

R&D Efforts towards Net Zero Emissions

Atindra Mohan Banerjee, Dimple Dutta, Mrinal R. Pai and
Jyotirmayee Mohanty

Preamble:

A brief compilation of the recent accomplishments of Chemistry Group towards the realization of the greater national goal of net zero emissions by 2070 is presented in this overview. Chemistry Group has made significant contributions in the last two decades on directed research towards realizing the net zero targets which include R&D on hydrogen generation and storage, material development for Li-ion and Na-ion batteries, and carbon dioxide capture, storage and utilization. Spanning from fundamental research for basic understanding to applications for deployment of materials have been carried out. Extensive research has been undertaken on development of novel materials for photocatalytic water splitting, CO₂ reduction along with mechanistic understanding of the fundamental processes involved via wide variety of tools viz. material characterization, density functional theory, femtosecond spectroscopy etc. Research and development of hydrogen storage materials from metal hydrides to porous materials/MOF's and complex hydrides have been explored. Catalysts/electrocatalyst have been developed and deployed at engineering scale processes for thermochemical hydrogen generation. Extensive research on lithium and sodium ion batteries has led to the development of novel anode and cathodes and also transfer of technology to private firms for synthesis of specific electrode materials.

Introduction:

Research and development on the efficient utilization of renewable energy, transition to hydrogen fuel and carbon capture, utilization and storage (CCUS) are going to play a critical role for India to halve CO₂ emissions by 2050 and to accomplish net-zero by 2070, as envisioned by the Hon'ble Prime Minister of India. Energy transition faces technological hurdles and hence it is important for targeting the R&D contribution towards accomplishing the above goal and make a meaningful contribution to decarbonization in India.

Chemistry Group has made rich contributions towards directing research on realizing the net zero targets. R&D on hydrogen generation and storage, material development for Li-ion and Na-ion batteries, and carbon dioxide capture and utilization have been initiated in past few decades and significant contributions have been achieved as documented in next sections.

Hydrogen generation and storage:

Studies related to hydrogen generation using thermochemical water-splitting processes:

In 2005, work on hydrogen generation via thermochemical splitting of water by Iodine-Sulfur (I-S) process with an aim to utilize nuclear heat (from Compact High Temperature Reactor) was initiated and was later proposed as an XI plan activity at BARC. Several groups in BARC viz., Chemical Technology Group, Chemistry Group, Chemical Engineering Group, Materials Group, Reactor Design and Development Group participated in this XI plan project entitled “*Hydrogen Energy*”. This activity was also in line with the National Hydrogen Energy Road Map (proposed by National Hydrogen Energy Board, setup under the aegis of MNRE, Government of India) wherein hydrogen production, storage, power, transport and systems integration solutions were considered for utilisation of hydrogen energy (a clean and renewable energy carrier) to solve the country’s energy security problems and meet environmental quality standards. Work on I-S process was initiated in Chemistry Group which involved: (i) kinetic and catalysis aspects of sulfuric acid and hydriodic acid decomposition steps, (ii) speciation of products in Bunsen step and (iii) influence of impurities (present in sulphuric acid and hydriodic phases produced during Bunsen step) on acid decomposition catalysts. In his concluding remarks during a review meeting on hydrogen generation and storage held at BARC in September, 2007, former Chairman, AEC, Dr. R. Chidambaram expressed his satisfaction that BARC with its multidisciplinary capabilities has taken up such important project on hydrogen generation and storage. He emphasized the role of basic research as important component for addressing to today’s energy related problems of national interest.

