

SYMPOSIUM ET14/BI01/NM04

TUTORIAL: Life Cycle Analysis from an Industrial Perspective
November 25 - November 25, 2018

* Invited Paper

TUTORIAL Life Cycle Analysis from an Industrial Perspective

Sunday Afternoon, November 25, 2018
Hynes, Level 2, Room 200

Environmental issues keep steadily increasing, thus there is a strong urge to discuss how materials scientists could more rapidly respond to the worldwide concerns. This joint tutorial effort would be organized by the three symposia together. To ensure the success of such synergistic efforts it is also urged a close dialogue with society so to establish guidelines for policymakers, thus this tutorial will incorporate both the societal and the engineering aspects of life cycle analysis (LCA) would be covered. The main objective of this tutorial is to explore communications pathways between companies and materials researchers that further elevate the profile and challenges of sustainability that represents a societal necessity and a viable and critical topic for research.

1:30 PM

Societal Aspect of LCA Jean-Pierre Birat; ArcelorMittal

Materials are not simply the product of an engineering discipline, Materials Science, but also "social constructs" that have entertained a close relationship with society all through the historical timeline and remain a core element of our modern world, what is called a Key Enabling Technology. How this can be analyzed by parallel approaches of hard and soft sciences will be explained in the class as well as the tryptic of economic, environmental and social values of materials. Examples reported in the 13 past SAM conferences will be used as examples.

2:45 PM BREAK

3:15 PM

Engineering Aspect of LCA Alan Rae; IncubatorWorks, USA

The instructor will provide an overview on all the aspects considered in a life cycle analysis aimed to the engineering design of an industrial process. A part of the tutorial will involve the interaction with the audience in order to apply some of the concepts described in the first part of the tutorials to common objects.

4:15 PM Sustainability Challenge

The symposia organizers will divide the participants into groups and a sustainability challenge will integrate the concepts presented by the instructors so to review and facilitate networking among participants and instructors

4:45 PM

Final Remarks

SYMPOSIUM ET14

Materials Science Facing Global Warming—Practical Solutions for Our Future
November 26 - November 27, 2018

Symposium Organizers

Klaus Lackner, Arizona State University
Fabrizio Passarini, Università di Bologna

Jenny Vitillo, University of Minnesota
Tao Wang, Zhejiang University

Symposium Support
Hiden Isochema Ltd.

* Invited Paper

SESSION ET14.01: DAC/CCS by Sorption in Materials I
Session Chairs: Darren Broom and Jenny Vitillo
Monday Morning, November 26, 2018
Hynes, Level 3, Room 305

8:30 AM INTRODUCTORY COMMENTS ON DAC BY KLAUS LACKNER

8:45 AM ET14.01.01

The Material Science Challenges of a Closed Carbon Cycle with Moisture Swing Technology Klaus S. Lackner; Arizona State University, Tempe, Arizona, United States.

A large class of strong-base anionic exchange resins with quaternary ammonium ions as the fixed cationic charge and carbonate, bicarbonate or hydroxide for mobile anions exhibit equilibria with gaseous CO₂ that are strongly affected by the presence of water. At room temperature, changing the relative humidity of air over the resin from 20% to 100% changes the equilibrium pressure of CO₂ in the gas phase for a fixed dissolved inorganic carbon loading of the resin five hundredfold. This novel phenomenon is of interest for capture of CO₂ from ambient air as it can support novel sorption/desorption cycles driven by moisture rather than temperature or pressure changes. It can support novel membranes where a concentration gradient in moisture can pump CO₂ against a chemical potential across the membrane. The impact of water on CO₂ sorption is so large that it cannot be explained through simple competition for sorption sites. Instead, theoretical analysis suggest that the effect is mediated through changes in the hydration states of the ions present in the resin. The emergence of superacids in nano-droplets as was described by Colussi and his group provides an analogy. The analysis suggests that the process is complicated and goes to the heart of the nature of water and its behavior in confined spaces and its interactions with ions. A better understanding and more detailed experimental analysis would be extremely valuable. There are a number of unanswered questions a more detailed research program would need to answer: how does the interaction of water with ions affect the ionic equilibrium; how does the nature of the polymer structure of the resin impacts this behavior, in terms of equilibrium conditions, but also transport conditions. The nature of the cation is also of great interest. If indeed the simple models which suggest that the nature of the cation and the polymer structure are of secondary concern proves correct under experimental scrutiny, then one can focus on cost, and long-term stability in choosing among different polymer structures and cations. Answers to these questions would open a new field of sorbent technologies that could have impact well beyond the immediate application in direct air capture.

9:00 AM ET14.01.02

Nano Porous Polymeric Composite Membranes—Excellent Carbon Dioxide Separation Performance and with Processible Membrane Properties Ali Sekizkardes^{1,2}, Surendar Venna^{1,2}, Victor Kusuma^{1,2} and David Hopkinson¹; ¹National Energy and Technology Laboratory (NETL), U.S. Department of Energy, Pittsburgh, Pennsylvania, United States; ²AECOM Pittsburgh, Pittsburgh, Pennsylvania, United States.

Nano porous polymers such as polymers with intrinsic microporosity (PIMs) have attracted great interest in Materials Science to applied as gas separation membranes. PIMs are constructed by contorted monomer backbones and given its inefficient polymer chain packing, PIM-1 possesses an intrinsic micro porosity with an unprecedented amount of free volume for a polymeric membrane. The unique polymer structure of PIM-1, however, constitutes two major drawbacks: Average pore size of PIM-1 (~1nm) is too large, hence permeate most of small gas molecules such as H₂, N₂, CO₂, CH₄ and consequently PIMs show lower gas selectivity properties compared to other polymeric membranes. The second drawback is weak mechanical properties for PIM due to the lack of sufficient hydrogen bonding capability between polymer chains, affording brittle film formation. Here we study novel composite membrane fabrication and characterization by incorporation of flexible in house synthesized polyether (NETL-PE) and porous organic fillers in PIMs. PIM/NETL-PE membranes show distinct improvement in brittle film properties of PIM-1 by greatly improving low strain to failure (< 1%) of PIM-1 to as high as 10.5%, which is indicative of a very flexible and durable film formation. The resultant membranes showed an excellent CO₂/N₂ selectivity of 40 while maintain high CO₂ permeability of up to 2500 barrer. Comparing these membranes with reported polymeric membranes above the 2008 Robeson upper bound shows that these membranes are one of best materials for CO₂/N₂ separation applications while having good mechanical properties. Fabrication and characterization of the membranes with pure and mixed gas permeation tests will be presented.

9:15 AM ET14.01.03

Quaternary-Ammonium Grafted Macroporous Resin for Direct Air Capture of CO₂ Yusong Wu, Chenglong Hou, Xinru Wang, Tao Wang and Mengxiang Fang; Zhejiang University, Hangzhou, China.

