficiency (Current efficiency and fuel production, Eq. 13, and Table 2), which dropped from 95% at 1.0 V to about 10% at 4.0 V, indicating that energy loss caused by cell resistance and water splitting approaches 90% of total energy input. Even with such a high energy loss (a specific energy consumption of $2.32 \text{ kWh kg}^{-1}\text{-NH}_3$, EDI had 55.9% to 80.5% less energy demand compared to the conventional nitrification-denitrification⁵³, and AS⁵⁴. On the consensus, R_{NEB} varies with the increase in $\text{NH}_4^+\text{-N}$ content in synthetic wastewater as summarized in Table 5. R_{NEB} was below one as influent $\text{NH}_4^+\text{-N}$ lower than 0.1 mol L^{-1} while it rose to 1 and even close to 2.3 as influent $\text{NH}_4^+\text{-N}$ increasing to 0.5 mol L^{-1} , implying that when feeding with concentrated $\text{NH}_4^+\text{-N}$ waste streams the EDI-SOFC system turns to a complementary alternative to integrating anaerobic treatment.

Table 5 Energy benefits from different concentrations of ammonium wastewater through the EDI-SOFC system

NH ₄ ⁺ -N (mol L ⁻¹)	Deionization	Treatment Capacity	Energy Recovery through SOFC	Energy Input through EDI	Net Energy Revenue	R _{NEB} *
	%	mol m ⁻³ d ⁻¹	kWh m ⁻³ d ⁻¹			
0.025	95±4.75	18,000±900	905±45.25	2,015±100.75	-1,110±-55.5	0.45±0.03
0.05	92±4.60	36,000±1,800	1,725±86.25	3,455±172.75	-1,730±-86.5	0.5±0.03
0.10	87±4.35	36,000±1,800	1,660±83	1,845±92.25	-185±-9.25	0.9±0.05
0.25	83±4.15	90,000±4,500	3,885±194.25	1,850±92.5	2,035±101.75	2.1±0.11
0.50	76±3.80	120,000±6,000	4,895±244.75	2,125±106.25	2,770±138.5	2.3±0.13
* Energy recovery through SOFC is calculated based on 50% electricity conversion efficiency ⁵⁵ .						

[0087] When biogas from anaerobic treatment is taken into consideration as a fuel, ED-SOFC's benefits would be more attractive. Table 6 summarizes the performances of the EDI-SOFC system in comparison with the conventional nitrification-denitrification, partial nitrification-Anammox, and CANDO. These calculations indicate that the EDI-SOFC system increased by 11-75% in

energy production and 2-6 times in R_{NEB} but reduced by 15-50% in sludge yield, respectively. Additionally, to obtain an overall assessment of the integration of anaerobic treatment and the EDI-SOFC system, the NEB is made for the Hong Kong West New Territories (WENT) Landfill. The plant's capacity, biogas yield, and raw leachate properties are summarized in Table 3, and its

5 techno-economic evaluation is shown in Fig. 4 and Table 4. The effective energies captured by the existing system (AS-CHP) and the EDI-SOFC of the present invention are 3.46×10^5 and 4.02×10^5 MWh year⁻¹, respectively, while the energy inputs required for either NH₃ stripping or recovery in the respective systems were 3.29×10^5 and 1.0×10^5 MWh year⁻¹. Consequently, R_{NEB} values for the respective systems were 1.11 and 1.75, implying that the EDI-SOFC system could

10 output about 60% more electricity. Given the fact that the energy uncaptured in the EDI-SOFC system was 4.04 MWh year⁻¹, prompting that this uncaptured energy sink leaves a great potential for further studies.

Table 6 Comparisons of ammonium removal/recovery processes integrated with anaerobic treatment per removal of 1 mole of NH₄⁺ with accompanying of 3.47 mole of BOD_L (a BOD_L/N ratio of 7.9) in a typical of U.S. medium strength wastewater^{56, 57}.

15

Processes	Sludge	Oxygen	Energy Sources				Energy	Energy	R _{NEB}	Reference
	Yield	Requirement	CH ₄	N ₂ O	NH ₃	H ₂	Potential*	Input**		
	g		mol				kJ			
Nitrification-denitrification	26.0±1.30	52±2.60	0.85±0.04	-	-	-	753±37	219.21±10.95	3.43±0.02	Yang et al. ⁵⁸
Partial Nitrification-Anammox	18.3±0.92	42±2.10	1.29±0.65	-	-	-	1142±57	176.90±8.85	6.45±0.32	Dongen et al. ⁵⁹
CANDO	15.8±0.79	42±2.10	1.29±0.65	0.58±0.03	-	-	1186±60	176.90±8.85	6.70±0.34	Kim et al. ⁶⁰
EDI-SOFC	13.3±.67	-	1.80±0.90	-	0.80±0.04	1.86±0.09	2388±120	113.58±5.68	21.02±1.05	This study

*Estimated according to ΔH_R⁰ of Eqs.3a, 3b, and 4a-4c.

**1.17 kWh kg⁻¹-O₂ for aeration⁶¹ and 2.32 kWh kg⁻¹-NH₃ for recovery (this study)

[0088] As mentioned above, the continuing system demonstrates the net energy balance ratio of 1.75. As NH₄⁺-N concentration rise to 0.1 mol L⁻¹, energy recovery balances of EDI is over

1.0. Furthermore, the ratio of CH₄ to CO₂ (6:4 in v/v) approaches peak power density of 1,000 mW cm⁻² at 750 °C. In addition, 20-30% (v/v) of NH₃ in H₂ does not significantly affect the peak power density of SOFC.

- [0089] An unprecedented EDI-SOFC integrated system is established for energy capture from carbonaceous (10.0 g L⁻¹ COD) and nitrogenous pollutants (0.5 mol L⁻¹ concentrated NH₄⁺-N) in waste (waters). The energy producing system of the present invention obtains 57% more net energy output over the conventional system. Particular interests are the NH₄⁺-N reduction rather than oxidation and CH₄ reformation with CO₂ avoiding carbon deposition, along with appropriate doubling the energy conversion efficiency.
- 10 [0090] In summary, the present invention developed a facile and sustainable process of EDI-SOFC capable of integrating anaerobic treatment processes for extracting more energy from waste(water) streams. The result was the successful demonstration of upgrading anaerobic processes from the extraction of both carbonaceous and nitrogenous pollutants energy potentials and upgrade of energy converting efficiencies. This study paves a creative way in practice to
- 15 achieve greater waste (water) management sustainability.

