Chem4Energy Annual Conference
Materials and Processes for a Sustainable Energy Future
Monday 7 – Friday 11 April 2025

Conference Programme (may be subject to amendment)

Wednesday 9 April 2025

08:50 – 09:00	*Chair's comments*	*Professor Phuti Ngoepe, University of Limpopo, South Africa*
09:00 – 09:45	**Keynote** The development of advanced fuel cell supports with improved cathode durability	**Dr Thelma Ngwenya, Mintek, South Africa**
09:45 – 10:10	CO_2 sorption studies of two isostructural Co(II) and Zn(II) mixed ligand metal organic frameworks containing substituted diimide ligands	Dr Eustina Batisai, University of Venda, South Africa
10:10 – 10:25	Highly photocatalytic Cu-doped TiO_2 thin films fabricated by the aqueous spray method	Klaudia Mwatile, University of Namibia
10:25 – 10:40	Experimental investigation on electrical discharges as an ignition source for Ammonia/Hydrogen/Air mixtures	Ndapanda Musole, University of Namibia
10:40 – 11:10	*Refreshment break*	
11:10 – 11:35	Computational modelling of carbon dioxide sequestration by zeolites or cerium dioxide	Professor Georgi N. Vayssilov, University of Sofia, Bulgaria
11:35 – 12:00	The role of Cu_5Pd cluster during CO_2 hydrogenation on ZnO (010) surface	Dr Tshegofatso Michael Phaahla, University of Limpopo, South Africa
12:00 – 12:15	Photocatalytic activities of aluminium-doped zinc oxide thin films via aqueous spray method	Wilka Titus, University of Namibia
12:15 – 13:25	*Lunch*	
13:25 – 13:30	*Chair's comments*	*Professor Likius Daniel, University of Namibia, Namibia*
13:30 – 14:15	**Keynote** Energetics and chemistry at the reactive electrocatalyst-liquid interface	**Professor Jan-Philipp Hofmann, Technical University of Darmstadt, Germany**
14:15 – 14:40	Alkaline water electrolysis: Electrocatalyst and binder innovations	Dr Anzel Falch, University of the Witwatersrand, South Africa

Wednesday 9 April 2025 continued

14:40 – 15:05	Perchlorate fusion–hydrothermal synthesis of Nano-Crystalline IrO_2: Leveraging stability and oxygen evolution activity	Dr Rhiyaad Mohamed, University of Cape Town, South Africa
15:05 – 15:35	*Refreshment Break*	
15:35 – 16:00	Efficient formic acid dehydrogenation mediated by novel pyridyl-formamidine ligated Ru(II) complexes	Professor Andrew Swarts, University of the Witwatersrand, South Africa
16:00 – 16:25	Materials design for better catalysis: how simulation can inform the production of more sustainable fuels	Dr Matthew Quesne, University of Leeds, UK
16:30	*Close of Session*	
17:00	*Optional dinner*	*Tiger Reef Beach Bar & Grill, Swakopmund*

Advanced Fuel Cell Catalyst Support Materials

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Introduction

PEM fuel cells have gained a lot of interest over the years as a cleaner energy production technology, primarily using Pt/C catalysts for both the anodic and cathodic reactions. The extensive adoption of this technology has been hindered by the slow cathodic oxygen reduction reaction, that requires high Pt content to overcome overpotential[1]. The degradation of the carbon support observed at the cathode negatively affects the catalyst durability thus impairing their widespread utilisation.

Materials and Methods

Several materials have been investigated as alternative supports for Pt catalyst in the cathodic oxygen reduction reaction. This work explores these different materials with an emphasis on the development of N-doped carbon. Nitrogen-doped Ketjenblack EC300J was synthesised via a modified addition-condensation[2] method with targeted 3 and 5% N content. The extent of the modification of Ketjenblack was determined via XPS, XRD, Raman spectroscopy and surface area and porosity analysis. Pt was loaded onto these doped supports via an aqueous deposition chemical reduction method. The synthesised catalysts' activity was assessed using ex-situ TF-DRE, employing the Nissan ADT protocol for durability testing.

Results and Discussion

The chemical addition of N onto Ketjenblack, has resulted in the formation of pyridinic and graphitic N on the surface of the carbon, which showed improved durability of the catalyst, tested ex-situ with up to 83% of the initial ECSA remaining after 7200 cycles between 0.6 and 1.0V compared to 65.3% of the remaining initial ECSA of commercial Pt/C (Platalite®-K40) catalyst. The modification of the support is further supported by results from XRD showing a slight shift to higher 2θ values for the C(002) peak.

References

1. Torihata M, Nakamura M, Todoroki N, Wadayama T, Hoshi N. Activity for the ORR on Pt-Pd-Co ternary alloy electrodes is markedly affected by surface structure and composition. *Electrochem commun*. 2021;125:107007.
2. Subramanian NP, Li X, Nallathambi V, et al. Nitrogen-modified carbon-based catalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells. *J Power Sources*. 2009;188(1):38-44.