Global warming, believed to be triggered by the emission of CO₂, has become the focus of the sustainable development of human society nowadays. It is imperative and urgent to take some effective actions to reduce the global CO₂ emissions. Considered to be one of the key technologies to achieve the negative CO₂ emissions, Direct Air Capture (DAC) has attracted worldwide attention since 2000. After decades of fundamental research on DAC sorbents, the low sorption kinetics, higher energy consumption for regeneration, and the insufficient stability become the major obstacles for DAC application in practical processes. Aiming to solve the problem above, this paper proposed a novel resin sorbent synthesized by chemical grafting the quaternary ammonium groups onto the nonpolar macroporous resins. Three different support materials (XAD-4, XAD-16, D101) with preferred porosity were selected as supports and the CO₂ adsorption performance were demonstrated with isothermal experiments. The structure-activity relationship of the sorbent were further revealed with multiple characterization methods including FESEM, FTIR, MIP and elemental analysis. Results indicated that the CO₂ adsorption isotherms of quaternary- ammonium grafted resins were in line with the classic Langmuir model. Quaternized XAD-16 sample, with a moderate pore size, had the highest CO₂ adsorption capacity of 0.42 mmol/g, and the quaternized XAD-4 and D101 samples were only 0.28 mmol/g and 0.21 mmol/g, respectively. Combined with the results of elemental analysis and pore analysis, it was inferred that the macropores in the resin are conducive to the grafting density of quaternary ammonium groups, while the quaternary ammonium groups confined in the micropores could reach a higher CO₂ adsorption efficiency. The adsorption kinetics of the optimized adsorbents could be one magnitude higher than commercial resin at 400 ppm CO₂. The stability of the

adsorbents were verified with a cyclic adsorption-desorption test based on moisture swing technique, showing no evident decline in working capacity in 10 cycles under 25 °C. Owing to higher kinetics and the energy-efficient moisture swing process, it can be suggested that the quaternary-ammonium grafted macroporous resin could be a promising and cheap material for direct air capture.

9:30 AM DISCUSSION TIME

9:45 AM BREAK

10:15 AM *ET14.01.04

Carbon Dioxide Capture in Diamine-Appended Metal-Organic Frameworks Rebecca Siegelman^{1,2}, Phillip Milner^{1,2}, Jeffrey Martell¹, Alex Forse^{1,2}, Miguel Gonzalez¹, Eugene Kim¹, Tomce Runcevski¹, Jarad Mason^{1,2}, Thomas McDonald^{1,2,3}, Jeffrey Reimer^{1,2} and Jeffrey R. Long^{1,2}; ¹University of California, Berkeley, Berkeley, California, United States; ²Lawrence Berkeley National Laboratory, Berkeley, California, United States; ³Mosaic Materials, Inc., Berkeley, California, United States.

Owing to their high surface areas, tunable pore dimensions, and adjustable surface functionality, metal-organic frameworks (MOFs) can offer advantages for a variety of gas storage and gas separation applications. In an effort to help curb greenhouse gas emissions from power plants, we are developing new MOFs for potential use as solid adsorbents in post- and pre-combustion CO₂ capture, and for the separation of O₂ from air, as required for oxy-fuel combustion. In particular, MOFs with diamine-functionalized surfaces have been demonstrated to provide high selectivities and capacities for the adsorption of CO₂ over N₂ under dry flue gas conditions. Thermogravimetric cycling and multicomponent adsorption measurements now further show that compounds of this type remain highly effective in the presence of water, while calorimetry data reveal a low regeneration energy compared to aqueous amine solutions. Most significantly, as determined by *in situ* nuclear magnetic resonance, infrared, x-ray absorption spectroscopy experiments, crystal structure determinations, and computational simulations, the unusual stepped CO₂ adsorption isotherms exhibited by these materials arise from a unique cooperative insertion mechanism to form one-dimensional chains of metal-bound ammonium carbamates. A detailed understanding of this mechanism now enables us to design new materials for the low-energy separation of CO₂ from a wide variety of key gas mixtures, including flue gases, air, biogas, and natural gas deposits.

10:45 AM ET14.01.05

Nano Fabricated Polybenzimidazoles with Chemically Robust Membrane Jung Ji Hye, Moon Ki Jeong and Sang Yong Nam; Gyeongsang National University, Jinju, Korea (the Republic of).

Polybenzimidazole is well known for its superior heat resistance and good mechanical properties. Due to an excellent various property, PBI has been used in a lot of fields such as gas separation, OSN and secondary battery membrane.

This work is focused on fabrication of meta-Polybenzimidazole(m-PBI) and control of morphology according to concentrations or manufacturing conditions. The membranes were prepared via the phase inversion method from casting solutions with predetermined amounts PBI, dimethylacetamide (DMAc) and tetrahydrofuran (THF). The polymer solutions were cast on a clean glass plate by using casting knife. The membrane was immersed in IPA to remove the residual solvent and dried in vacuum oven for 24 h. The membrane was crosslinked by α, α' -Dibromo-p-xylene. Also, this membrane can be prepared by electro-spinning. Electro-spinning can make highly porous non-woven fabrics consisted of nanofibers with the small diameters and overall porous structure. Also, electrospun fabrics have high specific surface area. To observe morphology, Scanning electron microscope (SEM) was used. In case of gas transport properties, H₂, CO₂ Permeability and selectivity of this membrane was measured via pure gas.

11:00 AM ET14.01.06

Ultra-Selective Defect-Free Interfacially Polymerized Molecular Sieve Thin-Film Composite Membranes for H₂ Purification and Carbon Capture Zain Ali, Federico Pacheco, Ingo Pinnau and Yingge Wang; King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Ultra-selective defect-free interfacially polymerized molecular sieve thin-film composite membranes for H₂ purification and carbon capture Purification is a major bottleneck towards generating low-cost commercial hydrogen from syngas mixtures. According to reports published by United States Department of Energy (USDOE), reduction in hydrogen purification costs can immediately increase the hydrogen market by 10-fold promoting its use in desulfurization, hydrotreating, chemical manufacture, power generation and use as a potential energy carrier. In this work, inexpensive high-performance H₂ separating membranes were fabricated by modifying the commercially successful reverse osmosis membrane production method. Defect-free thin-film composite membranes were formed that demonstrate unprecedented mixed-gas H₂/CO₂ selectivity of ≈ 50 at 140 °C with H₂ permeance of 350 GPU, surpassing the permeance/selectivity upper bound of all known polymer membranes by a wide margin.

Coupled with excellent H₂/CH₄ separation properties, given the targets specified by the USDOE, the membranes are excellent candidates for pilot-scale testing aimed at hydrogen purification from syngas while simultaneously promoting capture of accompanying CO₂. Fortuitously, these ultra-high-performance membranes can be produced by making only small changes to existing commercial membrane manufacturing processes. Therefore, their fabrication cost should be similar to standard RO membranes – only $\approx 1 - 2$ \$/ft², which would lower the membrane cost by 50-100-fold based on the USDOE target value of 100 \$/ft². This study demonstrated that varying fabrication parameters can tune permselectivity to meet the needs of specific processes. A few simple modifications to a time-tested commercial membrane fabrication process can produce membranes that meet a key industrial need. These membranes also demonstrated remarkable selectivity for O₂/N₂, CO₂/CH₄, H₂/N₂ and CO₂/N₂ separations. With rapidly developing economic and environmental pressures to increase efficiencies for separation processes, such highly-selective, low-cost, commercial barrier materials fabricated as ultra-thin films show potential for a paradigm shift to streamline industrial use of membranes for a large number of gas separation applications, including but not limited to hydrogen separations, air separations as well as a number of liquid-bases separations. The combination of exceptional separation performance and low manufacturing cost makes interfacially polymerized thin-film composite molecular sieves excellent candidates for cost-effective hydrogen purification from steam cracking and similar processes.

11:30 AM ET14.01.07

Tailoring Molecular Architecture of Graphene Oxide for CO₂-Selective Membrane Jae Eun Shin, Jun Kyu Jang, Inho Park and Ho Bum Park; Hanyang University, Seoul, Korea (the Republic of).