References

1. T. Abbasi, S. Tauseef and S. Abbasi, *Renew. Sust. Energ. Rev.*, 2012, **16**, 3228-3242.
2. D. O. Hall, G. W. Barnard and P. Moss, *Biomass for energy in the developing countries: current role, potential, problems, prospects*, Elsevier, 2013.
- 5 3. P. Jain, J. T. Powell, J. L. Smith, T. G. Townsend and T. Tolaymat, *Environ. Sci. Technol.*, 2014, **48**, 2920-2927.
4. M. R. Daelman, E. M. van Voorthuizen, U. G. van Dongen, E. I. Volcke and M. C. van Loosdrecht, *Water Res.*, 2012, **46**, 3657-3670.
5. O. P. Karthikeyan and C. Visvanathan, *Rev. Environ. Sci. Biotechnol.*, 2013, **12**, 257-284.
- 10 6. M. Raboni, V. Torretta, P. Viotti and G. Urbini, *Rev. Ambient. Água*, 2013, **8**, 22-32.
7. M. Lantz, *Appl. Energ.*, 2012, **98**, 502-511.
8. S. Wongchanapai, H. Iwai, M. Saito and H. Yoshida, *J. Power Sources*, 2013, **223**, 9-17.
9. A. Bogusch and R. T. Grubbs, *J Water Pollut Control Fed.*, 2014, **2014**, 1-14.
10. N. de Arespacochaga, C. Valderrama, C. Peregrina, A. Hornero, L. Bouchy and J. Cortina,
- 15 *Fuel Process. Technol.*, 2015, **138**, 654-662.
11. D. Wu and R. Wang, *Prog Energy Combust Sci.*, 2006, **32**, 459-495.
12. G. Venkatesh and R. A. Elmi, *Energy*, 2013, **58**, 220-235.
13. A. L. Smith, L. B. Stadler, L. Cao, N. G. Love, L. Raskin and S. J. Skerlos, *Environ. Sci. Technol.*, 2014, **48**, 5972-5981.
- 20 14. P. McKendry, *Bioresour. Technol.*, 2002, **83**, 47-54.
15. L. Lin, S. Yuan, J. Chen, Z. Xu and X. Lu, *J. Hazard. Mater.*, 2009, **161**, 1063-1068.
16. K. Cheung, L. Chu and M. Wong, *Water Air Soil Poll.*, 1997, **94**, 209-221.
17. A. Serna-Maza, S. Heaven and C. J. Banks, *Bioresour. Technol.*, 2015, **190**, 66-75.
18. S. Hussain, H. A. Aziz, M. H. Isa, M. N. Adlan and F. A. H. Asaari, *Bioresour. Technol.*,
- 25 2007, **98**, 874-880.
19. A. Klerke, Christensen, C. H., Nørskov, J. K., & Vegge, T., *J. Mater. Chem.*, 2008, 18(20), 2304-2310.
20. F. Schüth, R. Palkovits, R. Schlögl and D. S. Su, *Energ. Environ. Sci.*, 2012, **5**, 6278-6289.
21. L. Green, *Int. J. Hydrogen Energy*, 1982, **7**, 355-359.
- 30 22. P. W. Atkins and J. De Paula, *Physikalische chemie*, John Wiley & Sons, 2013.
23. J. Desloover, A. Abate Woldeyohannis, W. Verstraete, N. Boon and K. Rabaey, *Environ. Sci. Technol.*, 2012, **46**, 12209-12216.
24. J. H. Ahn, S. Kim, H. Park, B. Rahm, K. Pagilla and K. Chandran, *Environ. Sci. Technol.*, 2010, **44**, 4505-4511.
- 35 25. W. Wang, R. Ran, C. Su, Y. Guo, D. Farrusseng and Z. Shao, *J. Power Sources*, 2013, **240**, 232-240.
26. F. Siavashi, M. Saidi and M. R. Rahimpour, *J. Power Sources*, 2014, **267**, 104-116.
27. H. Tsukuda, A. Notomi and N. Histatome, *J. Therm. Spray Technol.*, 2000, **9**, 364-368.
28. Y. Shiratori, T. Oshima and K. Sasaki, *Int. J. Hydrogen Energy*, 2008, **33**, 6316-6321.

29. A. B. Stambouli and E. Traversa, *Renew. Sust. Energ. Rev.*, 2002, **6**, 433-455.
30. Y. Lin, R. Ran, Y. Guo, W. Zhou, R. Cai, J. Wang and Z. Shao, *Int. J. Hydrogen Energy*, 2010, **35**, 2637-2642.
31. E. Idelovitch and M. Michail, *J Water Pollut Control Fed.* , 1981, 1391-1401.
- 5 32. L. Zhang, Y.-W. Lee and D. Jahng, *J. Hazard. Mater.* , 2012, **199**, 36-42.
33. H. U. Cho, S. K. Park, J. H. Ha and J. M. Park, *J. Environ. Manage.* , 2013, **129**, 274-282.
34. M. Parmar, & Thakur, L. S, *Int. J. Plant. Anim. Environ. Sci*, 2013, 3(3), 143-157.
35. S. Srivastava, & Goyal, P, *Novel biomaterials: decontamination of toxic metals from wastewater*, Springer Science & Business Media., 2010.
- 10 36. M. Mondor, L. Masse, D. Ippersiel, F. Lamarche and D. I. Masse, *Bioresour. Technol.* , 2008, **99**, 7363-7368.
37. M. Mehanna, P. D. Kiely, D. F. Call and B. E. Logan, *Environ. Sci. Technol.*, 2010, **44**, 9578-9583.
38. Y. D. Scherson, G. F. Wells, S.-G. Woo, J. Lee, J. Park, B. J. Cantwell and C. S. Criddle, *Energ. Environ. Sci.*, 2013, **6**, 241-248.
- 15 39. Y. D. Scherson, S.-G. Woo and C. S. Criddle, *Environ. Sci. Technol.*, 2014, **48**, 5612-5619.
40. D. J. Griffiths and R. College, *Introduction to electrodynamics*, prentice Hall Upper Saddle River, NJ, 1999.
41. X. Chen, Y. Tang, S. Wang, Y. Song, F. Tang and X. Wu, *Electrophoresis*, 2015, **36**, 1953-1961.
- 20 42. P. Biesheuvel, R. Zhao, S. Porada and A. Van der Wal, *J. Colloid Interface Sci.* , 2011, **360**, 239-248.
43. P. Biesheuvel and A. Van der Wal, *J Memb Sci.*, 2010, **346**, 256-262.
44. Q. Ma, J. Ma, S. Zhou, R. Yan, J. Gao and G. Meng, *J. Power Sources*, 2007, **164**, 86-89.
- 25 45. G. Meng, C. Jiang, J. Ma, Q. Ma and X. Liu, *J. Power Sources*, 2007, **173**, 189-193.
46. G. N. Krishnan, P. Jayaweera, J. Perez, M. Hornbostel, J. R. Albritton and R. P. Gupta, *Effect of coal contaminants on solid oxide fuel system performance and service life*, Sri International, 2007.
47. N. S. Spinner, J. A. Vega and W. E. Mustain, *Catal. Sci. Tech.*, 2012, **2**, 19-28.
- 30 48. I. Dincer, C. O. Colpan, O. Kizilkan and M. A. Ezan, *Progress in Clean Energy*, Springer, 2015.
49. B. Suddhasatwa, *Recent trends in fuel cell science and technology*, New York, USA, Springer press, 2007.
50. M. Kuhn and T. W. Napporn, *Energies*, 2010, **3**, 57-134.
- 35 51. D. Singh, E. Hernández-Pacheco, P. N. Hutton, N. Patel and M. D. Mann, *J. Power Sources*, 2005, **142**, 194-199.
52. Y. Yi, A. D. Rao, J. Brouwer and G. S. Samuelsen, *J. Power Sources*, 2004, **132**, 77-85.
53. B. Wett, *Water Sci. Technol.* , 2007, **56**, 81-88.
54. S. G. Sommer, M. L. Christensen, T. Schmidt and L. S. Jensen, *Animal manure recycling: treatment and management*, John Wiley & Sons, 2013.
- 40