CO_2 sorption studies of two isostructural Co(II) and Zn(II) mixed ligand metal organic frameworks containing substituted diimide ligands

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Introduction

Metal-organic frameworks (MOFs) are porous compounds composed of metal ions or clusters coordinated to organic ligands.[1] MOFs have potential applications in gas storage and sequestration, separation, drug delivery, and catalysis.[2–5] Flexible MOFs, often referred to as soft porous crystals, exhibit dynamic structural changes in response to external stimuli.[6] Unlike rigid MOFs, their flexibility allows them to undergo reversible transformations, enhancing their performance in applications such as selective gas adsorption and sensing.[6] Herein, we report the synthesis, characterization, and carbon dioxide sorption studies of two isostructural flexible MOFs, namely $[Co(OBZ)(L1)_{0.5}]\cdot 2DMF$ (**1**) and $[Zn(OBZ)(L1)_{0.5}]\cdot 2DMF$ (**2**), where L1 is 2,7-bis(pyridin-3-ylmethyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone, and OBZ is 4,4′-oxybis(benzoic acid).

Materials and Methods

MOFs **1** and **2** were prepared solvothermally and characterized using single-crystal and powder X-ray diffraction (SCXRD and PXRD) and thermogravimetric analysis (TGA). CO_2 sorption studies were conducted up to 20 bar at 298 K using an intelligent gravimetric analyzer (IGA).

Results and Discussion

Single-crystal XRD analysis revealed that the structures of **1** and **2** are three-dimensional with 12% solvent-accessible volume. PXRD indicated that the crystals undergo a phase transition upon activation. CO_2 sorption studies showed that MOF **1** follows a type IV adsorption isotherm with hysteresis in the desorption curve. Initially, it adsorbs 0.6 mmol/g at 15 bar, after which the structure expands, allowing for an additional uptake of 1.3 mmol/g up to 20 bar. In contrast, MOF **2** follows a type I isotherm and achieves a total CO_2 uptake of 1.2 mmol/g at 20 bar.

References

1. *S.L. James. Chem. Soc. Rev., 32, (2003), 278.*
2. *P. Horcajada, et al, Chem. Rev., 112, (2012), 1232.*
3. *H. Li, et al, EnergyChem, 1, (2019), 10000.*
4. *L. Mbonzhe, et al, Results Chem., 4, (2022), 100648.*
5. *X. Zhao et al, Adv. Mater., 30, (2018), 1705189.*
6. *Z. Chang et al, Adv. Mater., 27, (2015), 5432.*

Highly photocatalytic Cu-doped TiO_2 thin films fabricated by the aqueous spray method

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Introduction

The need for efficient photocatalytic materials has prompted significant research into materials such as titania (TiO_2), due to its excellent photocatalytic activity, non-toxicity and chemical stability [1]. TiO_2's wide bandgap, however, limits its activity under visible light, prompting researchers to explore methods for narrowing the bandgap, such as doping with metals like copper (Cu) [2].

Materials and Methods

Undoped and Cu-doped TiO_2 thin films were deposited onto quartz glass substrates *via* the aqueous spray method. Aqueous precursor solutions were prepared by combining Ti^{4+} complexes with Cu^{2+} complexes, with molar percentages varying from 0 to 6%. The thin films were heat treated at 500℃ for 30 minutes and characterised through x-ray diffraction (XRD) and UV-Vis spectrophotometry). The photocatalytic properties of the resultant thin films were evaluated by irradiating a methyl orange (MO) solution under visible light, for 4 hours.

Results and Discussion

XRD analysis confirmed that all samples maintained the anatase phase. Regarding photocatalytic activity, the 6% Cu-doped films showed an increased degradation efficiency of MO by 28.82%. The findings highlight the ease of using the aqueous spray method for the fabrication of thin film for Cu-doped TiO_2 photocatalysts.