Graphene Oxide (GO) has been extensively investigated as a membrane material for CO₂ separation due to their high CO₂ sorption properties and 2-dimensional nanosheets structure for membrane formation. Although GO membrane is considered as one of promising membrane, it has a limitation to apply for practical application because of low gas permeability. In general, gas molecules are passed along the layered structure, which lead to increase of diffusional pathway and resistance to oxygen functional groups on the basal plane of GO. As such, in this study, we prepared modified GOs to reducing the diffusional pathway and increasing structural stability by adjusting the architecture of GO using the following methods; (1) surface porosity and interlayer distance control by sol-gel reaction, (2) tailoring sp²-graphitic and sp³-oxidized regions with mild hydrothermal treatment, (3) creating and decorating pores on the basal plane of GO nanosheets without thermal reduction. Finally, we fabricated membranes to confirm gas transport behaviors. From these

results, the CO₂ permeability was significantly increased up to 30 times compared to the pristine GO membrane and CO₂/N₂ selectivity was increased up to as high as 30. These results have the potential to open up new approaches for an improvement in the transport properties of two-dimensional membrane materials for use in next-generation membrane for CO₂ separation.

11:45 AM DISCUSSION TIME

SESSION ET14.02: DAC/CCS by Sorption in Materials II

Session Chair: Klaus Lackner

Monday Afternoon, November 26, 2018

Hynes, Level 3, Room 305

1:30 PM *ET14.02.01

Design of CO₂-Sorbing Materials and Their Compatibility with Practical, Scalable Direct Air Capture Processes Christopher W. Jones; Georgia Institute of Technology, Atlanta, Georgia, United States.

A variety of classes of materials have been established for CO₂ adsorption from gaseous mixtures. One particular challenge that has emerged in recent years is the design of materials that bind CO₂ suitably strongly and selectively that they can efficiently extract CO₂ from ultra-dilute mixtures, such as ambient air (400 ppm). Such materials and processes will play an important role in future climate mitigation strategies if society chooses to try and limit global climate change, being one of the only highly scalable approaches to achieve negative CO₂ emissions. In this contribution, I will discuss various classes of materials that have been proposed for use in such “direct air capture” technologies, highlighting strengths and weaknesses of assorted compositions in these applications, as well as critical research challenges that the field should address.

2:00 PM ET14.02.02

Fabrication of Large and Free-Standing Nanomembranes Preferential CO₂ Separation Under Atmospheric Pressure Shigenori Fujikawa, Toyoki Kunitake and Roman Selyanchyn; WPI-I2CNER, Kyushu University, Fukuoka, Japan.

Biological lipid bilayer membrane is an ideal example for precise and efficient molecular separation. One of its characteristics is a free-standing property with molecular thickness, and molecular scale phenomena become dominant in the direction of the membrane thickness. Thus, artificial membrane with a free-standing properties and nanometer thickness would be a unique property different from conventional thicker membrane. Especially in membrane separation, the thickness plays an important role for the efficient separation. Based on this idea, we have developed free-standing nanomembranes (thickness: 100 nm or less) with preferential CO₂ permeation ability over nitrogen even under low partial pressure difference of CO₂ across a membrane. Our developed nanomembranes showed very high CO₂ flux (about ~10,000 GPU, 1GPU=7.5×10⁻¹² m³/m²•s•Pa), without losing CO₂ selectivity which is identical to that of thicker membranes. This unique feature of free-standing nanomembranes, high CO₂ flux with preferential CO₂ separation, would be beneficial to capture CO₂ from the air, so-called “direct air capture”. Indeed, our free-standing nanomembrane showed preferential CO₂ separation even under very small pressure difference.

2:15 PM ET14.02.03

Techno-Economic Analysis of Membrane-Supported H₂O Splitting with CO₂ capture Xiao-Yu Wu, Yu-Dong Chen and Ahmed F. Ghoniem; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

In this presentation, we show the techno-economic analysis of an advanced hydrogen production technology: membrane supported water splitting with CO₂ capture. Oxygen permeable membranes such as La_{0.9}Ca_{0.1}FeO_{3-δ} (LCF) [1,2] and BaCo₃Fe₃Zr₂O_{3-δ} (BCFZ) [3, 4] are used to *in situ* separate the water splitting products. On the feed side of the membrane, H₂O splitting occurs and high purity hydrogen is produced. On the sweep side, methane oxidation takes place to consume the permeated oxygen and to maintain the oxygen potential gradient across the membrane. CO₂ produced from methane oxidation is ready to be captured at high pressure.

First, we built a thermodynamic model to compare the membrane reactor with the conventional methane reforming for high purity hydrogen production. Results show that membrane reactors have higher efficiency (as high as 8 percent points), especially when renewable heat source, e.g., solar and geothermal energy is incorporated into the system. The energy cost of hydrogen production with CO₂ capture is lower for the membrane reactors.

Secondly, a high-fidelity reactor model is built to simulate a monolith membrane reactor with 100 kmol/h H₂ production rate. The dimensions and operating conditions are similar to the solid oxide fuel cell stacks, and 90% methane conversion is achieved. Two well-studied perovskite membrane materials, i.e., LCF and BCFZ are compared. Results show that BCFZ membrane can produce more hydrogen per unit surface area, so the required LCF membrane surface area is 5.3 times larger than the BCFZ membrane area.

As the BCFZ membrane contain critical minerals, e.g., cobalt and zirconium, the membrane reactor cost can be impacted by the fluctuating mineral prices. Based on the quoted prices from Alibaba website on April 2018, the raw materials to produce the BCFZ membrane is 2.3 times more expensive than those for the LCF membrane. However, as the required LCF membrane surface area is larger, the cost for the LCF membrane reactor is 2.4 times more expensive than that for the BCFZ reactor. Sensitivity analysis shows that if cobalt price increases by 2.82 times, the cost for the BCFZ reactor can be more expensive.

Furthermore, it has been showed that BCFZ membrane is susceptible to performance instability due to the cobalt segregation [5], while LCF membrane can perform stably under both oxidizing and reducing environments [1]. Life-cycle analysis will be carried out to compare the costs of these two membrane reactors for a hydrogen plant designed with 20-year operating life.

Reference:

- [1] Wu, X. Y., et al., *PCCP*, 2015, **17**(15): 10093-10107
- [2] Wu, X.-Y., et al., *AIChE J.*, 2016, **62**(12): 4427-4435
- [3] Jiang, H., et al., *Angew. Chem. Int. Ed.*, 2008, **47**(48): 9341-9344
- [4] Jiang, H., et al., *Catal. Today*, 2010, **156**(3-4): 187-190
- [5] Jiang, H., et al., *Angew. Chem. Int. Ed.*, 2010, **49**(33): 5656-5660

2:30 PM DISCUSSION TIME

2:45 PM BREAK

SESSION ET14.03: CO₂ Fixation by Biological Systems
Session Chair: Edda Aradottir
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 305

3:15 PM *ET14.03.01

Nano-/Microscopic Design for the Hybrid Biological | Inorganic System of Electricity-Driven CO₂ Reduction Chong Liu; University of California, Los Angeles, Los Angeles, California, United States.

A hybrid biological | inorganic (HBI) system combines the benefits of both inorganic and biological catalysts and leads to high energy efficiency of electricity-driven CO₂ reduction to commodity chemicals. However, the reactor throughput and the versatility of chemical feedstock may not be optimal yet, as biocatalysts can be kinetically slow and have stringent requirements of substrates and liquid environment. In this talk, we will discuss some design strategies at micro-/nanoscopic scale to address these questions.