During the course of work, non-noble metal iron oxide-based catalysts (Fe_2O_3 and $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$) were developed as a better substitute (avoiding leaching and sintering problems associated with the noble metal catalysts) for the supported noble metal catalysts ($\text{Pt}/\text{Al}_2\text{O}_3$) for sulfuric acid decomposition step of I-S process. For this purpose, two acid decomposition setups were developed indigenously (Fig. 1, a, b). The setup involving a quartz reactor, equipped with a syringe pump (for dispensing sulphuric acid to preheater) and a carrier gas was used for screening the catalysts in powder form (Fig. 1 a) while the other comprising of a sulphuric acid reservoir, an integrated boiler cum decomposer and a two-temperature zone furnace (Fig. 1,b) was utilized for evaluation of activity of granular/foam based catalysts (selected for deployment in engineering scale operation) in temperature range, 600 - 850°C. The developed catalysts were also found to be resistant towards HI and I_2 impurities present in the sulfuric acid phase. The study further revealed the role of the oxide surface in catalyzing the formation and decomposition of sulfate transient species and helped in elucidation of mechanistic aspects of sulphuric acid decomposition process. These findings were published in reputed peer reviewed international journals. The $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ catalyst in granular form was deployed during closed-loop operation of the I-S cycle for 20 h (India became 5th country in the world to achieve this) producing hydrogen @ 30 NLPH at Chemical Technology Division in 2013. This catalyst was also deployed during demonstration of sulfuric acid decomposition using solar heat (from 1.8 m solar dish at Mod. Labs, terrace). More recently in 2019, $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ catalyst with improved porosity has been developed (in collaboration with Powder Metallurgy Division, BARC) in foam form, whose

performance was found to be superior to the granular form of catalyst during sulphuric acid decomposition at elevated temperatures at Chemical Technology Division, BARC. Subsequently, the foam based $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ catalyst was successfully deployed in the I-S process metallic closed-loop (MCL) demonstration of hydrogen generation at 150 NLPH in Chemical Technology Division in 2022.

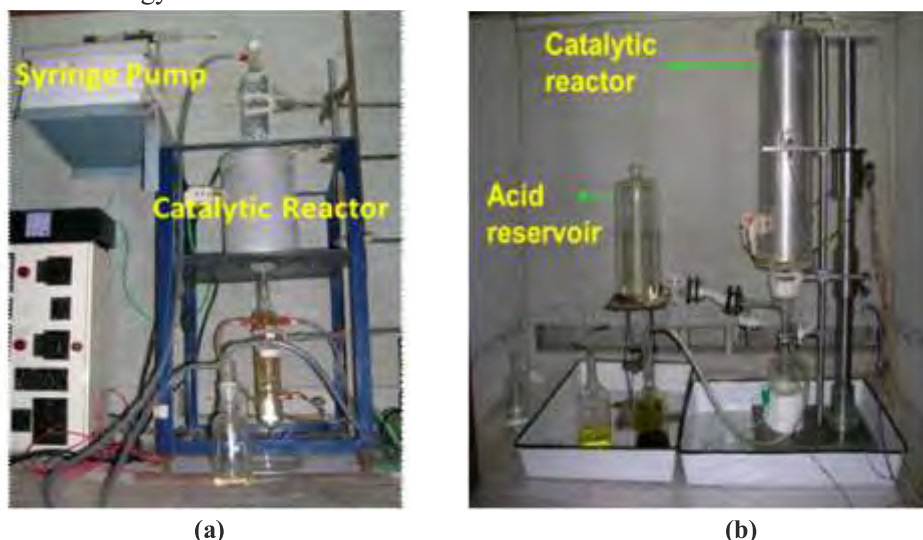


Fig. 1: Indigenously developed sulfuric acid decomposition set ups for (a) screening of catalysts in powder form and (b) and in granular/foam form (selected for deployment in engineering scale operations)

Similarly, several carbon and oxide supported catalysts such as Pt/C, Pt/ZrO₂, Pt/TiO₂ and Pt/CeO₂, were developed for liquid phase HI decomposition conditions. Oxide supported Pt catalysts were comparable or even better than Pt/C catalysts in terms of catalytic activity for HI decomposition.

Subsequently, the work expanded to other thermochemical cycles such as Hybrid-sulfur (Hy-S) and Copper-Chlorine (Cu-Cl). Suitable carbon supported platinum electrocatalysts were developed and membrane electrode assemblies (MEA) incorporating these electrocatalysts were fabricated. Also, proton exchange membrane based electrolyzers (active area- 4 cm²) were designed and fabricated indigenously to evaluate the performance at lab scale for the aforementioned electrolysis steps. Large sizes MEAs (active area-256 cm²) were fabricated and deployed in aqueous SO₂ electrolyser during closed loop demonstration of Hy-S cycle producing hydrogen @ 2 NLPH for 25 h at ChTD in 2018.