55. M. Dokiya, *Solid State Ionics*, 2002, **152**, 383-392.
56. Safoniuk and Mike, *Chem. Eng. J.* , 2004, **111**, 10-12.
57. M. Henze, *Biological wastewater treatment: principles, modelling and design*, IWA publishing, 2008.
- 5 58. Q. Yang, Y. Peng, X. Liu, W. Zeng, T. Mino and H. Satoh, *Environ. Sci. Technol.*, 2007, **41**, 8159-8164.
59. Van Dongen, LGJM, Jetten, MSM van Loosdrecht and M. CM, *The Combined Sharon/Anammox Process-A Sustainable Method for N-removal from Sludge Water*, 2007.
60. J. Kim, K. Kim, H. Ye, E. Lee, C. Shin, P. L. McCarty and J. Bae, *Environ. Sci. Technol.*,
10 2010, **45**, 576-581.
61. A. Fenu, J. Roels, T. Wambecq, K. De Gussem, C. Thoeve, G. De Gueldre and B. Van De Steene, *Desalination*, 2010, **262**, 121-128.
62. P. Jain, J. T. Powell, J. L. Smith, T. G. Townsend and T. Tolaymat, *Environ. Sci. Technol.*, 2014, **48**, 2920-2927.
- 15 63. M. R. Daelman, E. M. van Voorthuizen, U. G. van Dongen, E. I. Volcke and M. C. van Loosdrecht, *Water Res.* , 2012, **46**, 3657-3670.
64. O. P. Karthikeyan and C. Visvanathan, *Rev. Environ. Sci. Biotechnol.*, 2013, **12**, 257-284.
65. M. Raboni, V. Torretta, P. Viotti and G. Urbini, *Rev. Ambient. Água*, 2013, **8**, 22-32.
66. L. Lin, S. Yuan, J. Chen, Z. Xu and X. Lu, *J. Hazard. Mater.* , 2009, **161**, 1063-1068.
- 20 67. K. Cheung, L. Chu and M. Wong, *Water Air Soil Poll.*, 1997, **94**, 209-221.
68. A. Serna-Maza, S. Heaven and C. J. Banks, *Bioresour. Technol.* , 2015, **190**, 66-75.
69. S. Hussain, H. A. Aziz, M. H. Isa, M. N. Adlan and F. A. H. Asaari, *Bioresour. Technol.*, 2007, **98**, 874-880.
- 70 Yang, Y. Peng, X. Liu, W. Zeng, T. Mino and H. Satoh, *Environ. Sci. Technol.*, 2007, **41**,
25 8159-816
71. van Dongen, LGJM, Jetten, MSM van Loosdrecht and M. CM, *The Combined Sharon/Anammox Process-A Sustainable Method for N-removal from Sludge Water*, 2007.
72. Y. D. Scherson, G. F. Wells, S.-G. Woo, J. Lee, J. Park, B. J. Cantwell and C. S. Criddle, *Energ. Environ. Sci.*, 2013, **6**, 241-248.
- 30 73. Y. D. Scherson, S.-G. Woo and C. S. Criddle, *Environ. Sci. Technol.*, 2014, **48**, 5612-5619.
74. M. Taky, G. Pourcelly, F. Lebon and C. Gavach, *J. Electroanal. Chem.* , 1992, **336**, 171-194.
75. G. Wisniewska and T. Winnicki, *Desalination*, 1991, **84**, 163-176.
76. D. J. Griffiths, *Electrodynamics*, 1999.
- 35 77. W. F. Schmidt, G. Bakale, A. Khrapak and K. Yoshino, 2011.
78. E. Simons, E. Cairns and D. Surd, *J. Electrochem. Soc.* , 1969, **116**, 556-561.
79. K. Kordes, J. Gsellmann, M. Cifrain, S. Voss, V. Hacker, R. R. Aronson, C. Fabjan, T. Hejze and J. Daniel-Ivad, *J. Power Sources*, 1999, **80**, 190-197.
80. N. Dekker and G. Rietveld, *J. Compos. Tech. Res.* , 2006, **3**, 499-502.
- 40 81. A. Fuerte, R. Valenzuela, M. Escudero and L. Daza, *J. Power Sources*, 2009, **192**, 170-

- 174.
82. M. Boudart and G. Djéga-Mariadassou, *Kinetics of heterogeneous catalytic reactions*, Princeton University Press, 2014.
83. M. C. Bradford, P. E. Fanning and M. A. Vannice, *J. Catal.* , 1997, **172**, 479-484.
- 5 84. A. Vitvitskii, T. Gaidei, M. Toporkova, E. Kiseleva and E. Melikhov, *J. Appl. Chem., USSR*, 1990, **63**, 1883-1886.
85. E. Shustorovich and A. T. Bell, *Surf. Sci.*, 1991, **259**, L791-L796.
86. A. Chellappa, C. Fischer and W. Thomson, *Appl. Catal. A Gen.*, 2002, **227**, 231-240.
87. M. Bradford and M. Vannice, *Cat. Rev. - Sci. Eng.* , 1999, **41**, 1-42.
- 10 88. S. Wang, G. Lu and G. J. Millar, *Energy & Fuels*, 1996, **10**, 896-904.
89. Z. Zhang, V. Tsiouriari, A. Efstathiou and X. Verykios, *J. Catal.* , 1996, **158**, 51-63.
90. R. E. Valdés-Pérez and A. V. Zeigarnik, *J Chem Inf Comput Sci.*, 2000, **40**, 833-838.
91. M. V. Iyer, L. P. Norcio, E. L. Kugler and D. B. Dadyburjor, *Ind. Eng. Chem. Res.*, 2003, **42**, 2712-2721.
- 15 92. D.-f. Fung and F. Lianhui, *HKU Theses Online (HKUTO)*, 2012.

What is claimed is:

1. A system for generating energy from pollutants, comprising:
 - (a) one or more chambers containing microorganisms for digestion of said pollutants into products comprising one or more hydrocarbons and ammonium;
 - 5 (b) one or more devices for converting said ammonium into ammonia gas and hydrogen gas;
 - (c) a first electric cell for converting said one or more hydrocarbons into carbon dioxide, H₂O and electrons;
 - (d) a second electric cell for converting said ammonia gas and said hydrogen gas into
10 nitrogen gas, H₂O, and energy; and
 - (e) one or more current collectors in electrical connection with said first electric cell to capture said electrons for energy generation.
2. The system of claim 1, wherein said one or more microorganisms comprise anaerobic microorganisms.
- 15 3. The system of claim 1, wherein said pollutants are carbonaceous or nitrogenous pollutants or a combination thereof.
4. The system of claim 1, wherein said one or more hydrocarbons are selected from the group consisting of methane, methanol and ethanol.
5. The system of claim 1, wherein said one or more devices comprise electrodeionization cells.
- 20 6. The system of claim 1, wherein said one or more electric cells comprise solid oxide fuel cells and proton exchange membrane (PEM) fuel cell.
7. The system of claim 1, wherein said first electric cell has an increased conversion efficiency in the presence of carbon dioxide.
8. The system of claim 1, wherein said second electric cell has an increased conversion
25 efficiency in the presence of hydrogen gas.
9. The system of any one of claims 1-7, wherein said carbonaceous pollutants has concentration ranging from 8 to 12 g L⁻¹ COD.