3:45 PM ET14.03.02

Photocatalyst-Biocatalyst Integrated Artificial Photosynthesis System for Highly Selective Solar Fuel Production from CO₂ Jin-ook Baeg; KRICT, Daejeon, Korea (the Republic of).

The natural photosynthetic process has fascinated chemists for long due to its high specificity in solar energy conversion to sugar. However, given the structural and functional complexity, it is a challenge to mimic this natural process. In recent years, these efforts have intensified due to increasing emphasis on the development of emission-zero systems/technologies for production of solar fuel/chemicals. Utilizing the natural photosynthesis as blueprint, a number of covalent, and non-covalent donor-acceptor conjugate dyes have been studied as systems for CO₂ fixation. Although capable of efficient photoinduced intra- and intermolecular electron transfer(ET), they suffer from low conversion efficiency, poor product selectivity and lack of photostability. This has led to emergence of the coupling of a highly visible light active photocatalyst to an enzyme as an exciting avenue of research in this area. In this regard, we developed the photocatalyst/ enzyme integrated solar chemical factory system that exemplified solar energy in synthesis of solar fuel & solar chemicals. Generating NAD(P)H in non-enzymatic light-driven process and coupling it to the enzymatic dark reaction catalysis for the tailor-made solar fuel/solar chemical synthesis *via* photo-biocatalysis. The present work demonstrates successfully a new and potentially promising solar chemical factory platform system for the ultimate goal of utilization of solar energy in fuel & fine chemical synthesis.

4:00 PM ET14.03.03

Perfluorocarbon Nanoemulsions Alleviate Kinetic Bottlenecks in Electricity-Driven Microbial CO₂ Reduction Roselyn Rodrigues, Daniel Estabrook, Xun Guan, Jesus Iniguez, Shengtao Lu and Chong Liu; University of California, Los Angeles, Los Angeles, California, United States.

Rising atmospheric carbon dioxide levels make CO₂ an abundant source of carbon for synthesis of commodity chemicals. One of the most promising methods of CO₂ reduction developed in recent years is the use of a hybrid biological inorganic system that couples an electrochemical cell and CO₂ reducing microbes to simultaneously split water and fix carbon dioxide. While this system is highly energy efficient, the low solubility of the redox carrier, H₂ gas, in aqueous environments is hindering the scale-up of the hybrid biological inorganic system. We propose that biocompatible perfluorocarbon nanoemulsions can serve to increase the H₂ gas solubility to overcome this kinetic limitation. We discovered that perfluorocarbon nanoemulsions not only increase the average concentration of H₂ generated from electrochemical water splitting, but also accelerated the local H₂ transfer rate in proximity to the microbes. Both factors contributed to an average 20% (n ≥ 3) enhancement in overall device efficiency with high device throughput. We believe that our improved hybrid system could be used at point sources of CO₂ emissions to generate important chemical building blocks while reducing atmospheric CO₂.

4:15 PM *ET14.03.04

Carbon Negative Production of Living Biofertilizers Daniel G. G. Nocera and Daniel Loh; Harvard University, Cambridge, Massachusetts, United States.

Global soils store 2-3 times more carbon than the atmosphere, acting as a massive reservoir for carbon sequestration. Increasing soil carbon reservoirs by 0.4% per year would completely halt the increase of atmospheric CO₂ levels from human activity. These efforts to sequester carbon simultaneously enrich agricultural soils, supporting soil biology and reducing the need for synthetic fertilizers, a production system responsible for >245 million tons CO₂/year. To both sequester atmospheric CO₂ and replace synthetic fertilizer production, we have developed a living, CO₂-negative biofertilizer. This work adapts the Bionic Leaf, a bioelectrochemical cell that uses water, sunlight, and atmospheric CO₂ to cultivate microbes. Bionic Leaf growth of the soil microbe *Xanthobacter autotrophicus* produces an active, living biofertilizer capable of using CO₂-derived intracellular energy stores to synthesize NH₃ as a plant nutrient in the field. This biofertilizer demonstrates both potent plant-beneficial features as well as a route to increasing soil carbon reservoirs.

4:45 PM ET14.03.05

Photosynthesis-Mimicking Cell with 15.6% Solar-to-CO Efficiency Junlang Liu, Yuhang Wang and Gengfeng Zheng; Fudan University, Shanghai, China.

The vigorous growth of atmospheric CO₂ level has posed a threat on sustainable development of our blue planet. The solar-energy-driven electrochemical CO₂ conversion into various value-added chemicals (namely artificial photosynthesis) is regarded as one of the most promising solutions to alleviate this urgent environment pressure and energy crisis. Compared to the other configurations of artificial photosynthesis systems such as photocatalysis and photoelectrochemical conversion, electrocatalysis powered by photovoltaics has shown the highest solar-to-fuel efficiency to date, which has achieved over 10-fold enhancement compared to natural photosynthesis. Nonetheless, the operation of all artificial photosynthesis systems still strongly relies on sunlight illuminations, which are altered significantly over time of a day, weathers and regions. Thus, **designing artificial photosynthesis devices capable of CO₂ reduction reaction (CO₂RR) under different sunlight conditions is of crucial significance.**

Delighted by the temporary energy storage function of ATP and NADPH in green plants, we propose that a redox medium can be introduced between oxygen evolution reaction (OER) and CO₂RR. The redox medium forms a loop with OER electrode to store the photogenerated electrons in the step of light reaction, as the charging of battery. These photogenerated electrons can be released spontaneously to reduce CO₂ in the following artificial carbon fixation step, as the battery discharge.

Therefore, we develop a green-plant-mimicking artificial photosynthesis-battery system, by introducing Zn/Zn(OH)₄²⁻ redox pair as the energy transfer medium between artificial light reaction and carbon fixation to simulate ATP/ADP. Nano-Au and NiFe hydroxides were employed as electrocatalysts for CO₂RR and OER, respectively. A GaAs solar cell was utilized to drive oxygen evolution reaction and store electrons in Zn/Zn(OH)₄²⁻. The further release of electrons proceeded without light and led to an unassisted CO₂ electroreduction. The solar conversion efficiency of artificial light reaction is 28.7%. During carbon fixation, the unassisted electrochemical CO₂ reduction achieved a **record-high solar-to-CO efficiency peaking at 15.6%** under 1-sun intensity at the current density of 10 mA/cm². By tuning CO₂ electroreduction current density in the range of 2 to 10 mA/cm², **a tunable and light-independent selectivity of CO production was realized.**

Our two-step, artificial photosynthesis-battery design possesses **high efficiency, tunable selectivity, excellent stability and flexibility to various sunlight conditions even in the dark**, owing to the mutual independence of light reaction and carbon fixation. Combining with further robust electrocatalysts as well as new redox media able to provide higher potential difference for carbon fixation, our design actually suggests new opportunities in anthropogenic manufacture of fossil fuels from CO₂ and sunlight with such a green-plant-mimicking approach.

SESSION ET14.04: Poster Session: Carbon Dioxide Capture, Separation and Utilization
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET14.04.01

Sequestration of CO₂ and SO₂ from Flue Gas Using 3-D Graphene Sponge Manish Maurya and Jayant K. Singh; Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, India.