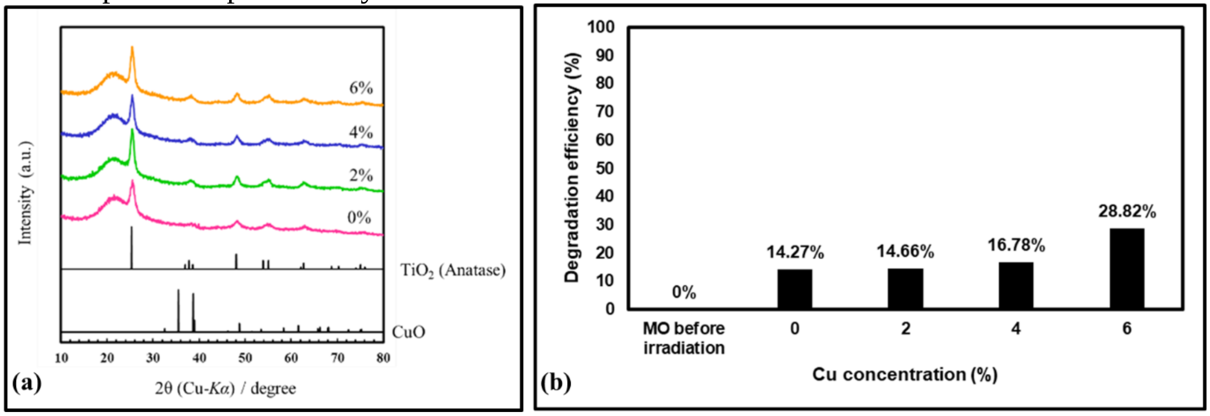

Figure 1. *(a)* XRD pattern of the resultant thin films, and (b) MO degradation efficiency under visible light.

References

1. *Komaraiah D, et al. Mater Today Proc, 3, (2016), 3770–3778.*
2. *Vidhya Rajendran, et al. Mechanics, Materials Science & Engineering, 9, (2017).*

Experimental Investigation on Electrical Discharges as an Ignition Source for Ammonia/Hydrogen/Air Mixtures

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Introduction

Hydrogen's role as a clean energy carrier is gaining popularity due to its potential to significantly reduce greenhouse gas emissions, particularly in transportation and power generation sectors[1]. However, its high flammability and low ignition energy necessitate safety research to mitigate risks associated with accidental ignition[2]. The recent explosion at a hydrogen fuelling station in Augsburg, Germany, has highlighted the hazards of hydrogen infrastructure, especially under high-pressure conditions[3]. This study aims to study characteristics of electrical discharge as a potential ignition source for ammonia/hydrogen/air mixtures, focusing on how factors such as electrode spacing impact required discharge energy.

Materials and Methods

The study employs Schlieren imaging techniques to visualize the effects of electrical discharges on gas mixtures[4]. A camera captures the temporal evolution of hot gas kernels and pressure waves following discharge events in the ignition chamber.

Results and Discussion

Fig. 1 below shows a successful experimental setup on the left, and on the right, it represents a schlieren image capture. The image clearly shows the localized density variations caused by the thermal expansion of ionized air, as well as the formation of a pressure wave propagating outward from the discharge site.

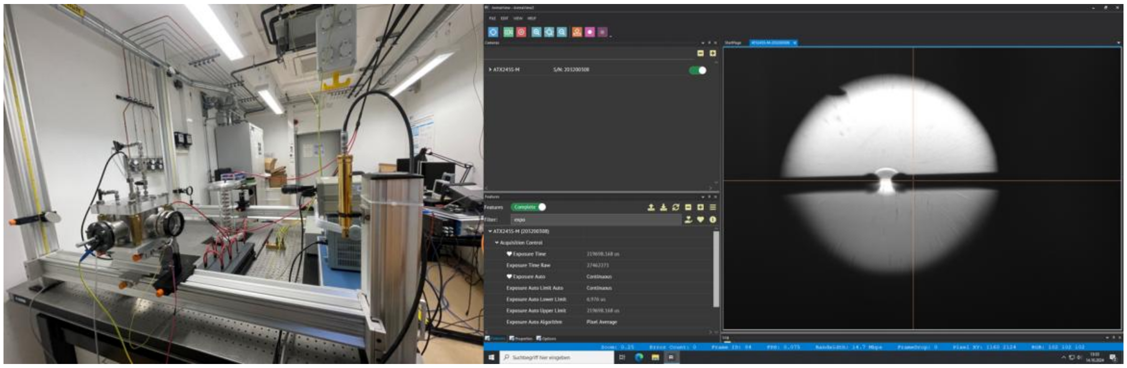

Figure 1 Final experimental set up and schlieren image

References

1. *Maas, U. et al., J. (1988) 'Ignition Processes in Hydrogen-Oxygen Mixtures', 69, pp. 53–69.*
2. *Essmann, S. et al. (2024) 'Ignition characteristics of hydrogen-enriched ammonia/air mixtures', 17. Available at: https://doi.org/10.1016/j.jaecs.2024.100254.*
3. *Hazardex (2023) Explosion damages newly opened hydrogen fuelling station in Germany, Hazardex, (Accessed: 11 October 2024).*
4. *Essmann, S., et al., (2015) 'Schlieren measurements of the pressure wave induced by low energy electrical discharges', European Combustion Meeting 2015.*

Computational modelling of carbon dioxide sequestration by zeolites or cerium dioxide

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Introduction

Due to their high specific surface area and the presence of positively charged metal ions, alkaline and alkaline-earth exchanged zeolites are very suitable for CO_2 adsorbents for controlling carbon dioxide emissions and its sequestration. Alternative approach to molecular adsorption of CO_2 is formation of surface carbonates on oxide surfaces. To contribute to clarification of the questions related to adsorption energies, spectral features and stability of surface species we report series of computational model studies based on periodic density functional theory calculations.[1]

Materials and Methods

The calculations for carbon dioxide adsorption on NaY and CaX zeolites and formation of surface carbonates on cerium dioxide were performed with periodic DFT method with PBE exchange-correlation functional and D2 dispersion correction of Grimme, as implemented in VASP code.[2] For the ab initio molecular dynamic simulations we used CP2K code with the same functional.[1] For the modelled systems we also calculated vibrational frequencies.

