

# Research Portal

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## Application - Research Tools and Instruments

### Identification

#### Applicant

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**Family Name:** Dinh

**First Name:** Cao Thang

**Middle Names:**

**Current Position:** Assistant professor

#### Administering Organization

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**Organization** Queen's University

**Department/Division** Chemical Engineering

#### Application

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**Application Title** Metal Cluster Catalysts for Electrochemical Carbon Dioxide Conversion

**Language of the Application**  English  French

**Suggested Evaluation Group** 1511 Materials and Chemical Engineering

**Hours per month to be devoted to the research/activity, or use of equipment or facility** 40

### Summary of Proposal

#### Summary

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Limiting global warming to 2°C above pre-industrial levels would imply reducing greenhouse gas emission

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by 80% of the 1990 level by 2050 and a net-zero emission by 2100. Achieving this climate target means replacing traditional fossil fuels with renewable energy and accelerating carbon dioxide (CO<sub>2</sub>) capture and utilization technologies. Renewable energies, such as wind and solar, are very abundant and, taken together, could exceed today's global electricity demand > 10,000 times. However, the intrinsic intermittency of solar or wind resources limits their further deployment as replacements of fossil fuels.

Electrochemical CO<sub>2</sub> conversion (ECC) to fuels and chemicals provides compelling solution to both the CO<sub>2</sub> emission and renewable energy storage problems. The ECC to fuels enables renewable energy storage in the form of chemical energy. The most critical component in ECC system is the catalyst where CO<sub>2</sub> is converted to desired products. In this research program, we will develop next-generation catalysts based on metal clusters that are active, selective, and stable for converting CO<sub>2</sub> into fuels and chemicals. To achieve this goal, it is essential to understand the correlation between the surface structural characteristics and the catalytic performance of the catalysts.

We are requesting a chemi- and physisorption analyzer that will provide an in-depth understanding of the surface structure and chemistry of ECC catalysts. Specifically, we will use this gas sorption analyzer to determine the specific surface area and porous structure, the two important factors of an ECC catalyst. We will also employ this instrument to characterize the nature of the metal active sites for CO<sub>2</sub> reduction using chemisorption and temperature-programmed techniques. By combining this tool with our electrochemical testing systems, we will be able to identify key surface physical and chemical features that govern the performance of the ECC catalyst. From the insights gained using the chemi- and physisorption analyzer, we will be able to develop more active, selective, and stable catalysts for CO<sub>2</sub> conversion.

Advancing ECC technology will position Canada as the leader in developing clean technologies that provide solutions to the global problem of climate change. The specialized gas sorption analyzer will also contribute to the training of next generation of HQP on a versatile state of the art research tool. We anticipate that over the next five years more than 50 HQP will directly benefit from using this tool.

## **Second Official Language Translation**

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## Proposed Expenditures

	Year 1 Amount
<b>Equipment or facility</b>	
Purchase or rental	\$154,340
<b>Subtotal</b>	\$154,340
<b>Other (specify)</b>	
	\$0
<b>Subtotal</b>	\$0
<b>TOTAL PROPOSED EXPENDITURES</b>	\$154,340
<b>Total Cash Contribution from Industry (if applicable)</b>	\$0
<b>Total Cash Contribution from University (if applicable)</b>	\$0
<b>Total Cash Contribution from Other Sources (if applicable)</b>	\$4,340
<b>TOTAL AMOUNT REQUESTED FROM NSERC</b>	\$150,000

## Activity Details

### Certification Requirements

Does the proposed research involve humans as research participants?

Yes  No

Does the proposed research involve animals?

Yes  No

Does the proposed research involve human pluripotent stem cells?

Yes  No

Does the proposed research involve hazardous substances?

Yes  No

### Impact Assessment

Will any phase of the proposed research take place outdoors?