Increasing atmospheric carbon dioxide and sulfur dioxide emissions from combustion of fossil fuels, such as coal and oil, are considered as a globally alarming environmental issue. Hence, the quest for an immediate solution for sequestration and storage of carbon dioxide and sulfur dioxide is warranted. Recently, amine and ionic liquid based absorption process have attracted widespread attention to capture these gases but this process passes several disadvantages such as severe corrosion, highly energy intensive, and low contact area. One viable alternative is adsorption technology, which is recognized to be attractive to replace current absorption technology. Therefore, development of novel porous carbon based materials has become one of the hot areas due to their extensive applications in gas storage and separation. In this regard, first we have modeled an experimentally observed 3-D porous structure of graphene sponge (GS) using molecular dynamics simulations (MD). The initial structure is composed of randomly distributed graphene flakes and inclusion particles of variable dimensions following the lognormal distribution. [1] MD simulations are performed using Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential to mimic the synthesis of 3-D graphene sponge. Further, we have used this graphene sponge as an adsorbent to capture CO₂/SO₂. We have performed Grand Canonical Monte Carlo (GCMC) simulation to get adsorption isotherm and to examine selectivity for CO₂ and SO₂ in graphene sponge. Our simulation results show that graphene sponge obtained using smaller size inclusion particles have large uptake capacity at post combustion conditions. We first tested pure component flue gas adsorption capacity in graphene sponge then we moved on for more realistic ternary mixture (CO₂/SO₂/N₂) of flue gas adsorption. Pure component adsorption results show that SO₂ adsorbs preferably over CO₂ and N₂. At 1 bar, extent of excess adsorption of SO₂ and CO₂ in GS of 10 Å pore size are found to be 13 mmol/g and 2.6 mmol/g, respectively. Upon increasing pore size to 20 Å excess amount decreases by 56 % and 58 % for SO₂ and CO₂, respectively. In case of ternary mixture, we have found that adsorption follow the same order as in the pure component flue gas adsorption but adsorption amount decreases significantly. Selectivity analysis of adsorption show that adsorption selectivity of SO₂ over N₂ is highest followed by selectivity of CO₂ over N₂ and SO₂ over CO₂. Thus, our results indicate that graphene sponge obtained using smaller size inclusion particles is a promising material for treatment of flue gas at post combustion conditions.

References

[1] Z. Qin, G. S. Jung, M. J. Kang, M. J. Buehler, "The mechanics and design of a lightweight 3-dimensional graphene assembly", Science Advances, 2017, 3, 1601536.

ET14.04.02

Determining the Role of the Ionic Radii of Interlayer Cations for CO₂ Capture in Synthetic Smectite Clay Kristoffer W. Hunvik¹, Leide Cavalcanti², Matthias Daab³, Barbara Pacakova¹, Paulo H. Brito¹, Kenneth Knudsen^{2, 1}, Josef Breu³ and Jon O. Fossum¹; ¹Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway; ²Institute for Energy Technology, Kjeller, Norway; ³Lehrstuhl für Anorganische Chemie, University of Bayreuth, Bayreuth, Germany.

Large amounts of clays are found in cap-rock formations and can act as flow barriers in storage sites for anthropogenic CO₂ [1,2]. Clays are also relevant as capture elements for combustion gases, such as methane or CO₂. Recent experiments and simulations have shown that CO₂ (like H₂O) can intercalate in smectite clays, both in the supercritical (scCO₂)[3], and in the gaseous/liquid phase[4]. Understanding how clay swells and adsorbs CO₂ interacts with clay is vital for CCS and capturing applications. The group has previously demonstrated that CO₂ intercalates into dry synthetic (Na, Ni and Li)-Fluorohectorite (Fh), with Li-Fh clay being able to retain CO₂ (0.23 ton of CO₂/m³ captured) up to a temperature of 35°C, at ambient pressure, and that the captured CO₂ can be released by heating above this temperature. Na⁺ showed much slower intercalation dynamics than the Ni²⁺ and Li⁺, which might relate to its larger ionic radii, and thus a lower ability polarize CO₂. [5]

We have studied (Li, Ca, Ba, Ni)-fluorohectorite [6] with a capillary based high-pressure cell with synchrotron X-ray powder diffraction. Here we show preliminary results on the dynamics of the intercalation depends on the specific cation, initial space in the interlayer of the clay and at which temperatures the CO₂ enters the clay. Our studies show that dehydrated Ni-Fh is able to adsorb at higher temperatures range than Li-Fh, and that dehydrated Ca-Fh and Ba-Fh is not able to adsorb CO₂.

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- [6] Nanoplatelets of Sodium Hectorite Showing Aspect Ratios of ≈20 000 and Superior Purity, M. Stoter, D.A. Kunz, M. Schmidt, D. Hirsemann, H. Kalo, B. Putz, J. Senker, J. Breu, *Langmuir* 29, 1280-1285 (2013)

ET14.04.03

Efficient CO₂ Conversion to CO Catalyzed by Metal Nanoclusters Hoeun Seong, Yongjin Lee and Dongil Lee; Department of Chemistry, Yonsei University, Seoul, Korea (the Republic of).

Significant progress has been made recently in the electrochemical CO₂ conversion to value-added products. Various polycrystalline metal electrodes have been investigated as electrocatalysts for electrochemical CO₂ conversion, but they typically require high overpotentials and show relatively low catalytic activities. In this poster, we present that atomically precise metal nanoclusters, such as Au₂₅(SR)₁₈, where SR is thiolate ligand, can efficiently catalyze the CO₂ conversion to CO with high selectivity. The electrochemical CO₂ reduction was studied with Au₂₅ nanoclusters immobilized on gas diffusion electrode in CO₂-saturated aqueous solution containing KHCO₃ and KCl. We found that Au₂₅ nanoclusters can catalyze the CO₂ conversion to CO with high selectivity (>90%) at high current density of nearly 100 mA cm⁻². Additional studies on the effects of compositions and pH of the media on the electrocatalytic activities reveal the key factors controlling the catalytic activities of the nanoclusters. To further circumvent CO₂ mass transport limitations in aqueous solutions, we explored the possibility of using flow electrolyzer that supplies continuous CO₂ stream at the electrode-electrolyte interface. The electrocatalytic activity of the Au₂₅ nanoclusters was found to be drastically enhanced with high CO selectivity when the electrocatalysis was conducted with the flow electrolyzer.

ET14.04.04

Electrochemical CO₂ Reduction Catalyzed by Atomically Precise Copper-Hydride Nanoclusters Yongjin Lee¹, Woojun Choi¹, Dongil Lee¹, Qing Tang², De-en Jiang², Dai-Ying Li³ and Chen-Wei Liu³; ¹Department of Chemistry, Yonsei University, Seoul, Korea (the Republic of); ²Department of Chemistry, University of California, Riverside, Riverside, California, United States; ³Department of Chemistry, National Dong Hwa University, Hualien County, Taiwan.

Electrochemical CO₂ conversion into valuable fuels and feedstocks has been the focus of recent research in electrocatalysis. In particular, copper-based electrocatalysts have received much attention because they can catalyze the formation of significant amounts of hydrocarbons at high reaction rates. However, the mechanistic understanding of CO₂ reduction on nanostructured Cu catalysts has been lacking. In this poster, we show that the atomically precise Cu-hydride nanoclusters, such as Cu₃₂H₂₀L₁₂, where L is dithiophosphate ligand, offer unique selectivity for electrocatalytic CO₂ reduction at low overpotentials. Density functional theory (DFT) calculations have predicted that the presence of the negatively charged hydrides in the copper cluster plays a critical role in determining the selectivity of the reduction product, producing HCOOH over CO at lower overpotential. To confirm the DFT prediction, electrochemical CO₂ reduction was performed on the Cu₃₂H₂₀L₁₂ loaded electrode in aqueous media. Analysis of the reaction products demonstrated that HCOOH was indeed produced with 89 % selectivity at low overpotential, while H₂ production dominated at higher overpotential. The unique selectivity observed in this system can be understood by the lattice-hydride mechanism offered by the unique Cu-hydride nanocluster.