Results and Discussion

As some of the most promising adsorbents we considered NaY, CaNaY or CaX zeolites with faujasite framework due to their high aluminium content leading to large number of alkaline/alkaline-earth cations, respectively. The computational modelling showed that CaNaY zeolites possess a high CO_2 adsorption capacity at ambient temperature as both sodium and calcium cations act as adsorption centers.[2] In CaX zeolite, with Si/Al ratio close to 1, our results suggested that up to three carbon dioxide ligands can be coordinated at each calcium cation as the average interaction energy decreases with the number of ligands, from 102 to 80 and 69 kJ/mol.[3] In order to compare the computational results with real systems, we calculated vibrational frequencies of adsorbed CO_2 in all modelled complexes and compared to obtained values with experimental infrared spectra. The calculated frequencies of the complexes with one and two ligands in a model with one calcium cation, 2367 and 2371/2358 cm^{-1}, respectively, fit well to the corresponding experimental values, 2364 and 2367/2354 cm^{-1}.

On cerium dioxide as surface intermediates we considered various structures of carbonates, hydrogen carbonates, and formates.[4] Based on the relative stability and simulated vibrational spectra we suggested assignments of different bands in the experimental infrared spectra, which allowed correct interpretation of such spectra obtained not only after CO_2 adsorption but also formed during various catalytic processes involving oxidation of C-containing compounds.

Acknowledgements: The support by the Bulgarian Science Fund is gratefully acknowledged.

References

1. E. B. Clatworthy et al. Journal of the American Chemical Society, 145 (2023) 15313.
2. N. Drenchev et al. Journal of Physical Chemistry Letters, 14 (2023) 1564.
3. N. Drenchev et al. Separation and Purification Technology, 349 (2024) 127662.
4. G. N. Vayssilov et al. Journal of Physical Chemistry C, 115 (2011) 23435.

The role of Cu_5Pd cluster during CO_2 hydrogenation on ZnO (010) surface

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Introduction

Carbon dioxide, which is thought to be one of the primary causes of global warming, has increased as a result of the significant depletion of fossil fuels [1]. The process of turning CO_2 into industrial resources with additional value, like methanol (CH_3OH) [2], formic acid (HCOOH), and methane (CH4), has received a lot of attention in recent years [3]. The synthesis of methanol ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) is an exothermic process among these products. Reaction can be facilitated by lowering the temperature or raising the pressure, however practically lowering the temperature will decrease the rate of reaction. Finding a catalyst that can significantly increase the conversion efficiency is necessary for the production of methanol from CO_2 hydrogenation.

Materials and Methods

The dispersion-correction density functional theory (DFT-D) method was carried out to investigate the impact of doped Cu_5Pd nanocluster on ZnO (010) surface. The CASTEP code was used to investigate the adsorption of all intermediates and products of CO_2 hydrogenation on (010) ZnO surface. A plane wave energy of 380 eV and k-point mesh of (4x4x1) for bulk and (2x2x1) for the surface propose by Monkhorst Pack grid for Brillouin zone integration were used.