Yes  No

### Research Subject Codes

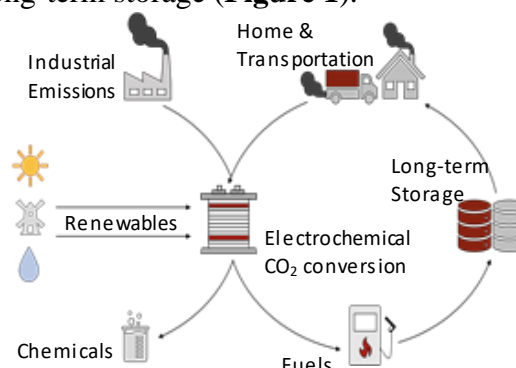
## Metal Cluster Catalysts for Electrochemical Carbon Dioxide Conversion

Reducing carbon dioxide (CO<sub>2</sub>) emissions is widely acknowledged as a major priority to limit global warming. Electrochemical conversion of CO<sub>2</sub> into fuels and chemicals powered by renewable energies such as wind and solar provides a promising solution to achieving this goal. This NSERC-RTI proposal aims to develop next-generation catalysts for electrochemical CO<sub>2</sub> conversion (ECC). We are requesting a chemi- and physisorption analyzer, which provides an in-depth understanding of the surface structure and surface chemistry of catalytic materials - the fundamental insights for the rational design of high-performance ECC catalysts.

### 1. Need and Urgency and Suitability of Equipment

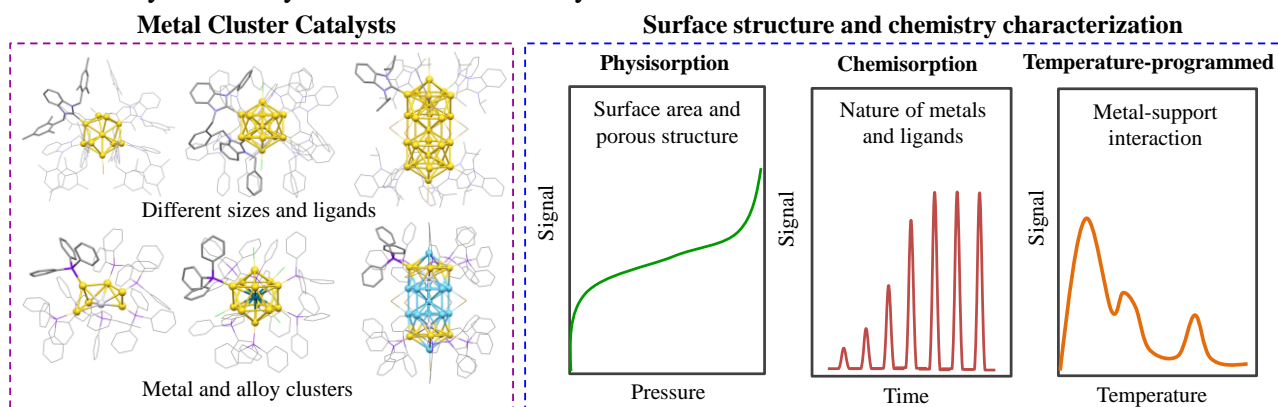
**Research program.** The conversion of CO<sub>2</sub> to fuels and chemicals powered by renewable electricity can simultaneously address the CO<sub>2</sub> emission and the intermittency issue of renewable energy sources [1]. The carbon-neutral fuels produced from CO<sub>2</sub> captured from air or industrial emissions can be readily integrated into current infrastructures for convenient transportation and long-term storage (**Figure 1**).

In ECC systems, CO<sub>2</sub> is reduced to chemicals at the surface of a catalyst. The critical features of an ECC catalyst are the nature of the active sites and their immediate environment, both of which govern how the CO<sub>2</sub> molecule and reaction intermediates interact with the active sites of the catalyst. These interactions determine the reaction pathways, and therefore, the overall CO<sub>2</sub> conversion efficiency. Currently, ECC catalysts are designed mainly based on metallic nanostructures with various morphologies [2]. In these catalysts, control over the reaction pathways remains challenging because they exhibit different types of catalytic sites and local environments on a single catalyst particle.