10. The system of any one of claims 1-8, wherein said nitrogenous pollutants has concentration ranging from 0.4 to 0.6 mol L⁻¹ NH₄⁺-N.
11. The system of any one of claims 1-8, wherein said one or more devices comprise one or more titanium bat coated mixed metal oxide iridium-ruthenium (MMO Ir-Ru),
 5 La_{0.8}Sr_{0.2}MnO_{3-δ} (LSM), La_{1-x}Sr_xCoO₃ (LSC), La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF), Sm_{0.5}Sr_{0.5}CoO_{3-δ} (SSC), PrBaCo₂O_{5+δ} (PBC), La_{0.7}Sr_{0.3}FeO₃ (LSF) cathodes.
12. The system of any one of claims 1-8, wherein said one or more electric cells comprise one or more NiO+(ZrO₂)_{0.92}(Y₂O₃)_{0.08} (YSZ, NiO:YSZ=6:4 by weight), Sr₂MgMoO_{6-δ} (SMM), Sr₂Mg_{1-δ}Mn_δMoO_{6-δ} (SMMO) anodes.
- 10 13. The system of any one of claims 1-8, wherein the volume ratio of said one or more hydrocarbons and said carbon dioxide feed to said first electric cell ranges from 40:60 to 80:20.
14. The system of any one of claims 1-8, wherein the volume ratio of said ammonia gas and said hydrogen gas used in said second electric cell ranges from 100:0 to 40:60.
- 15 15. A process for generating energy from pollutants, comprising the steps of:
 - (a) digesting said pollutants with microorganisms to form products comprising one or more hydrocarbon, and ammonium;
 - (b) converting said ammonium to ammonia gas and hydrogen gas;
 - (c) feeding said one or more hydrocarbon from step (a) to an anode of a first electric cell
 20 to produce carbon dioxide, H₂O and electrons;
 - (d) feeding said ammonia gas and said hydrogen gas from step (b) to an anode of a second electric cell to produce nitrogen gas, H₂O and energy; and
 - (e) capturing the electrons from step (c) with one or more current collectors to generate energy.
- 25 16. The process of claim 15, wherein the total energy potential ranges from 0.5 x 10⁵ MW h year⁻¹ to 200 x 10⁵ MW h year⁻¹.

17. The process of claim 15, wherein the net energy captured ranges from 0.5×10^5 MWh year⁻¹ to 100×10^5 MWh year⁻¹.
18. The process of claim 15, wherein the energy conversion efficiency ranges from 50% to 80%.
19. The process of claim 15, wherein the net energy balance ratio ranges from 0.4 to 2.45.

1/10

Figure 1A

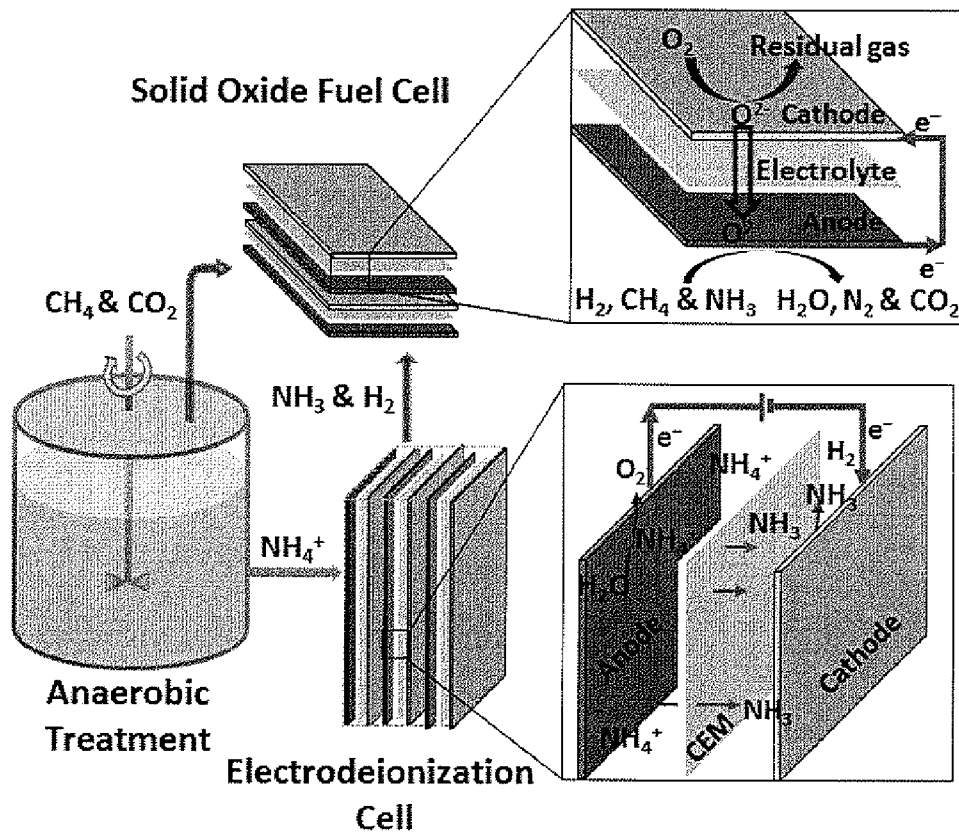
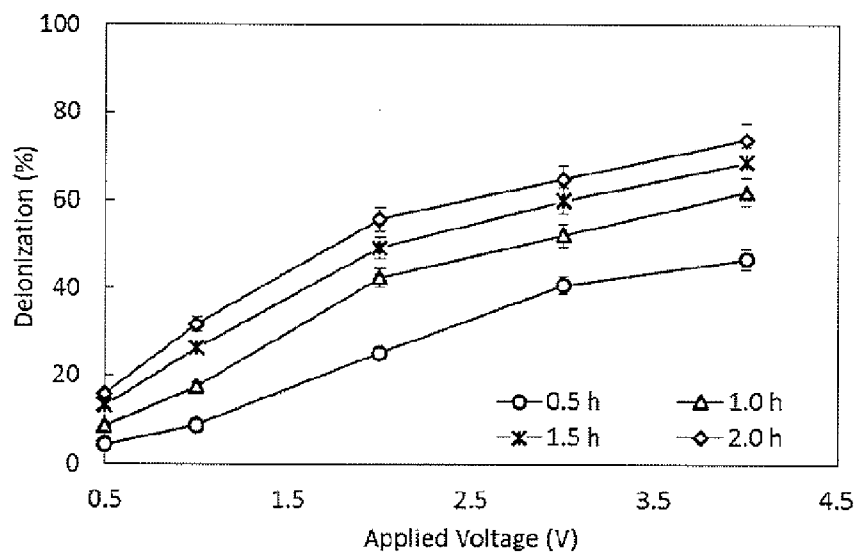