Results and Discussion

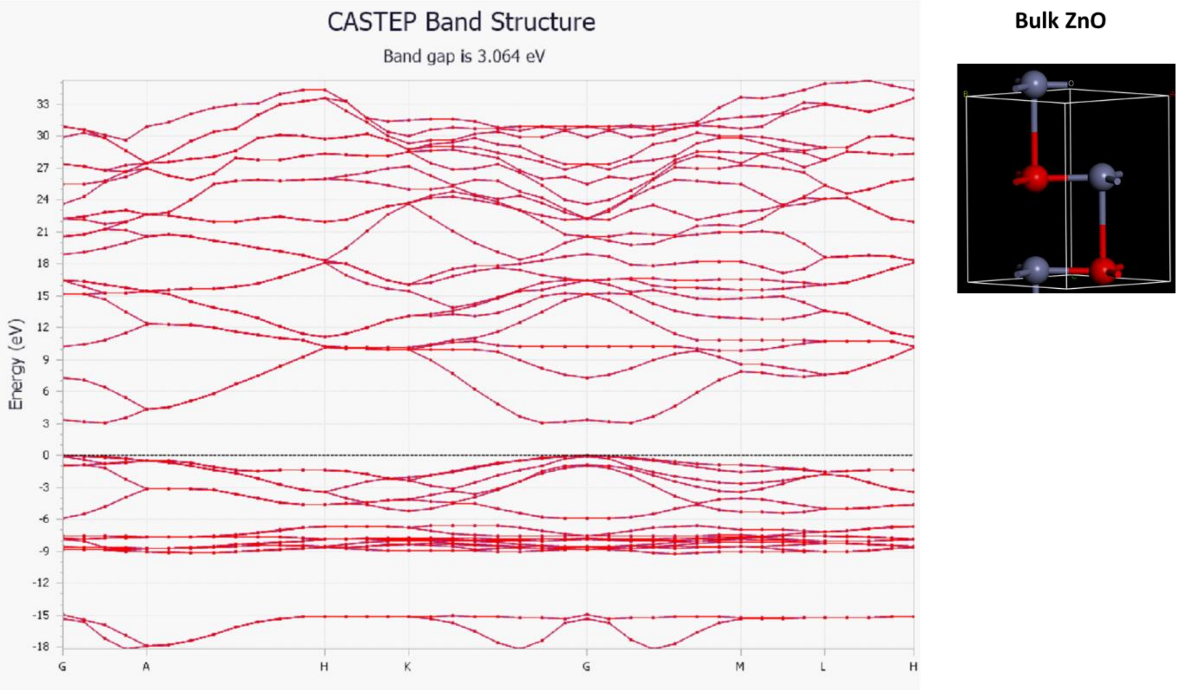

Figure 1: The band gap energy for bulk ZnO bulk structure.

Fig. 1 shows the band gap of 3.064 eV for the bulk ZnO structure, whereas, the band gap of 3.439 eV for ZnO (010) surface was found to be higher as compared to that of bulk ZnO structure.

However, the 6 atom Pd doped Cu cluster adsorbed on ZnO surface displayed a reduced band energy of 0.186 eV.

References

1. *P. M. Cox et al, Nat, 408, (2000), 84–187.*
2. *K. C. Waugh, Catal Lett, 142, (2012),1153–1166.*
3. *L. Yawei et al, Nanoscale, 7, (2015), 8663–8683.*

Photocatalytic activities of aluminium-doped zinc oxide thin films via aqueous spray method

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Introduction

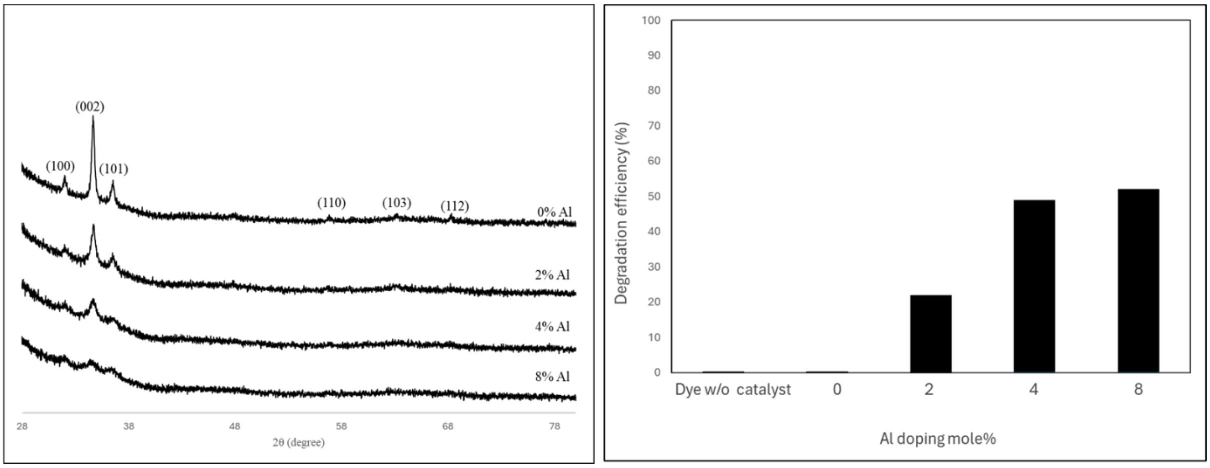
Thin films can be used as photocatalysts for environmental remediation due to their large surface area and their ease of use.[1] However, the fabrication of thin film materials that are eligible for such applications is not facile. The techniques utilised currently are not environmentally friendly, use costly instruments, and are complicated.[2]

Materials and Methods

In this research, the aqueous spray-coating method was used to fabricate aluminium-doped zinc oxide thin films. Aqueous precursor solutions containing Zn^{2+} complexes with varying mole percentages (0, 2, 4, and 8%) of Al^{3+} complexes were prepared and spray-coated onto quartz glass substrates pre-heated to 180°C. The as-sprayed films were heat-treated at 450°C for 30 minutes to obtain the final thin films.