**Figure 1.** Closing carbon cycle with electrochemical CO<sub>2</sub> conversion.

Our research program focuses on developing next-generation ECC catalysts based on metal clusters with high stability and well-defined structures. Metal clusters with a tunable number of metal atoms, stable surface ligands, and specific nature of the metals used represent an exciting class of material for efficient ECC (**Figure 2**). Because the size of the metal clusters is ultrasmall (1-5 nm), the unsaturated coordination environment effectively alters the interaction of CO<sub>2</sub> molecules and reaction intermediates with the active sites. The ligands on the surface of the metal clusters can be modified to control the number of active metal atoms exposed. This will allow us to tune the catalytic activity of metal clusters at the atomic level. Controlling the particle size and the identity of the metal atoms offer another powerful tool to fine tune the intrinsic catalytic activity of metal cluster catalysts.



**Figure 2.** Schematic illustration of metal clusters with various sizes, ligands and compositions (left); and surface characterization of the catalysts using chemi- and physisorption analyzer (right).

**Importance of the equipment.** There have been significant advances in ECC catalyst design over the last decade. Particularly, Cu-based catalysts with various morphologies and compositions have been developed for producing valuable hydrocarbon products from CO<sub>2</sub> (Dinh *et al.*, *Science* 2018, 360, 783; de Arquer *et al.*, *Science* 2020, 367, 661; Miao *et al.*, *Nature* 2020, 581, 178). However, these nanostructured catalysts still exhibit insufficient activity and selectivity for practical ECC application. Thus, there is an urgent quest for developing efficient catalysts for CO<sub>2</sub> conversion to desired fuels and chemicals. Recently, we reported that metal clusters can be used as selective catalysts for CO<sub>2</sub> conversion to carbon monoxide (Narouz, Dinh, Crudden *et al.*, *Nature Chemistry* 2019, 11, 419). While the results obtained were promising, further insights into the structure-performance properties of metal cluster catalysts are critical for rational design of highly efficiency ECC catalysts. The requested chemi- and physisorption analyzer will provide us with these key insights, enabling us to develop next-generation ECC catalysts. Combining the requested tool with the ECC testing systems available in our lab, will enable us to understand and optimize the link between the nanocluster surface structure and its catalytic activity. We will also identify the structural changes of the catalysts after the reaction. These insights will provide guidance for the design of more active, selective, and stable ECC catalysts - the bottleneck to the development of ECC technology.

While the surface area of the catalyst can be obtained from a physisorption analyzer, details about the nature of active sites and surface chemistry of metal cluster catalysts will require a sophisticated method such as X-ray absorption spectroscopy. This characterization can be done only at Canadian Light Source. Given that the applicants currently have no or limited access to either of these above techniques, a chemi- and physisorption analyzer represents a highly cost-effective way for the applicants to advance ECC technology.

**Impact of a delay in the acquisition of equipment.** The research to advance ECC technology described in this proposal will not be possible without the requested chemi- and physisorption analyzer. While some elements of research, such as specific surface area measurement, would continue via applicants' collaborations, those requiring nature of active sites and ligands, and metal-support interaction characterization would not. A delay in obtaining the equipment will significantly restrict our research capability in this program.

Dr. Dinh and Dr. Crudden have established collaboration on studying metal clusters for CO<sub>2</sub> conversion [3]. Our recent unpublished results show that the ligands on the surface of Au clusters dramatically affect their catalytic properties. We also found that doping Pt atoms into Au clusters significantly changes CO<sub>2</sub> conversion performance. The requested instrument will provide critical insights into how Pt doping and tuning the surface ligands change CO<sub>2</sub> reduction. Dr. Dinh has also established several collaborations with other researchers at Queen's university and other institutions directed towards developing efficient ECC catalysts. For example, he is working with Dr. Dominik Barz on exploring graphene-based catalysts for CO<sub>2</sub> conversion and hydrogen production (funded by NSERC Alliance). The requested gas sorption analyzer is a powerful tool for characterizing physical and chemical properties of graphene surface. Thus, a delay in acquiring the requested instrument will severely affect collaborations in place. It also reduces the impact of the research and the ability to train students on this important piece of instrumentation.