Figure 1B



2/10

Figure 1C

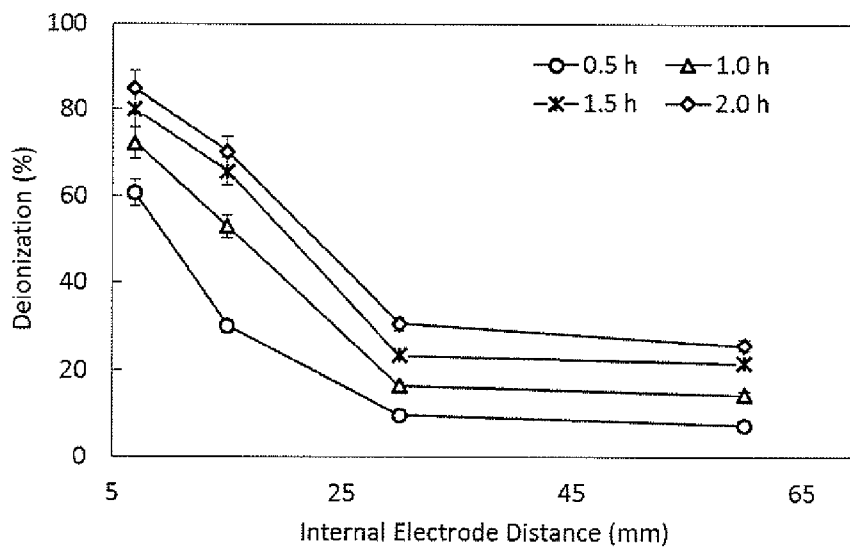
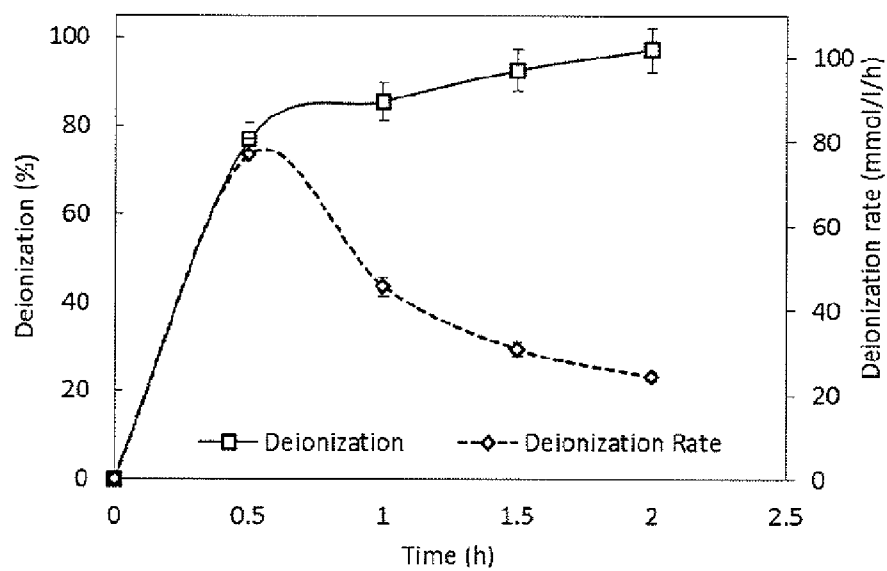


Figure 1D



3/10

Figure 2A

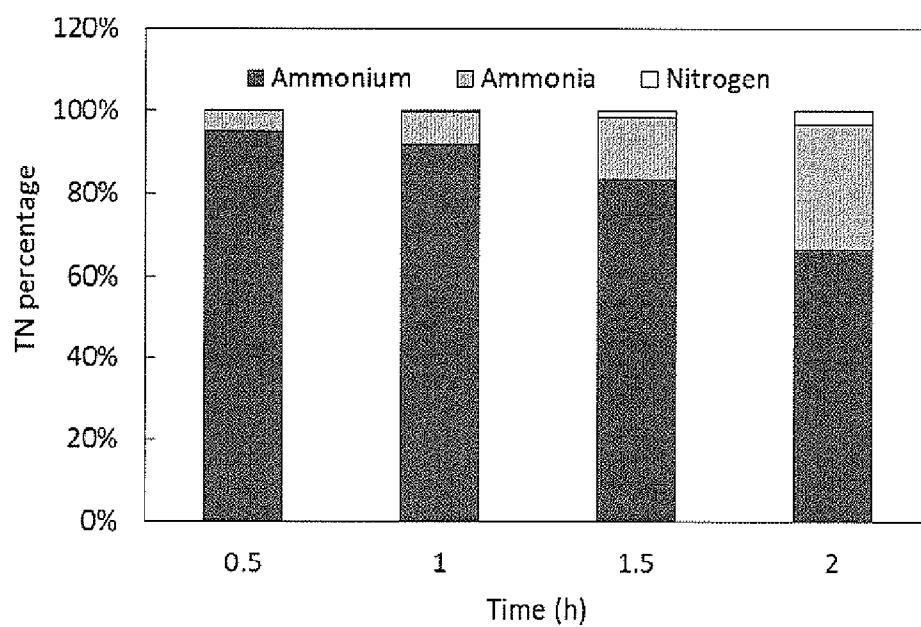
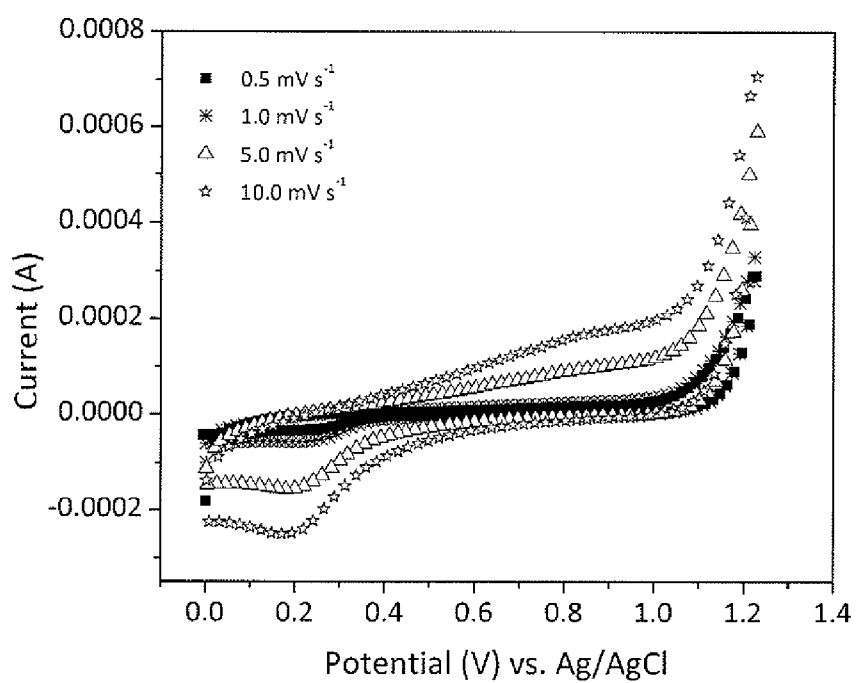
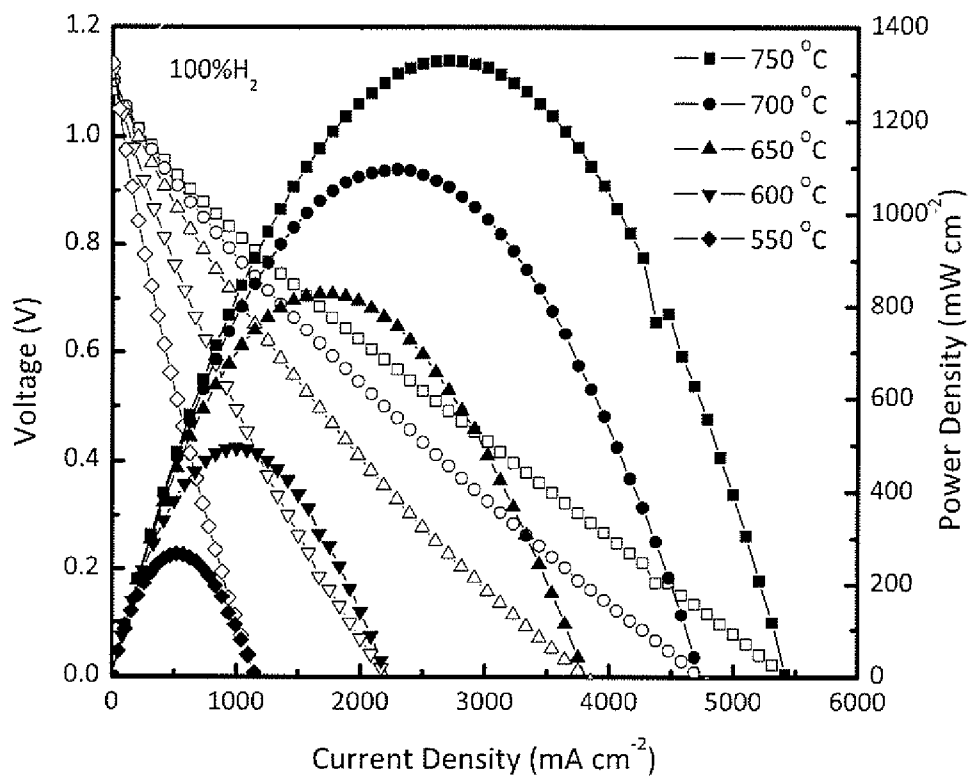