Results and Discussion

According to the X-ray diffraction (XRD) patterns, the fabricated thin films are of zinc oxide, having a hexagonal structure. The resultant thin films promoted the degradation of methyl orange under visible light, and the degradation efficiency was observed to increase with Al doping percentage.



(a) (b)

Figure 1. (a) XRD patterns of the resultant thin films and (b) methyl orange degradation efficiency under visible light irradiation.

References

1. *M. Nadareishvili, et al, Eng Technol Appl Sci Res, 4, (2020) 2.*
2. *P.N. Hishimone, et al, Intech, (2020), 15.*

Energetics and Chemistry at the Reactive Electrocatalyst-Liquid Interface

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Sustainable energy storage and conversion are key for the transition to a CO_2-neutral energy system. In the required transition technologies, solar energy conversion to and storage of the intermittently available electricity in chemical bonds, i.e., solar fuels (here H_2), will play a major role. To achieve the targeted scale, abundant, active, and stable converter materials and their integration into efficient devices, i.e., electrolyzers or artificial leaves, are needed. This requires an in-depth understanding of interface chemistries and energetics, especially at the reactive solid-liquid interface.

In this perspective talk, I will focus on characterization and control of interfacial properties governing the functioning of electrocatalysts and photoelectrodes. I will introduce the requirements for successful solar water splitting devices and discuss the electronic structure of the involved functional materials. At the example of $CuBi_2O_4$ as a promising p-type oxide photoabsorber, the experimental and theoretical characterization of interfacial energetics and chemistry will be discussed.[1,2] Measurement strategies to assess the chemistry and energetics at the solid-liquid interface, using synchrotron experimentation and lab-based operando spectroscopies will be introduced. The application of multi-method approaches in (photo)electrocatalysis will be discussed, also in light of new developments of synchrotron radiation experimentation.[3]

References

1. *F. E. Oropeza, B. T. Feleki, K. H. L. Zhang, E. J. M. Hensen, and J. P. Hofmann, Influence of reduced Cu surface states on the photoelectrochemical performance of $CuBi_2O_4$, ACS Appl. Energy Mater.,* ***2****, 6866-6874,* ***2019****.*
https://doi.org/10.1021/acsaem.9b01333
2. *F. E. Oropeza, N. Y. Dzade, A. Pons-Martí, Z. Yang, K. H. L. Zhang, N. H. de Leeuw, E. J. M. Hensen, and J. P. Hofmann, Electronic Structure and Interface Energetics of $CuBi_2O_4$ Photoelectrodes, J. Phys. Chem. C, 124, 22416-22425,* ***2020****.*
https://doi.org/10.1021/acs.jpcc.0c08455
3. *S. Vadilonga, P. Dumas, U. Schade, K. Holldack, K. Hinrichs, G. Reichardt, T. Gerber, A. Vollmer, J. P. Hofmann, H. Oertel, B. Rech, R. Schlögl, J. Viefhaus, and H. Bluhm, Optical layout and endstation concept for the Enhanced Liquid Interface Spectroscopy and Analysis (ELISA) beamline at BESSY-II, Synchrotron Rad. News,* ***35****, 67-72,* ***2022****.*
https://doi.org/10.1080/08940886.2022.2082213

Alkaline Water Electrolysis: Electrocatalyst and Binder Innovations

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Introduction

Green hydrogen production through alkaline water electrolysis suffers from hampered water dissociation kinetics and the need for optimized components. Manganese as an electrocatalyst component shows promise for OER, while a novel poly(vinyl alcohol) (PVA)-based binder enhances HER, outperforming traditional Nafion™ ionomer in alkaline media.

Materials and Methods

Manganese based electrocatalysts were synthesized using a hydrothermal method. For polymer preparation, physical crosslinking was achieved through freeze-thaw cycles to enhance structural integrity. The electrocatalyst and polymer binder were physically characterized using SEM/EDX and potentiodynamic electrochemical techniques.

Results and Discussion

The combination of nickel and manganese presents a promising strategy due to nickel's high oxidation states and adaptable 3d electrons, which facilitate rapid electron transfer and improve reaction kinetics for oxygen evolution activity.[1] However, these advantages require optimization to be fully realized. Adjusting metallic ratios and synthesis temperatures can enhance the overpotentials of Mn:Ni combinations compared to individual NiO and MnO counterparts, demonstrating a synergistic effect between the two metals.