**Availability of similar equipment.** There is currently a physisorption analyzer available at Queen's that allows measurement of specific surface area. This instrument is heavily used. In addition, it lacks the critical ability to perform chemisorption and temperature-programmed measurements that are crucial for us to analyze the surface chemistry of active metal clusters. These characterizations are critical for developing highly active and selective ECC catalysts based on metal clusters with well-defined structures.

**Utilization of the equipment by the applicants and other users.** Given a very high demand for the requested equipment from the applicant and other main users, the equipment will be located at the shared facility center of the Department of Chemical Engineering. It will, therefore, be of immediate use to all our HQP, not only from the applicants' groups but also from various groups at the Department and across Queen's campus. HQP working on developing next-generation ECC catalysts will greatly benefit from

this innovative technology. The synthesized catalysts can be immediately characterized to understand their surface properties, confirming the formation of the desired catalytic structure. These catalysts will also be characterized after use in the ECC reaction to understand the surface changes and degradation mechanism of the catalysts. With these analyses, HQP will be able to correlate the catalyst's surface characteristics with its catalytic performance. From there, they will be able to efficiently and effectively adjust the synthesis conditions to design better ECC catalysts.

The equipment will also be available for our colleagues at Queen's University working on various materials which require a delicate tool for surface structure and chemistry characterization. These research programs include developing catalysts for hydrogen production (Brant Peppley, Chemical Engineering); 2D electronic devices (Shideh Kabiri Ameri, Electrical and Computer Engineering); electrodes for sensors (Zhe She, Chemistry, and Carlos Escobedo, Chemical Engineering), electrodes for battery application (Dominik Barz, Chemical Engineering), graphene-based nanocomposites (Marianna Kontopoulou, Chemical Engineering), metal oxide catalysts for CO<sub>2</sub> conversion (Paul Duchesne, Chemistry), surface metal oxidation (Suraj Persaud, Mechanical and Material Engineering). The capacity and availability of the instrument will also be posted on Department and personal websites so that it can attract diverse potential users throughout Queen's campus and industries.

## 2. Feasibility and Impact

**Plan to use the equipment.** With this instrument, we will be able to characterize the detailed surface structure and surface chemistry of a variety of metal cluster catalysts. First, we will measure the specific surface area and pore structure of metal clusters supported on carbon via physisorption (**Figure 2**). The specific surface area and pore structure are important characteristics of ECC catalysts, especially for ultrasmall metal clusters supported on a porous substrate. Second, this instrument allows us to determine the reactivity of the exposed metal atoms, which are expected to be the active sites, from chemisorption measurements (**Figure 2**). These analyses provide insights into the nature of the active sites of the catalysts and the effect of surface ligands on the catalytic structure of the clusters. Finally, we will characterize the interaction of the metal clusters with the support and the stability of the surface ligands by performing temperature-programmed reduction and oxidation. The metal-support interactions and stability of the ligands directly affect both the activity and stability of the catalysts. These temperature-programmed measurements will provide a guide to the modification of the support for optimizing ECC performance.

In this collaborative research program, metal clusters will be synthesized by Dr. Crudden's group. The clusters will be immobilized on a conductive carbon support (graphene, graphite and carbon nanotube) and their performance will be evaluated by Dinh's group using gas phase CO<sub>2</sub> conversion systems. Characterization of catalysts using chemi- and physisorption apparatus will be performed at the Department of Chemical Engineering by students and PDFs from both groups.