ET14.04.05

Gas Separation Membrane of poly(ethylene glycol)-polyimide Copolymer for Separating Carbon Dioxide Sang Yong Nam, Jin Woo Jo and Ji Hyun Kim; Gyeongsang National University, Jinju, Korea (the Republic of).

The study of polymer separation membrane for carbon dioxide separation for global warming is drawing attention. Among various polymer membranes materials, Polyimide (PI) has excellent thermal and mechanical properties, good chemical stability and high gas transport property. Many researchers have studied gas transport property of polyimide membrane for gas separation. However, polymer membrane still have low performance compared with ceramic membrane and absorption process. Many researchers have been studied to complement this weak point, and can improve permeability of membranes by controlling diffusivity and solubility. Poly(ethylene glycol)(PEG), rubbery polymer, can improve solubility. The moieties with high fractional free volume (FFV) such as cardo fluorene and durene group can improve diffusivity. In this work, Diamines containing cardo fluorene and durene group were used to obtain polyimide having the high FFV. we synthesized PI-PEG copolymer to improve solubility. Finally, chemical structure, thermal property (thermal degradation and glass transition temperature) were investigated and PI-PEG copolymer membrane formed via immersion precipitation process and then membrane morphology was observed and gas transport property of PI-PEG membrane was investigated.

ET14.04.06

Hydrogen Production by Methane Decomposition Over Carbon Catalysts with Different Structures Dai Miyamoto¹, Haruki Nishii¹, Yoshito Umeda², Hiroaki Hamaguchi³, Masashi Suzuki³, Toru Harigai¹, Tsuyoshi Tanimoto¹, Hirofumi Takikawa¹ and Suda Yoshiyuki¹; ¹Electrical and Electronic Information Engineering, Toyohashi University of Technology, Toyohashi, Japan; ²Toho Cryogenics Co., Ltd, Nagoya, Japan; ³Aichi Center for Industry and Science Technology, Toyota, Japan.

Thermo-catalytic decomposition (TCD) of methane is an attractive hydrogen production process to mitigate CO₂ emissions commonly associated with the conventional processes (such as steam methane reforming). However, the problem of the process is catalyst deactivation by carbon deposition^[1]. The purpose of this study is to investigate the relationship between the catalysts structure and the catalytic activity of produced carbon during TCD of methane by using four types of carbon catalysts with different structures.

Four types of carbon catalysts were tested in the TCD of methane: activated carbon (AC), mesoporous carbon (MC), carbon black (CB), and carbon nanofiber (CNF). Experiments were carried out in a fixed-bed reactor using 1.7 g of the catalysts with space velocity of 360 h⁻¹, at a reaction temperature of 1173 K. The produced gas was analyzed by a hydrogen detector and gas chromatography. Carbon catalysts before and after the experiments were analyzed by Raman spectroscopic analysis. The methane conversion ratio was derived from the hydrogen concentration obtained by gas analysis.

Temporal change of methane conversion ratio of each catalyst is evaluated by the concentration ratio of produced hydrogen and methane. Methane conversion ratios of all the tested catalysts eventually reached about 25%. We also investigated the temporal change of the intensity ratio of the G band and

the D band in Raman spectrum (I_D/I_G) of the produced carbon. I_D/I_G is used to evaluate the degree of graphitization of carbonaceous materials [2]. After 600 min elapsed, I_D/I_G of the produced carbons of all the tested catalysts was about 1.5. Therefore, we found that the produced carbon shows the same activity and degree of graphitization regardless of the structure of catalysts. We also found that Raman spectroscopy is an effective method for evaluating initial catalytic activity for methane decomposition.

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SESSION ET14.05: CO₂ Sequestration and Utilization
Session Chairs: Chong Liu and Tao Wang
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 305

8:30 AM *ET14.05.01

The Solar Electrochemical Refinery—An Industrial View [Emanuela Negro](#); Shell, Amsterdam, Netherlands.

In the coming decades the share of renewable electricity in the energy mix will expand substantially in all parts of the world. This development is driven by rapid reductions in solar and wind energy costs. Continued reductions in the cost of these renewable sources depends in part on developing economical solutions to intermittency and on optimizing the mismatch between the location of energy production and consumption. Storing electricity in an energy carrier that is low cost, abundant, dense, 24/7/365 available, clean and safe would solve intermittency and distribution problems.

Shell New Energies Research & Technology has launched a Long Range Research (LRR) platform as part of a Technology Strategy Refresh consisting of programs with specific focus on investigating energy storage solutions for intermittency, solar fuels production as an alternative to fossil fuels, and alternative outlets for methane in a future low-carbon emissions world.

Solar fuels refer to synthetic energy-rich molecules made using low-cost solar energy, water and atmospheric carbon dioxide. A diesel-like solar fuel could be produced using a hybrid process consisting of photovoltaic power generation, water electrolysis, direct air CO₂ capture, Reverse Water Gas Shift to produce CO, followed by integrated Fischer-Tropsch fuels synthesis. Essentially these technologies are all available today. However, such an integrated process is not currently competitive (economically) with fuels refined from fossil hydrocarbon sources. The capex of required supply chains is too high and CO₂ emission penalties are not effective. The optimal geographic location for sufficient levels of low-cost solar electricity generation may not coincide with the location of sufficient point sources of carbon emissions required by a commercial scale solar fuels production facility. The viability of solar fuels depends on a continual decline in the cost of renewable power and on realizing disruptive performance improvements in direct air CO₂ capture and conversion technologies.

Electrochemical routes, such as Co-electrolysis of H₂O and CO₂ to CO, may offer a competitive alternative for CO₂ conversion compared to "standard" catalytic technologies, both in terms of CAPEX and OPEX.

An overview of Shell's current co-electrolysis program will be presented along with an industrial view of what targets needs to be improved to make the "solar e-refinery" concept a success. Some examples of current projects designed to achieve these targets will be presented.

9:00 AM ET14.05.02

E-Refinery—Towards the Sustainable Electro-Refining of Chemicals and Fuels from Renewable Resources [Wilson Smith](#); Delft University of Technology, Delft, Netherlands.

Electrification is a key enabler towards reducing CO₂ emission. The availability of renewable electrical energy does however not remove the demand for fuels, chemicals and other materials. In addition, the variability of nature calls for electricity storage to safeguard continuous electricity supply.