In the context of alkaline water electrolysis (AWE), Nafion™ remains the most widely used ionomer but is suboptimal for alkaline conditions, expensive, and environmentally detrimental.[2] Its phased discontinuation has intensified the search for alternative binders designed specifically for alkaline environments. As a potential solution, (PVA)-based binders offer a cost-effective alternative. PVA's hydrophilic properties enhance the Volmer step in the hydrogen evolution reaction (HER), leading to improved performance. Although incorporating branched poly(ethylenimine) (bPEI) and poly(pyrrole) (PPy) into the binder system showed limited improvement, PVA alone outperformed Nafion™, demonstrating superior HER activity and stability.

References

1. *Hu, J; Zhou, et al.. International Journal of Molecular Science. 2023, 24*
2. *Di Virgilio, M; et al. Clean Technol. 2023, 5, 74-93*

Perchlorate Fusion–Hydrothermal Synthesis of Nano-Crystalline IrO_2: Leveraging Stability and Oxygen Evolution Activity

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Introduction

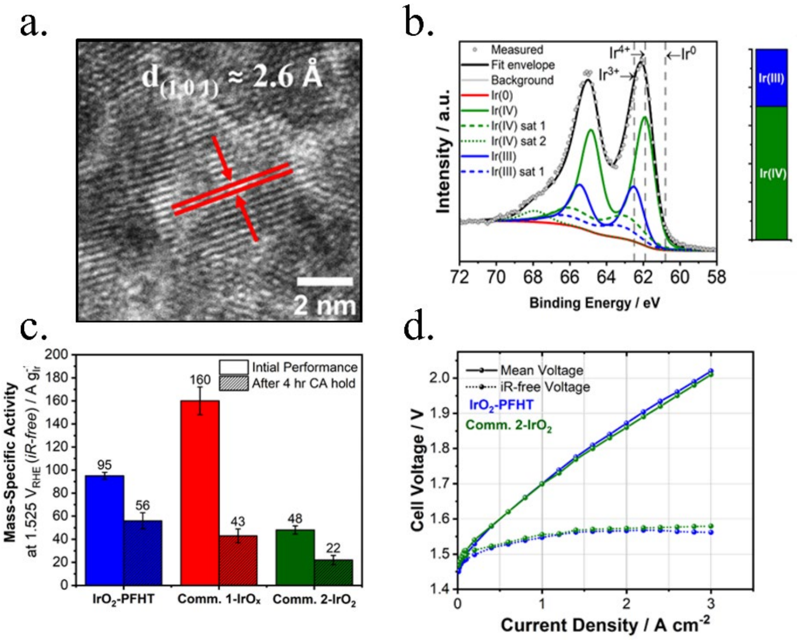
Iridium oxides are the best class of materials for the catalysis of the kinetically demanding oxygen evolution reaction (OER), the bottleneck of green hydrogen production through proton exchange membrane water electrolysers (PEMWE). Developing more robust, efficient materials will allow for significant breakthroughs in the cost and long-term durability of PEMWEs.

Materials and Methods

In this study, we introduce a novel perchlorate-fusion hydrothermal (PFHT) synthesis technique that enables the formation of rutile, nanocrystalline iridium dioxide nanoparticles. Notably, this method eliminates the need for high-temperature thermal treatment to achieve crystalline IrO_2 while effectively maintaining the high active surface area of the nanoparticulate catalyst.

Results and Discussion

Using the PFHT approach, we have successfully addressed the common activity-stability trade-off that often limits the performance of materials in the OER. The synthesised IrO_2 nanoparticles have demonstrated exceptional performance under *ex-situ* OER and *in-situ* PEM electrolyser conditions. Achieving high activity while maintaining electrochemical stability marks a significant advancement in developing cost-effective, efficient electrocatalysts for energy conversion.



Efficient formic acid dehydrogenation mediated by novel pyridyl-formamidine ligated Ru(II) complexes

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Introduction

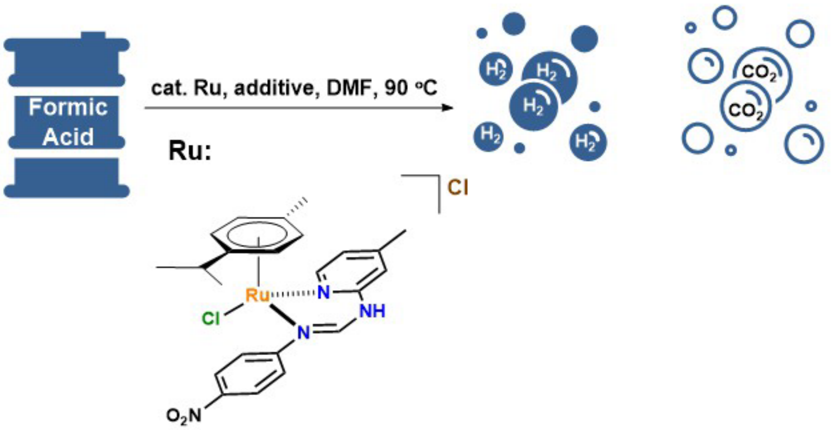
Hydrogen is a clean and renewable energy store, which provides an attractive alternative to fossil fuels.[1] Significant research efforts have been geared toward developing efficient hydrogen carriers. To this end, formic acid has emerged as the carrier of choice due to its favorable properties, which includes high hydrogen content by weight, ease of transport and handling.[2] The research efforts of the Swarts Research Group focus on the development of catalyst systems derived from earth-abundant metals.[3]

Materials and Methods

We report the preparation of Ru(II) half-sandwich complexes, bearing new pyridyl-formamidine ligands. This is accomplished via a one-step ligand synthesis, followed by ligation of Ru(II)-*p*-cymene dimer.