**Relevant experience of applicants.** Dr. Cao Thang Dinh has been developing technologies for chemical and fuel production from renewable energies since 2008. His research focuses on designing efficient catalysts and electrodes for CO<sub>2</sub> conversion. He has co-invented 4 patents and has published over 80 papers in impactful journals, including *Science*, *Nature*, *Nature Energy*, *Nature Chemistry* and *Nature Catalysis*. Notably, Dr. Dinh pioneered the design of a new gas diffusion electrode configuration for stable CO<sub>2</sub> conversion to ethylene (Dinh *et al.*, *Science* 2018, 360, 783). In 2019, Dr. Dinh and his colleagues designed a new catalyst layer structure for ECC to ethylene and ethanol at a current density beyond 1 A/cm<sup>2</sup>, which is on par with the best mature water electrolyzer technology for hydrogen production (Pelayo\*, Dinh\* *et al.* *Science* 2020, 367, 661). Dr. Dinh has extensive experience employing gas sorption analyzers to characterize the pore structure and surface area of nanostructured electrocatalysts and photocatalysts. Dr. Cathleen Crudden is Tier 1 Canada Research Chair in metal organic chemistry. She has been working on catalysis for over 25 years and is a recognized expert in NHC-protected metal clusters. She has extensive experience in characterizing the surface properties and porous structures of heterogenous catalysts using

gas sorption apparatus from her work with mesoporous silicates. The requested instrument will be located at the shared facility of the Department of Chemical Engineering and will be managed by Dr. Ying Zhang - the technician of the Department. Dr. Zhang has more than 10 years of experience working with gas sorption equipment. HQP working with the requested instrument will be trained directly by Dr. Zhang.

***Rationale of the team composition.*** We have brought together a team of applicants and users from multiple disciplines, including Chemical Engineering, Chemistry, Electrical and Computer Engineering, and Mechanical and Material Engineering. The team is made up of both early career and established researchers, and those from equity seeking groups (i.e., women and members of the BIPOC community). The success of our teams is a direct result of our implementation of EDI best practices. As leaders, the faculty and staff strive to be positive role models and mentors to all HQP while considering EDI at each step in the research process from study design to knowledge mobilization.

### **3. Importance of requested equipment in training HQP**

***Quality and extent of the training.*** Fundamental breakthroughs on developing new materials (e.g., metal clusters) for efficient CO<sub>2</sub> conversion are often published in very high impact journals, which will benefit the career of HQP tremendously. Since the chemi- and physisorption analyzer can be used to characterize multiple types of CO<sub>2</sub> reduction catalysts, all HQP working on developing ECC catalysts (7 current HQP in Dinh's group) will be trained on using this equipment for catalyst characterization. It is anticipated that this equipment will be directly used by over 20 HQP working on ECC technology in the first 5 years. About 5 HQP working on metal clusters for catalysis application in Crudden's group will also work with the requested instrument. Because of the high demand for this tool, we anticipate direct usage by another over 25 HQP from our collaborators at Queen's University in the first 5 years

***Opportunity for hands-on training.*** HQP working on the synthesis of metal clusters will receive hands-on experience on using various wet-chemistry synthetic techniques. HQP working on ECC testing will gain trainings on using electrochemical cells as well as multiple chemical analytic instruments, including gas chromatography and nuclear magnetic resonance spectroscopy. Regarding the gas sorption analyzer, all HQP will receive hands-on training directly from our department lab manager on various skills, including (i) safely handling of liquid nitrogen (for physisorption) and reactive gases (for chemisorption); (ii) using cutting edge experimental methods and adsorption/desorption models to understand the surface physicochemical properties of solid materials; and (iii) training in advanced data processing.

***Potential to provide marketable skills.*** Gas sorption is one of the most widely used techniques for characterizing surface properties of solid adsorbents and catalysts in chemical industries. The fundamental knowledge and hands-on skills that HQP will acquire when working with the requested chemi- and physisorption analyzer will be a great asset for them in future academic or industrial placements.