Electrosynthesis is a promising approach to electrify the manufacturing of fuels, chemicals and materials and to contribute to energy storage. Given the Dutch strategic position in the international chemical, renewable energy and transport sectors, TU Delft sees exciting opportunities to establish a national consortium taking the first steps towards industrialscale 'e-refinery' systems to convert electricity into molecular bonds. Flexible energy storage in the form of chemicals produced by using electrical energy offers prospects for the energy sector to deal with the growing challenge of demand versus supply mismatch. The large-scale production of synthetic fuels, for example for heavy long-distance transport and aviation, platform chemicals and other materials using electrical energy from renewable sources addresses sustainability demands and is a decisive step towards creating a circular economy. In this presentation, we explore the challenges that lie ahead, dividing them according to the three scales involved: the micro scale (Materials, Catalysts, Electrochemistry), the meso scale (Transport phenomena, Reactor Engineering & Process Intensification, Energy Technology & System Engineering) and the macro scale (Process and System Integration, Societal Embedding). We envision a national consortium and a long-term (10+ years) research and development programme to tackle these challenges, in line with the recent advice by the Electrochemical Conversion and Materials (ECCM) committee to the Dutch Top Sectors HTSM, Energy and Chemistry. TU Delft started the e-refinery initiative and is motivated to play a key role in such a national activity. Across all the disciplines involved, from fundamental research to societal implementation, TU Delft has the expertise to pioneer the topic of large scale electrosynthesis of chemicals and fuels from renewable feedstock. A systems integrated approach to CO₂ electroreduction will be given as an example of how process integration and intensification can provide relevant reaction conditions at the micro and nanoscale that differ significantly from current areas of academic research. Therefore, materials science and chemistry research can benefit from understanding the 'big picture', and lead to more rapid technological development.

9:15 AM ET14.05.03

Fe-Doped Carbon Spheres Architecture as a Catalyst for CO/CO₂ Methanation [Arturo Reza Ugalde](#), Hani E. Naguib, Pin Tsung Liao and Olivera Kesler; University of Toronto, Toronto, Ontario, Canada.

The CO₂ is one of the greenhouse gases with higher impact in the global warming. Although a natural cycle regulates the CO₂ concentration by the photosynthetic organism, the large-scale burning of fossil fuels has increased considerably the concentration in the atmosphere producing an unbalanced carbon cycle. Nowadays, the only solution available is the underground storage of the CO₂, however, this method is extremely expensive and require continuous monitoring. An alternative solution is the sequestration and utilization of the CO₂, where the greenhouse gas is captured and reduced into different products (mainly hydrocarbons), which then can be used to produce energy. With this system, the cycle of CO₂ can be completed reducing the environmental impact. Among the post-capture treatments of CO₂, the catalytic hydrogenation into methane is one of the most studied routes, nevertheless, the lack of a durable and cost-efficient catalyst is still a problem. This work presents the fabrication process (through nitration and

impregnation) of a Fe-doped carbon spheres architecture as the electrocatalyst for CO₂/CO methanation via hydrogenation. Through a thermodynamic analysis, we studied the degradation of carbon during the methanation process to ensure the longevity and stability of the carbon spheres. Furthermore, the selectivity and activation of the Fe and its transition into Fe²⁺ and Fe³⁺ were considered to guarantee the catalyst efficiency.

9:30 AM DISCUSSION TIME

9:45 AM BREAK

10:15 AM *ET14.05.04

C2CNT—The Inexpensive, Efficient Direct Transformation of Atmospheric or Emitted CO₂ to Valuable Carbon Nanotubes by Molten Electrolysis Stuart Licht; George Washington University, Washington, District of Columbia, United States.

“C2CNT” (CO₂ to carbon nanotube) is a Carbon XPRIZE technology for transforming CO₂ to the most valuable product.

An incentive to remove CO₂ is provided by a low energy, low cost, high yield conversion to valuable products such as carbon nanotubes. Displaying superior strength, conductivity, flexibility and durability, carbon nanotube (CNT) applications had been limited due to their cost intensive their synthesis. An inexpensive source of CNTs made from CO₂ will facilitate its adoption as an important societal resource for building, transportation, renewable energy, sporting and consumer electronics, while concurrently consuming CO₂. We present an inexpensive, high-yield and scale-able synthesis of CNTs.

A new chemistry for the effective capture of CO₂ and its high yield, low energy transformation is via dissolution in a molten carbonate electrolyte and electrolytic splitting to CNTs and O₂.¹⁻¹⁰ The CO₂ reactant is directly absorbed from air (without the need for pre-concentration), or can be used and removed from industrial emissions. CNTs are a compact, stable storage for the removal of anthropogenic CO₂.

We show that common metals act as CNT nucleation sites in molten media to efficiently drive high yield electrolytic conversion of CO₂ dissolved in molten carbonates to CNTs. The CNT structure is tuned by controlling the electrolysis conditions, such as nucleation sites, composition of the electrolyte, and the control of temperature and current density. Upward scalability of the process is demonstrated over several orders of magnitude.

Our goal is to transform CO₂ from a pollutant to a desired resource. Molten carbonate electrolysis production is significantly less expensive than contemporary CVD to produce CNTs, and uses CO₂ as the reactant. An inexpensive source of CNTs has demand as a preferred, lighter weight, stronger replacements to metals and plastics, which can provide a large market to mitigate anthropogenic CO₂.

C2CNT publications:

¹One-pot synthesis of carbon nanofibers from CO₂, *Nano Letters*, **15**, 6142 (2015).

²The minimum electrolytic energy needed to convert CO₂..., *J. Phys. Chem., C*, **119**, 23342 (2015).

³Carbon Nanotubes Produced from Ambient CO₂..., *ACS Central Science*, **2**, 162 (2015).

⁴Thermodynamic assessment of CO₂... transformation ... in a ... power plant, *Energy Cons./& Manag.*, **122**, 400 (2016).

⁵One-Pot Synthesis of Nanostructured Carbon Material from CO₂..., *Carbon*, **6**, 27760 (2016).

⁶Tracking airborne CO₂ mitigation and low cost transformation into valuable CNTs, *Scientific Reports*, **106**, 208 (2016).

⁷Co-Production of Cement and CNTs ..., *J. CO₂ Utilization*, **18**, 378 (2017).

⁸Data on ... CNTs made directly from CO₂ by molten electrolysis, *Data in Brief*, **14**, 593 (2017).

⁹Transformation of the greenhouse gas CO₂ by molten electrolysis into a wide controlled selection CNTs, *J. CO₂ Utilization*, **18**, 335 (2017).

¹⁰CNT Wools Made Directly from CO₂ by Molten Electrolysis, *Mat. Today Energy*, **5**, 230 (2017).

10:45 AM ET14.05.05

Selective Electrochemical CO₂ Reduction to CO on Ultrathin MXene Nanosheets Nuwan H. Attanayake¹, Akila C. Thenuwara¹, Babak Anasori¹, Yury Gogotsi² and Daniel R. Strongin¹; ¹Temple University, Philadelphia, Pennsylvania, United States; ²Material Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States.

Anthropogenic release of CO₂ is believed to be a leading cause of global climate change. An attractive proposed strategy to limit this change is to capture CO₂ after production and if possible to electrochemically convert it into value added chemicals using renewable energy. Research is presented that investigates the catalytic activity of Mo₂C and Ti₃C₂ MXenes towards the electrochemical CO₂ reduction reaction (CO₂RR) as a cheaper alternative to precious metals that are known to catalyze this reaction. The metallic nature, large surface area of the 2D nanosheets and the ability of these MXenes to spontaneously bind CO₂ are key factors that make them attractive materials for the CO₂RR. We report very high faradaic efficiencies, ~90% for the reduction of CO₂ to CO at low overpotentials, ~300 mV, in acetonitrile/ionic liquid electrolytes on Mo₂C MXene. Ti₃C₂ MXene shows ~65% FE at an overpotential of ~600 mV for the cathodic half reaction. The use of ionic liquid 1-ethyl-2-methylimidazolium tetrafluoroborate suppresses the competing H₂ evolution reaction and also acts as the electrolyte. High selectivity and high FE of CO₂ reduction to CO makes these MXenes, which are composed of earth abundant elements, an attractive non-precious metal electrocatalyst for the CO₂RR.