Work on Cu-Cl cycle was initiated in 2015 in Chemistry Group in collaboration in Chemical Engineering Group. Chemistry Group investigated the individual steps of Cu-Cl thermochemical cycle and the main focus was on the development of electrocatalyst and MEA for the electrolysis step and generation of kinetic and thermodynamic data for thermal steps. Hydrolysis of CuCl₂ was demonstrated using fixed bed and spray reactors (Fig.2a). The reaction products were characterized qualitatively and quantitatively. The kinetic parameters were derived for CuCl₂ hydrolysis and mechanistic insights were gained using *insitu* XAS and other probes. Studies were performed to understand the effect of impurity phase

associated with hydrolysis product on kinetics of subsequent O_2 evolution decomposition step. A thermal decomposition pathway involved during decomposition step using whether Cu_2OCl_2 feed or $CuO+CuCl_2$ feed was investigated. Their studies have established that $CuO+CuCl_2$ is an ideal substitute for Cu_2OCl_2 as feed for decomposition step. The preparation conditions for Cu_2OCl_2 synthesis were optimized. Electrocatalysts and membrane electrode assembly (MEA) were developed for $CuCl/HCl$ electrolysis. MEA's of Pt/C electrocatalysts were fabricated and tested in indigenous electrolyser for $CuCl/HCl$ electrolysis and shown in Fig. 2b. The MEA fabricated in Chemistry Group was successfully deployed in the closed loop demonstration of Cu-Cl cycle @ 4 NLPH of hydrogen generation in ChED for a prolonged 169 h in 2023.



Fig. 2: Indigenously developed (a) spray reactor for $CuCl_2$ hydrolysis and (b) $CuCl/HCl$ single cell electrolyser with Pt/C electrocatalyst based membrane electrode assembly (MEA)

Studies related to hydrogen generation using photocatalytic / photoelectrochemical / electrocatalytic water-splitting processes:

The photocatalytic water splitting involves conversion of solar energy into chemical energy (H_2) with the help of photocatalyst and was initiated in Chemistry Group in 2005. Its mechanism mainly involves absorption of photons in UV-vis region by semiconductor suspended particles (photocatalyst) having appropriate band gap and band potentials, followed by generation of e^-/h^+ pairs, transfer of charge carriers from bulk of the photocatalyst to the surface; catalytic reactions in which the photogenerated electrons and holes operate redox reactions over adsorbed water molecules to generate hydrogen and oxygen and recombination of e^-/h^+ pairs which occurs in competition with surface reactions and is detrimental for photocatalytic activity of the material.

Persistent efforts were made to develop visible-light active and stable photocatalysts for solar hydrogen generation. Numerous photocatalyst materials viz. TiO_2 , In_2TiO_5 (indium titanate), graphitic carbon nitride ($g-C_3N_4$) and novel organic semiconductor were modified in order to improve their photocatalytic properties. Several approaches were adopted to increase photocatalytic activity viz. Cu doping in TiO_2 , NiO/CuO composites with TiO_2 inducing *pn* heterojunctions, carbon inclusion in TiO_2 ($C@TiO_2$) to improve its electronic conductivity, surface modification of $g-C_3N_4$ by dispersing carbon nanodots (CND), noble metals (Pt, Pd, Cu, Ag and Au), oxides like $CaFe_2O_4$, Fe_2O_3 . The parameters optimized included illumination area, catalyst concentration, catalyst forms (powder/films) and type and concentration of

sacrificial agents. Performance of the screened photocatalysts was also tested in up-scaled photoreactors (vol = 0.5, 1 and 2L). H₂ yield @ 1.167 L/h/m² with apparent quantum efficiency (AQE) of 7.5 % and SFE of 3.9 % over Cu_{0.02}Ti_{0.98}O₂ was observed under sunlight suggesting that 0.96 m² illumination area will yield H₂ @ 1 L/h photocatalytically. Several CdS based photocatalysts active in sunlight were also investigated for photocatalytic splitting water. Notable among these are Pt-CdS-ZnS-Cd_{0.8}Zn_{0.2}S and Pt-Cd_{0.95}Pd_{0.05}S composite photocatalysts where hydrogen generation rates of 1-1.72 L/h/m² were achieved using sodium sulfide and sodium sulfite as sacrificial agent under sunlight irradiation (reactor volume- ~ 2 L; illumination area ~154 cm²).