Figure 2B



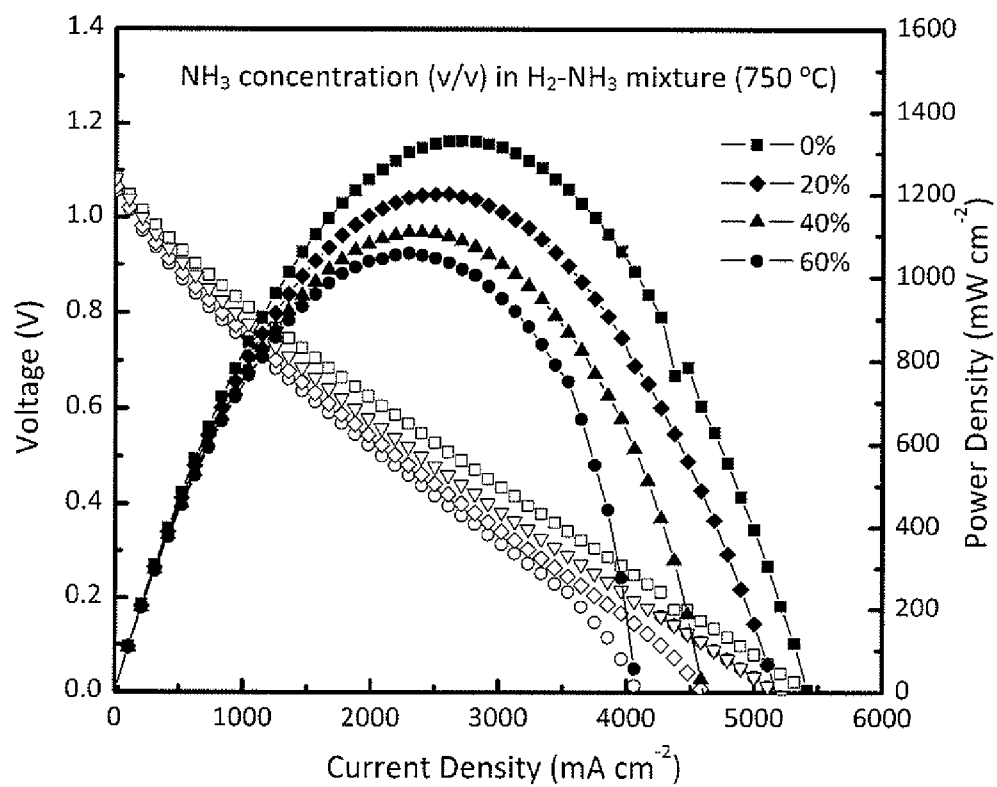
4/10

Figure 3A



5/10

Figure 3B



6/10

Figure 3C

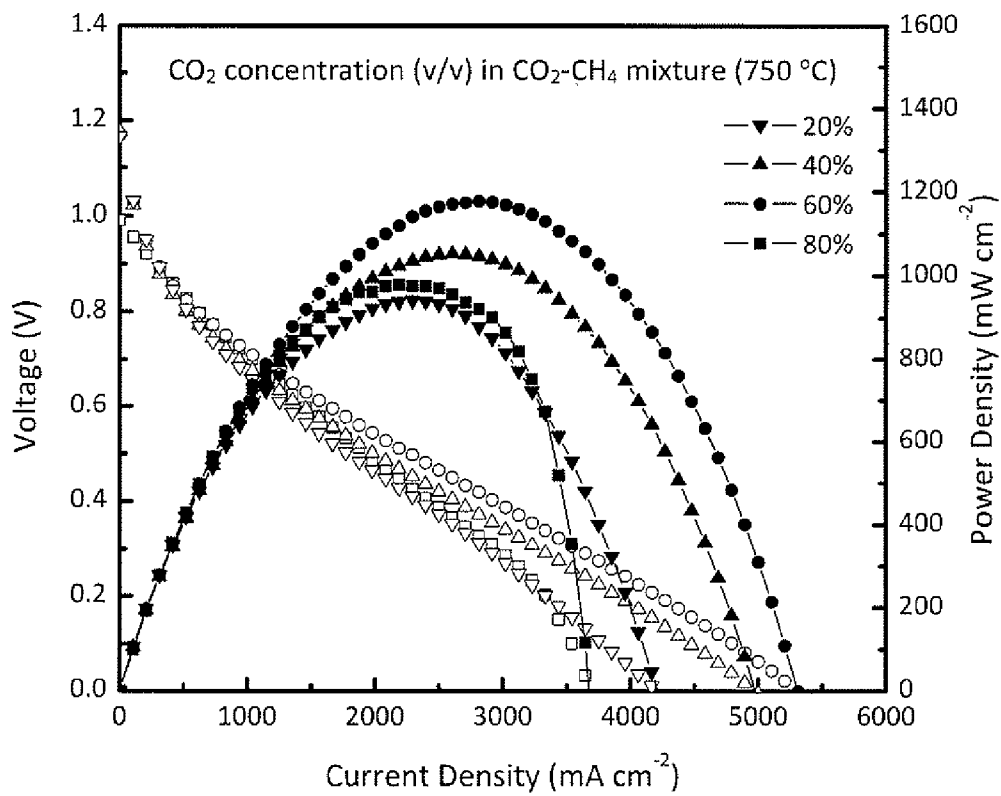
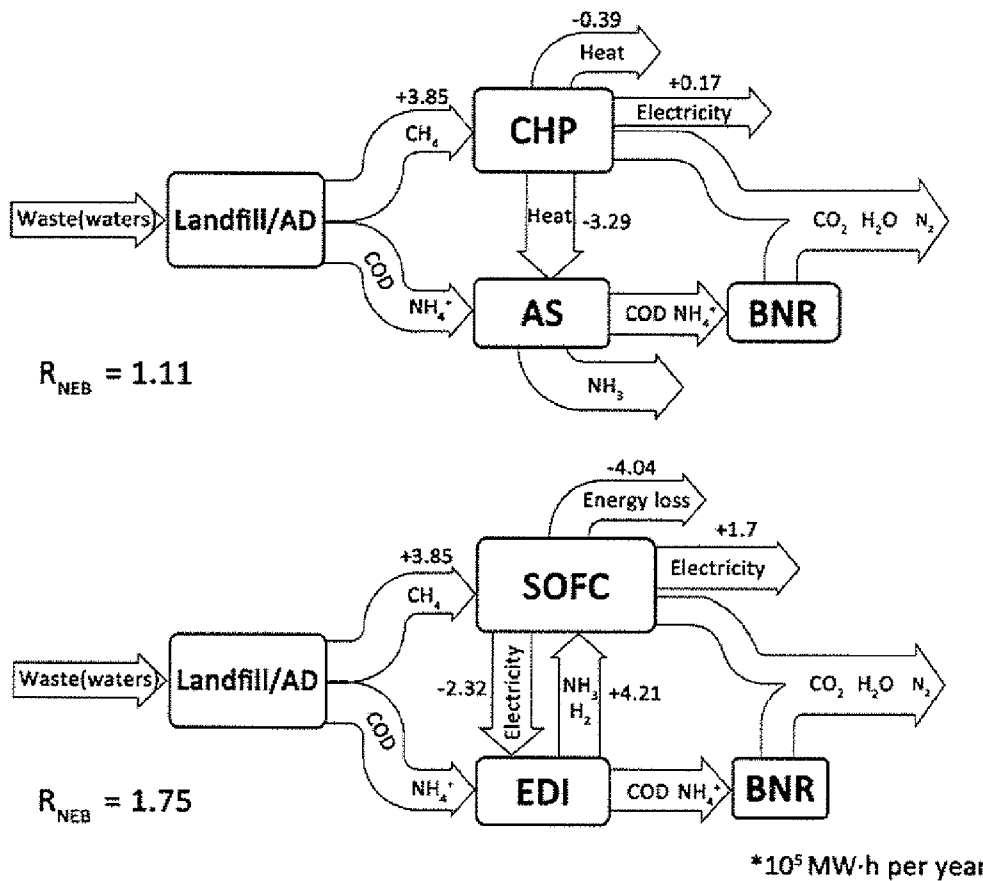