Results and Discussion

These complexes we found to be active catalysts for the selective dehydrogenation of formic acid to H_2 and CO_2, with turnover frequency of 9916 h^{-1} and turnover number of 347080 at 100 °C in DMF. Mechanistic studies by DFT and NMR spectroscopy shed light on the role of Ru-hydride and potential ligand cooperativity in the catalytic cycle.[4]



References

1. *G.W. Crabtree, et al, MRS Bull. 33, (2008), 421.*
2. *D. Mellman, et al, Chem. Soc. Rev, 45, (2016), 3954.*
3. (a) *V. Vermaak, et al, Adv. Synth. Catal, 362, (2020), 5788. (b) T. Makhado, et al, Sustain. Energy Fuels, 5, (2021), 2771.*
4. *J.M. Edor, et al, Eur. J. Inorg. Chem. [Manuscript in preparation].*

Materials Design for better catalysis: how simulation can inform the production of more sustainable fuels

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Introduction

Methane emissions now account for ~30 percent of anthropogenic warming. Centralised methane capture and conversion, is an extremely promising technology for future green chemistry research. This presentation will focus on two studies that explore selective methane conversion by: (1) the photoactive covenant framework material CFT-1[1] and (2) Au supported on ZSM-5.[2]

Materials and Methods

CFT-1: Catalyst activity of CTF-1 is compare to: (1) Anatase TiO2 and (2) g-C_3N_4. The photocatalytic reactions are carried out under irradiated by a 365 nm LED source. Computation uses Density Functional Theory (DFT) in combination with Perdew−Burke−Ernzerhof functional (PBE), as implemented in the Vienna Ab initio simulation (VASP) code. **Au-ZSM-5**: H-ZSM-5 with SiO2/Al_2O_3 ratio of 25 is loaded with Au by a deposition–precipitation. Methane oxidation with oxygen is carried out in an autoclave reactor. Calculations are performed using VASP in and PBE. Four models were constructed: (1) periodic slab calculations of Au(111) and Au(100) planes, (2) subnanometre Au particles, containing 38 atoms, (3) ZSM-5 with a Au extra framework cation and (4) a Au_{10} cluster supported on an Fe_2O_3(001) slab, examining iron leaching from the reactor.

Results and Discussion

CFT-1 This study demonstrates that the intrinsic molecular heterojunction in CTF-1 polymer is highly selective for solar-driven methane transformation towards ethanol. At a GHSV of 2000 mL h^{-1}, the photocatalytic methane-to-ethanol conversion at 65 °C represents a very high selectivity of *ca.* 80 % and a yield of 122.4 mmol h^{-1}. The study rationalises a process for methane transformation to ethanol via ethane, without the over-accumulation of strong oxidants, seen in C_3N_4-based catalysts. **Au-ZSM-5**: This study showed that Au nanoparticles supported on ZSM-5 can oxidize CH_4 to methanol and acetic acid with minimal formation of CO_2. In the batch experiments, a maximum oxygenate productivity at short times of 7.3 mol mol_{Au}^{-1} h^{-1}. This is much higher than that reported for the examplar Cu-based catalysts tested under similar conditions under flow conditions.[3] In contrast to the Cu-zeolite catalysts, for which only C1 products are observed, C2 oxygenates are the major products observed with the Au-ZSM-5 catalyst, demonstrating that the Au catalyst operates by a different mechanism.

References

1. *Xie, J., Fu, C., Quesne, M.G., Guo, J., Wang, C., Xiong, L., Windle, C.D., Gadipelli, S., Guo, Z.X., Huang, W., Catlow, C.R.A., Tang, J., Methane Oxidation to Ethanol by a Molecular Junction Photocatalyst (2024) Nature, [in press].*
2. *Qi, G. et al. Au-ZSM-5 catalyses the selective oxidation of CH4 to CH3OH and CH3COOH using O2. (2022) Nat. Catal. 5, 45–54.*
3. *Dinh, K. T. et al. Continuous partial oxidation of methane to methanol catalyzed by diffusion-paired copper dimers in copper-exchanged zeolites. (2019) J. Am. Chem. Soc. 141, 11641–11650.*