***Equity, diversity, and inclusion in the training of HQP.*** We will strive to identify and remove any barriers preventing EDI in the training of HQP in this research program. For the chemi- and physisorption analyzer users, each member will be trained individually based on their backgrounds and previous experience with this characterization technique. New users will also work alongside our lab manager until they can use the instrument independently and efficiently. An online booking system for this gas sorption analyzer will be made available so that all members have equal opportunities for equipment access and use them at flexible times. This will help accommodate the schedules of HQP with school-age children, caregiver responsibilities, or those who require time off for cultural or religious activities. The setup of the equipment, including its physical location (height and position) as well as supporting gas systems, will be carefully considered to accommodate users with various physical sizes and strengths.

#### **References:**

- [1] P. De Luna et al., *Science* **2019**, *364*, eaav3506.
- [2] T. N. Nguyen, C. T. Dinh, *Chemical Society Reviews* **2020**, *49*, 7488-7504
- [3] M. R. Narouz et al., *Nature Chemistry* **2019**, *11*, 419-425.

**BUDGET JUSTIFICATION**

The equipment requested in this RTI grant is pivotal to achieve the development of next-generation electrochemical CO<sub>2</sub> conversion catalysts. The tool below was carefully selected based on its specifications, which meets the essential requirements of the proposed research program. This research program does not have any financial overlap with other funding sources.

Our characterization tool includes a chemi- and physisorption analyzer Autosorb iQ-C-MP. The total cost of the instrument is \$154,340.46 (table below). ***\$150,000.00 are requested from the RTI Grant program; Dr. Dinh's Research Initiation Grant will supply the balance.***

Item	Quantity	Cost per unit in original currency (CAD)	Exchange rate	Total cost in Canadian dollars
Autosorb iQ-C-MP	01	149,251.00	NA	149,251.00
Subtotal:				149,251.00
Institutional tax rate (%):				3.41
Total tax:				5,089.46
Total cost:				154,340.46
Total confirmed from other source(s):				4,340.46
<b>Total requested from NSERC:</b>				<b>150,000.00</b>

Quantachrome Instruments (Acquired by Anton Paar in 2018) is a leading company in laboratory material characterization instrumentation for analyzing porous materials and powders. The Autosorb iQ-C-MP chemi- and physisorption analyzer is the model with a combined chemisorption-physisorption that significantly reduces the required bench space. Besides the physisorption function that allows measuring the surface area and different pore structures of the catalysts, it features built-in degassing stations and a built-in thermal conductivity detector for automated flow chemisorption methods. This feature enables the measurement of monolayer gas uptake on active metal areas of heterogeneous catalysts. Thus, the distribution and exposure of metal active sites in metal clusters can be analyzed. The temperature-programmed methods, such as temperature-programmed reduction and oxidation, integrated in the instrument can be used to determine the strength of metal-support interaction, a property that significantly affects the catalytic performance of ECC catalysts.

We have received another quotation from Micrometrics for a 3Flex Multiport chemi- and physisorption analyzer. While this instrument has similar functionalities compared to the Autosorb iQ-C-MP, its price is much higher, at \$209,936.00 CAD.

**Relationship to other support**

Conceptual and budgetary relationships between the current grant application and the research supports that are currently being held or applied for from the PI are described below.

PI: Cao Thang Dinh (currently being held grants)

1. Sponsor: **Queen's University – Research Initiation Grant**; Participants: Dinh (PI); Title: *Electrochemical CO<sub>2</sub> conversion*; 2019-2025; Total- \$200,000.  
This is a Research Initiation Grant from Queen's University to support Dr. Dinh as a new Faculty member. It can be used for supporting students, buying lab equipment, and paying costs related to user fees, materials, and supplies. This grant will mainly be used to buy equipment for the synthesis of the catalysts. ***An amount of \$4,340.46 from this fund will be used for the purchase of the requested equipment.***
2. Sponsor: **NSERC Discovery Grant and NSERC- Discovery Launch Supplement**; Participants: Dinh (PI); Title: *Electrode Engineering for Carbon Dioxide Electroreduction to Fuels and Chemicals*; 2020-2025; Total - \$177,500.