Strong visible light absorption followed by long lived charge carrier generation in high yield is a critical parameter for any potential photocatalyst for hydrogen generation. Femtosecond resolved transient absorption spectroscopy (state of art facility available in Chemistry Group) offers direct measurement of charge-carrier dynamics and provides an excellent tool to estimate suitability of potential photocatalysts in photocatalytic hydrogen production. In this regard, ultrafast transient dynamics of several organic nano-structured materials and metal organic framework (MOF) systems have been explored to correlate excited state dynamics with hydrogen production rate. Co-sensitization and defect controlled excited state dynamics has been shown to favorably influence hydrogen production rate. Correlation with molecular structure tuned photophysical parameters in organic nano-structured photocatalyst is currently being pursued.

Significant theoretical studies have also been undertaken in Chemistry Group towards identification of suitable materials for enhancing photocatalytic water splitting efficiency. Through *ab initio* investigations, it was proposed that poly s-triazine based graphitic carbon nitride (g-C₃N₃) as a possible metal-free photocatalyst for solar water splitting. The electronic band structure calculations on g-C₃N₃ indicated that the material has a band gap of 2.89 eV with appropriate band edge potentials for water splitting which can be further tuned through doping with non-metal elements as well as by metal decoration. A systematic study of different intermediate reaction steps involved in both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) on g-C₃N₃ surface was proposed.

Work on photoelectrochemical water splitting (PEC) for hydrogen generation has also been undertaken in Chemistry Group. PEC water splitting is a sustainable and environmentally clean hydrogen generation process using solar energy to achieve carbon neutral fuel generation. The n-type and p-type semiconductor photoelectrodes with appropriate band gap, capable to absorb in the visible light and band position proper with redox potential of water oxidation and reduction are targeted to be explored. Work has been carried out with several transition metal oxide and sulfides (BiVO₄, Fe₂O₃, WO₃, TiO₂, Cu₂O, MoS₂) and their performance tested for photoelectrochemical activity for water splitting. Further, combination of these electrodes is planned to be fabricated. Devices will be fabricated with full cell operational conditions and sustainable generation of hydrogen through the PEC route.

Electrocatalytic hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) – the two half-cell reactions of electrolytic water splitting are important process for green hydrogen generation. Platinum is known as the best catalyst for HER but it is not feasible to commercialize owing to its cost implications. In this direction work has been

carried out in Chemistry group on alternative homogeneous as well as heterogeneous electrocatalysts. Three different complexes of cobalt namely bis (iminodiacetate)- cobaltate (III) $\text{Co}(\text{IDA})_2$, cobalt(2,6-) bismethylhydroxy pyridine) $_2$ (acetate) $\text{Co}(\text{BHPy})(\text{OAc})$ complex and cobalt (2,6-bisimidazolyl pyridine) $\text{Co}(\text{BIP})$ complex showed very high catalytic activity for hydrogen generation in weak acid medium. On the other hand, molybdenum carbide based electrocatalysts have shown good potential as a replacement to costly Pt-based formulations. Pt-alloy based electrocatalysts with low-Pt content has also been explored for electrochemical HER. Fe-Co and Fe-Ni based layered double hydroxide (LDH's) with varied Fe/Co and Fe/Ni ratios have been investigated for electrochemical OER showing reasonable activity and stability. For alkaline water electrolysis, Ni-P, Ni-Mo and Ni-Mo-P based coatings on Cu and Ni substrates have shown good promise for electrochemical HER in alkaline media.

Studies related to development of materials for hydrogen storage:

Chemistry Group had rich traditions of R&D on metal hydrides since mid-1970's. This experience and facilities were directed towards development of hydrogen storage materials since 2005 onwards. Chemistry Group has been actively involved in research and development of hydrogen storage materials for specific applications. Among several transition metal-based alloys studied by the group, Ti_2CrV alloy is found to have 4 wt. % hydrogen storage capacity at room temperature and sub-atmospheric pressure, which is one of highest internationally reported so far for transition metal-based systems. The material has been selected for *in-situ* storage of hydrogen, produced by alkaline water electrolysis in Heavy Water Division. After successful demonstration for 18 L of hydrogen storage, the system is being scaled up for storage of 144 L of hydrogen. A photograph of the material and the system is shown in Fig. 3.