Figure 4



8/10

Figure 5A

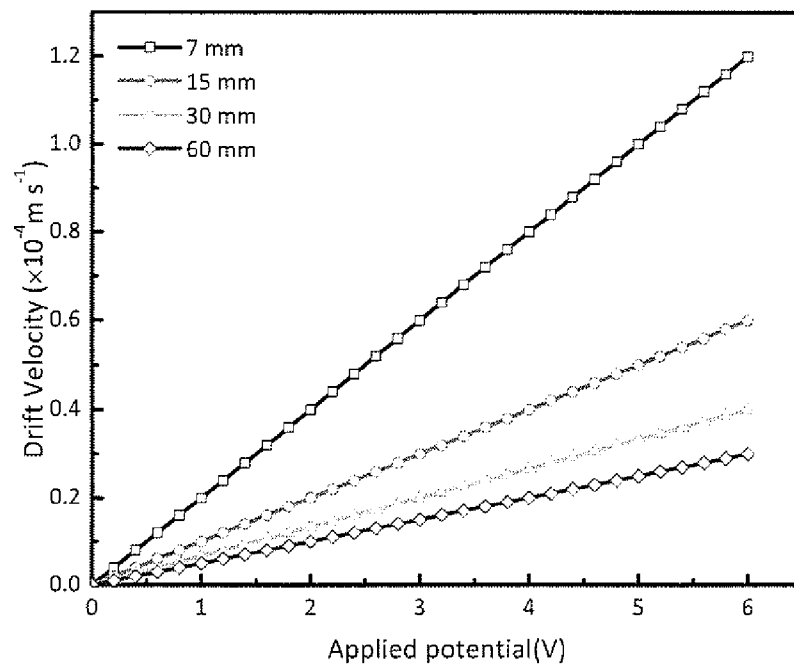
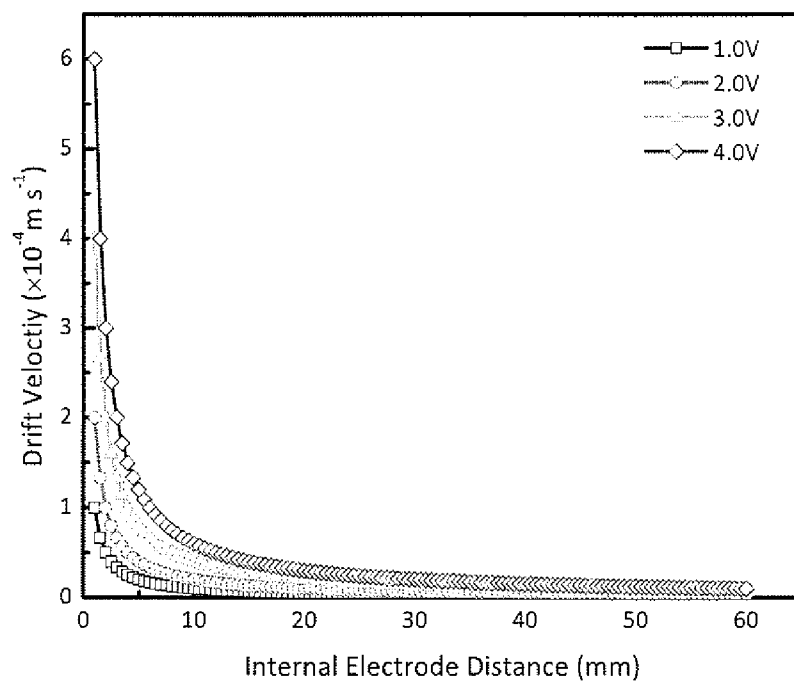


Figure 5B



9/10

Figure 6A

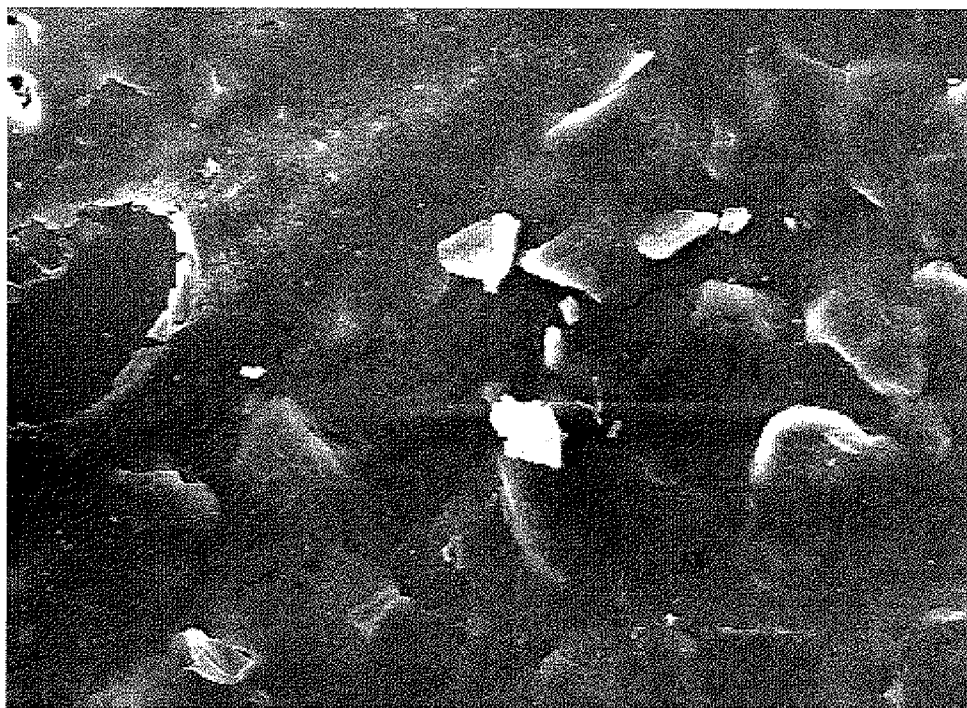
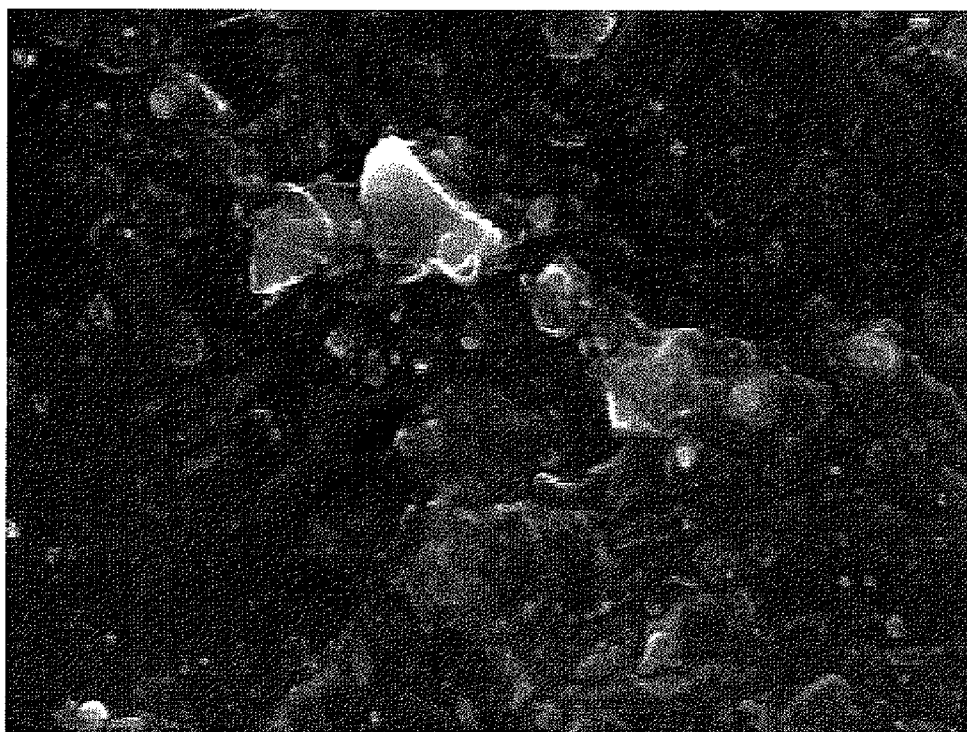