This operating grant supports research on the development of catalysts and electrode for electrochemical CO<sub>2</sub> conversion. The requested instrument for characterizing CO<sub>2</sub> conversion catalysts will significantly benefit this research program. There is no budgetary overlap.

3. Sponsor: **Canada Foundation for Innovation - John R. Evans Leaders Fund (CFI-JELF); Ontario Research Fund- Small Infrastructure Fund (ORF-SIF)**; Participants: Dinh (PI); Title: *Electrochemical CO<sub>2</sub> Conversion to Fuels and Chemicals*; 2021-2026; Total - \$250,000.

These grants support additional infrastructure for the applicant to carry out research in electrochemical CO<sub>2</sub> conversion technology. Specifically, these grants are used to purchase a thermal evaporator for catalyst preparation and an advanced system for electrochemical CO<sub>2</sub> conversion testing. The requested instrument for catalyst characterization will be combined catalyst synthesis and testing facilities to advance electrochemical CO<sub>2</sub> conversion technology. There is no budgetary overlap.

4. Sponsor: **NSERC- Alliance Grants** – Germany – hydrogen technologies; Participants: Barz (PI) with Dinh and Peppley (co-applicants); Title: *A road map to the development of the next generation of efficient water electrolyzers for the production of green H<sub>2</sub> from renewable power (RoadtoGreenH2)*; 2021-2022; Total - \$50,000.

This operating grant supports research on the development of hydrogen production catalysts based on metal supported on carbon. The requested instrument will enable characterizing highly efficient catalysts for hydrogen production. Thus, it will be of great importance to this project. There is no budgetary overlap.

5. Sponsor: **Queen's University, Faculty of Engineering and Applied Science – Dean's Research Funds**; Participants: Yang (PI) with Dinh (co-PI); Title: *Electro-bio Hybrid System for Sustainable Fuel and Chemical Production*; 2020-2022; Total - \$63,000.

This fund can be used to support HQP working on developing catalysts for CO<sub>2</sub> conversion to acetate which is coupled with a biological process. The requested instrument will allow characterizing CO<sub>2</sub>-to-acetate catalysts which will lead to the development of more efficient CO<sub>2</sub> conversion to acetate. There is no budgetary overlap.

Co-applicant: Cathleen Crudden (currently being held grants):

1. Sponsor: **New Frontiers Research Fund–Transformation 2020**; Participants: Crudden (PI), with 13 others; Title: *Protection of Metallic Surfaces from Bulk to Nano Through Molecular-level Innovation* 2021–2027, Level of Funding - \$4,000,000/year.

The aim of this project is to investigate the ability of NHCs in a variety of applications, including protecting metals and alloys corrosion, enabling patterning in the manufacture of semiconductors, and functionalizing metal nanoparticles for use in biomedical applications including precision radiation therapy, targeted chemotherapy and tumor imaging. This grant application focuses heavily on surface chemistry and applications and has no catalytic applications described.

2. Sponsor: **Semiconductor Research Corporation**; Participants: Crudden (PI), with Barry, S. and Ragona, P. (co-applicants); Title: *Area selective ALD using next-generation organic surfactants* 2021-2023, Level of Funding - \$90,000 US/year.

The aim of this project is to explore the use of NHCs to block and protect the surfaces of metals of interest to the semiconductor industry such as Ru, Cu and Mo, in area-selective atomic layer deposition (ALD) processes. There is no overlap with the current application.

3. Sponsor: **NSERC–Discovery Grant**; Participants: Crudden (PI); Title: *Nanoclusters, nanoparticles, and surfaces: Bridging the gap between homogeneous and heterogeneous catalysis*; 2021-2027, Level of Funding - \$126,000/year.