11:00 AM *ET14.05.06

Indirect Ocean Capture of Atmospheric Carbon Dioxide Matthew Eisaman; Stony Brook University, The State University of New York, Stony Brook, New York, United States.

Negative emissions technologies (NETs) are needed to limit the increase in average global temperature to less than 1.5 °C. In this talk, I will present the design, prototype performance characterization, and techno-economic analysis for a new negative emissions technology (NET) termed indirect ocean capture (IOC). IOC removes carbon dioxide gas from the atmosphere by leveraging both air-ocean gas exchange and the pH sensitivity of the ocean's carbonate buffer system. I will present the predicted net cost per ton of removed carbon dioxide for multiple scenarios, including co-location with desalination plants, and discuss the tradeoff between minimizing cost and maximizing impact. Finally, I will explain the results of a techno-economic sensitivity analysis to highlight the research and development areas that hold the most promise for future cost reduction.

11:30 AM DISCUSSION TIME

SESSION ET14.06: CO₂ Petrification
Session Chair: Matthew Eisaman
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 305

1:30 PM *ET14.06.01

CarbFix – Reducing Emissions by Rapidly Petrifying CO₂ in the Subsurface with Added Economic, Social and Economic Value [Edda S. Aradottir](#); Reykjavik Energy, Reykjavik, Israel.

Global emissions must be put on a permanent downward trend by 2020 if severe consequences of global warming are to be prevented. CarbFix involves capturing otherwise emitted CO₂, dissolving it in water and injecting it into basaltic geological formations. There, the CO₂ is turned into rock in less than two years and is thereby permanently removed from the atmosphere. The CarbFix team has developed the method from scratch over the past twelve years; moving from laboratory-scale and numerical simulations, through pilot-scale field injections, to stage-wise build-up of industrial-scale capture and injection. Innovative equipment and methods for capturing, injecting, and monitoring have been designed and built. The annual CO₂ emissions of Hellisheidi geothermal power plant, the home of CarbFix, were reduced by 34% since industrial scale CCS operations began in 2014 until 2017.

The CarbFix team, in collaboration with the Swiss company Climeworks, is currently running a pilot demonstration of a conjugated direct air capture and subsurface CO₂ mineral storage through support of the EU's H2020 framework program. Large worldwide potential lies in joint application of direct capture of CO₂ from ambient air and CCS technologies in favorable rock formations, as this allows for rapid, permanent removal of CO₂ from the atmosphere.

The CarbFix method provides a safe and efficient alternative to conventional CCS methods in which CO₂ is stored in less reactive rock formations as a supercritical phase. It only takes two years to petrify the injected CO₂ in CarbFix, whereas mineralization happens on the scale of hundreds to thousands of years in conventional CCS. Risks of leaks are also eradicated in CarbFix as the injected phase is denser than the surrounding groundwater and therefore sinks as opposed to rising to the surface through buoyancy forces.

CarbFix checks all three pillars for sustainability, providing added environmental, social and economic value. The method imitates and accelerates processes already happening in nature and is, as such, environmentally benign. Added social value from CarbFix e.g. involves dissemination of knowledge, training of next generation students, on-site access to facilities, and raised awareness of available climate solutions in mass media. Added economic value can be achieved by using the method to co-capture and mineralize other environmentally important gases. At Hellisheidi power plant, the method was used for co-capturing CO₂ and H₂S. Significant savings on both capital and operational expenses were achieved compared to conventional gas removal methods. The value of those savings is over US \$100 million for this single power plant.

2:00 PM ET14.06.02

Controlled Synthesis of MgO with Diverse Basic Sites and Its CO₂ Capture Mechanism Under Different Adsorption Conditions [Wanlin Gao](#) and [Qiang Wang](#); College of Environmental Science and Engineering, Beijing Forestry University, Beijing, China.

Mesoporous MgO adsorbents with diverse basic sites were prepared via a urea hydrolysis synthesis method for CO₂ capture. With elevated hydrolysis temperatures, the phase transition process made great contributions to the morphological changes of the precursor architectures. In situ DRIFTS analysis demonstrated that various carbonate surface species including bicarbonate, bidentate, and unidentate carbonates were formed on the obtained MgO during interaction with CO₂. Furthermore, the main component of adsorbed CO₂ surface species swings from bicarbonate to bidentate and unidentate carbonates with increase of adsorption temperature. The highest CO₂ uptake of 1.22–1.99 mmol g⁻¹ was attained for MgO sample at the lowest calcination temperature in a wide temperature range of 60–300 °C. High specific surface area (372.0 m² g⁻¹), large pore volume (0.38 cm³ g⁻¹) as well as diverse basic sites of the synthesized MgO make it an eligible candidate for CO₂ capture, with a nearly 20-fold enhancement of the commercialized light MgO. Additionally, the results of CO₂ uptake studied under diluted and wet (H₂O containing) CO₂ conditions for the as-prepared MgO adsorbent also suggested good prospect in practical applications.

2:15 PM ET14.06.03

Technoeconomics of Electrochemical Carbon Dioxide Conversion on the 100-kW Scale [Stafford W. Sheehan](#); Catalytic Innovations, Adamsville, Rhode Island, United States.

Key discoveries in the last century have demonstrated the breadth of products that could be made electrochemically from carbon dioxide, including carbon monoxide, formic acid, methanol, ethylene, and others. We conducted an economic assessment of both beachhead market opportunities and bulk commodity chemicals that use each of these compounds as feedstock material, with a focus on value propositions unique to products made from carbon dioxide (on-site production, cost tied to electricity prices, and use of renewable feedstock). Our findings identify pathways to implementation of electrochemical carbon dioxide conversion technologies across diverse industries that have been under-explored until now, and we identify technological roadblocks that remain for economically viable implementation.

2:30 PM DISCUSSION TIME

2:45 PM BREAK

SESSION ET14.07: Materials Science and CCUS—So What?
Session Chairs: Christopher Jones and Klaus Lackner

Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 305

3:15 PM ET14.07.01

Materials Science Facing Global Warming—So What? Jenny G. Vitillo; University of Minnesota, Minneapolis, Minnesota, United States.

More than the cost. Carbon capture, as any technology, is not free of costs, as evaluated in different ways: money, energy and carbon dioxide production itself. Unlike others, it is a technology that does not have a one-to-one correspondence with the person or the group paying for it, being the benefits of its application spread on a global scale. This is a problem because it makes less appealing to invest in it, unless driven by humanitarian or environmental interests. Nevertheless, it is clear from purely economical projections that investing in technologies aimed to the mitigation of the global temperature rise to 1.5 °C will allow significantly saving with respect to the cost to pay for the impact of climate change in terms of money.¹ And if extreme weather events are considered the cost to be paid will be not be restricted only to that.²

Several studies will be presented during the symposium giving different perspectives on the solutions envisaged for the reduction of the CO₂ concentration in the atmosphere and its possible use.

This presentation will summarize and compare the results presented along the symposium, trying to give a more general background to the conclusions made. A discussion involving the speakers, the organisers and the audience will be stimulated trying to understand which among the different technologies are the most mature working tools to face the global warming. The possibility to size down a direct air capture technology and the benefits/drawbacks of this will be envisaged, in order to evaluate if the large sensitization of the general public on this theme can be exploited through its direct involvement (person-sized DAC devices) or indirect involvement (carbon tax or carbon credits) and then centralized carbon capture centers are more viable solutions.

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3:45 PM DISCUSSION TIME

4:00 PM CLOSING REMARKS