Figure 6B



10/10

Figure 7A

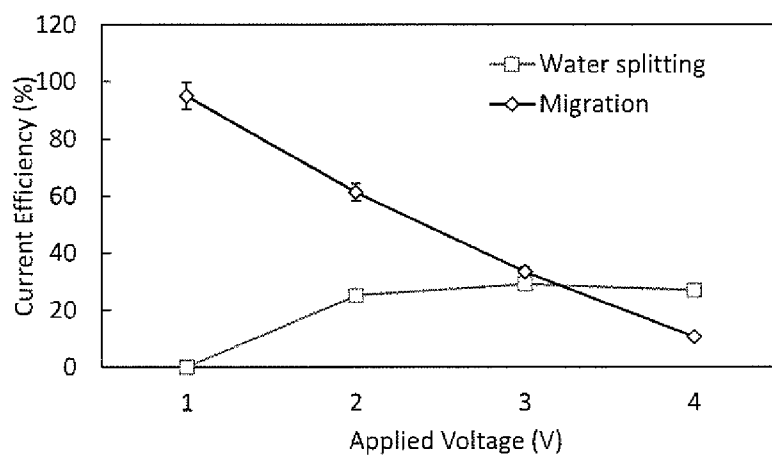
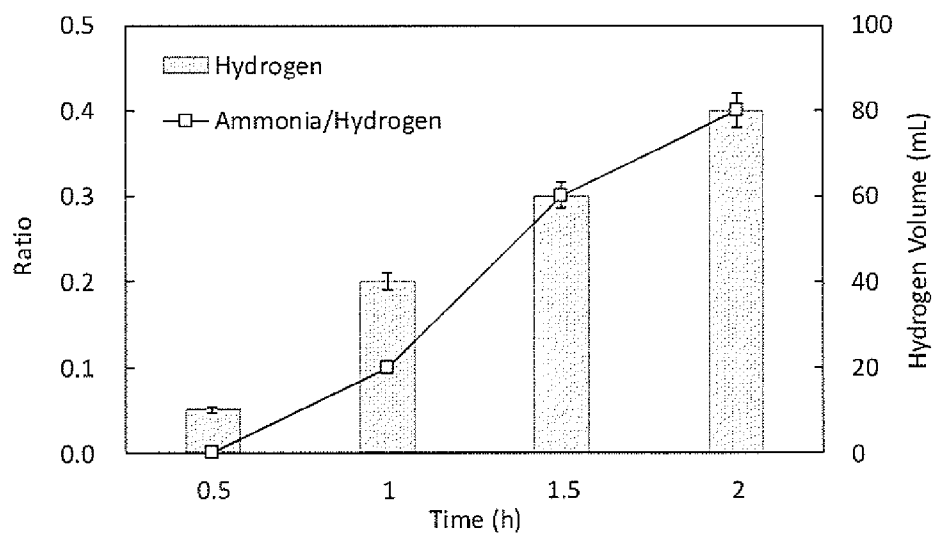


Figure 7B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2017/053741

A. CLASSIFICATION OF SUBJECT MATTER

C02F 3/28(2006.01)i; C02F 1/469(2006.01)i; B01D 61/44(2006.01)i; H01M 8/10(2016.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C02F1; C02F3; B01D61; H01M8

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI;EPODOC;CNKI;CNPAT;VEN:fuel cell?,EDI,electrodeionization,electroosmosis,electrodialysis,anaerate, anaerobic, digestion,ammonium,ammonia,hydrogen

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012189923 A1 (HEMMES KATRIEN ET AL.) 26 July 2012 (2012-07-26) claims 32 and 48 and description, paragraph [0041]	1-19
Y	US 2015014169 A1 (UNIVERSITY GENT) 15 January 2015 (2015-01-15) description, paragraph [0031]	1-19
A	US 3291713 A (IONICS) 13 December 1966 (1966-12-13) the whole document	1-19
A	CN 105552411 A (FUEL CELL RES & DEV BRANCH GUANGDONG ZHONGSHANG GUOTONG ELEC) 04 May 2016 (2016-05-04) the whole document	1-19
A	CN 101402497 A (WANG, FANG) 08 April 2009 (2009-04-08) the whole document	1-19
PX	Linji Xu et al. "energy upcycle in anaerobic treatment: Ammonium, methane, and carbon dioxide reformation through a hybrid electrodeionization-solid oxide fuel cell system" <i>Energy Conversion and Management</i> , No. 140, 08 March 2017 (2017-03-08), ISSN: 0196-8904, page 158, paragraph 4 to page 163, paragraph 1 and figure 1	1-19

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 October 2017

Date of mailing of the international search report

08 November 2017

Name and mailing address of the ISA/CN

STATE INTELLECTUAL PROPERTY OFFICE OF THE
P.R.CHINA
6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088
China

Facsimile No. (86-10)62019451

Authorized officer

CAO,Meng

Telephone No. (86-10)62084995

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/IB2017/053741

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2012189923	A1	26 July 2012	CN	102576889	A	11 July 2012
				EP	2474064	A1	11 July 2012
				US	8802323	B2	12 August 2014
				NL	2003429	C	03 March 2011
				ZA	201201198	B	28 November 2012
				EP	2474064	B1	16 October 2013
				WO	2011028104	A1	10 March 2011
US	2015014169	A1	15 January 2015	WO	2013113724	A3	07 November 2013
				EP	2809430	A2	10 December 2014
				ES	2564549	T3	23 March 2016
				CA	2861151	A1	08 August 2013
				EP	2809430	B1	30 December 2015
				DK	2809430	T3	07 March 2016
				WO	2013113724	A2	08 August 2013
US	3291713	A	13 December 1966	None			
CN	105552411	A	04 May 2016	CN	105552411	B	22 September 2017
CN	101402497	A	08 April 2009	CN	101648738	A	17 February 2010
				CN	101648738	B	04 July 2012