This research program centres around our group's discovery of the ability of carbon-based ligands called N-heterocyclic carbenes to form strong bonds to metal surfaces. This proposal describes the extension of this work to other metals and other nanostructures. This grant focuses on the understanding

of organic on metal films, and so will loosely inform the current grant, but there is no functional overlap since catalytic CO<sub>2</sub> chemistry was not described.

4. Sponsor: **New Frontiers Research Fund–Exploration**; Participants: Crudden (PI) with J. Hein (UBC, co-PI); Title: *Machine Learning Approach to Accelerated Nanomaterials Synthesis and Property Optimization*; 2020-2021, Level of Funding – \$125,000/year.

The aim of this project is to employ machine learning algorithms and robotics systems in the Hein lab at UBC to optimize nanocluster synthesis for properties rather than structure. In this case, we will optimize for stability and yield, and for photophysical properties, specifically looking for a red shift in adsorption, moving the adsorption frequency to closer to the near-IR, which is important for biological imaging applications. This approach will allow for complex multi-parameter searches that would be difficult or impossible in a regular lab. This project is targeted to developing the ML concept as well as improved nanocluster syntheses and properties. There is limited overlap with the current project, since catalysis is not the focus, but the work will help in terms of leading to new nanocluster syntheses.

5. Sponsor: **NSERC–CRD program**; Participants: Barry, S (PI, Carleton), with Ragogna and Crudden (co-applicants); Title: *Molecular Layer Deposition (MLD) of CapturePhos – A barriers for flexible electronics*; 2020-2022, Level of Funding – \$206,400 Total

This project, collaborative with chemical company Solvay, is focused on the preparation of cross-linkable molecules that can protect surfaces during molecular layer deposition. Our contribution will be the design of NHCs that can functionalize metal surfaces and then serve as a point for the formation of protective polymeric coatings. There is no overlap with the current application.

6. Sponsor: **World Premier Research Institute, Japan Society for Promotion of Science and Nagoya University**; Participants: Itami, (PI), with Crudden and 8 others; Title: *Institute of Transformative BioMolecules*; 2013-2022, Level of Funding - ca. \$300,000/year (to be spent exclusively in Japan).

This project aims to design novel organic structures, prepared via catalysis, and study their interaction with plant and animal species as a collaborative effort between synthetic chemists and plant/animal biologists. Crudden is one of three international PIs that are part of this institute. All funds are to be spent in Japan at the research institute. The funds allocated to my lab are in support of one Assistant Professor to run the lab in my absence, two postdoctoral fellows and my own travel. We carry out some nanoparticle and nanocluster work in Japan as relevant to biological applications, and synthetic work targeted to plant and animal biology. Federal funding for this position will end in 2022, and the institute will continue to enable overseas PIs to carry out research, but without allocated funding for postdoctoral fellows. There is limited conceptual overlap with the current application, and zero financial overlap.

7. Sponsor: **Queen's University Wicked Ideas Fund**; Participants: Stamplecoskie (PI) with Crudden, (co-applicant); Title: *Immortal Solar Cells Based on Metal Nanoclusters*; 2020, Total - \$75,000.

This research focuses on the use of metal nanoclusters in regenerable solar cells, with the plan being to employ thiol-stabilized nanoclusters in metal-cluster-sensitized solar cells (MCSSC). We will take advantage of the kinetic lability of thiol-stabilized metal clusters to enable regeneration of the clusters, and will determine whether this same feature can be employed in NHC-stabilized clusters and mixed thiol/NHC clusters. There is no overlap with the current application.

8. Sponsor: **NSERC CREATE program**; Participants: Fraser, J (PI) with Crudden and 9 others (co-applicants); Title: *Materials for Advanced Photonics and Sensing*; 2018-2024, Total - \$1,600,000.

This program focuses on the use of materials for photonics, and our involvement is limited to the study of the photophysical properties of NHC-stabilized Au nanoclusters. This grant supports the partial salary of 1-2 graduate students in my research group. There is no conceptual overlap with the current application and no financial overlap.