Fig. 3: Material developed for online hydrogen storage facility

Among light metals, in house study on magnesium-based system with extensive ball milling experiments revealed the usefulness of wet milling technique for development of Mg based particles with size in ~ 80 nm range with very little oxidation. Even without addition of any external catalyst, hydrogen storage capacity up to 6.2 wt.% has been achieved with excellent hydrogen absorption and desorption kinetics. The effect of nano-sizing has been established through first principle calculations and it has been seen at very low particle size

(<2 nm), there is considerable decrease in the activation barrier for hydrogen absorption and desorption. Apart from that in the basic research front, Chemistry Group has contributed to *in-situ* and *ex-situ* modification of carbon-based systems like graphene, porous carbon, activated carbons and carbon nanotubes, by both metals (Pd, Ni) and non-metals (B, N) doping for improved hydrogen storage properties. Prussian Blue analogues with inherent cage structures has been explored for low temperature hydrogen storage application. Chemistry Group has also developed metal-free supramolecular cucurbituril nanocavitands as catalyst (Fig. 4) for room temperature hydrolysis of ammonia borane, with hydrogen storage capacity as high as 19.6 wt%. The screening of cucurbituril-functionalized Co:Ni (Co:Ni:CB) nanocomposites as catalysts was carried out for the hydrolysis of ammonia borane (AB). Ammonia release during hydrolysis was prevented significantly in the presence of Co:Ni:CB nanocomposite. The reusability of the catalysis was examined for six cycles in 24 h interval each. The catalytic activity of Co:Ni:CB nanocomposite remained constant, whereas the activity of nanocomposite without cucurbituril, Co:Ni, decreased by 60% after three cycles. Apart from this, several metal organic frameworks based and zeolite imidazole framework-based catalysts were utilised for the room temperature hydrolysis of ammonia to generate ammonia free hydrogen. Efforts have also been made for the complete regeneration of the starting material from the by product generated during hydrolysis of ammonia borane to maintain sustained hydrogen release.

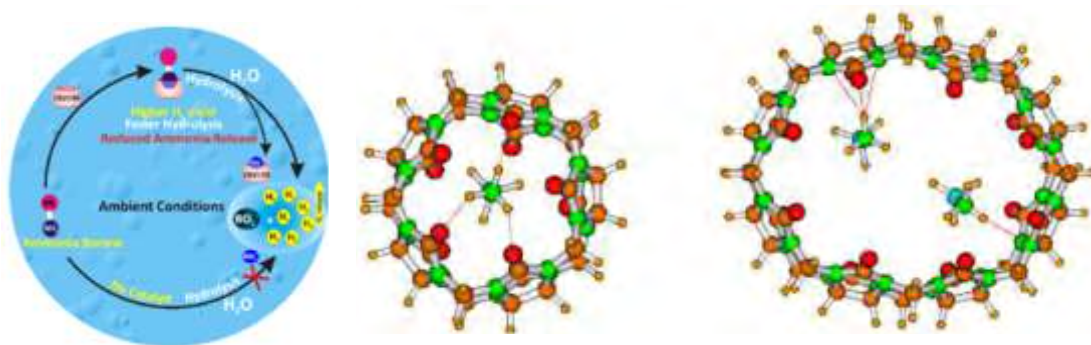


Fig. 4: Metal-Free Supramolecular Cucurbituril Nanocavitands (CB5 and CB8) for Catalytic Hydrolysis of Ammonia Borane

Significant contributions were made by Chemistry Group towards theoretical modelling of light metal decorated materials, like cyclic carbon molecular systems, fullerenes, boron hydrides, two-dimensional carbon materials, metal organic frameworks (MOFs) and porous carbon materials for their hydrogen adsorption characteristics. Alkali metal decoration over the C_{60} fullerene was shown to remarkably enhance the molecular hydrogen adsorption capacity of fullerenes with a hydrogen adsorption density of ~ 9.5 wt %. The hydrogen adsorption in cyclic carbon systems (C_nH_n) and the results reveal that the simple van der Waals surface is not capable of adsorbing hydrogen efficiently and the presence of charged sites can enhance the adsorption energy considerably. Hydrogen adsorption in metal

decorated MOFs has revealed that boron doping can improve the stability of the metal decorated MOFs and also prevents metal clustering thus leading to significant improvement of the hydrogen adsorption capacity. Studies on emerging two-dimensional carbon allotropes, graphyne and graphdiyne for their possible applications in hydrogen storage as well as in nano-electronics, Li ion batteries etc. were also carried out.

Studies related to energy storage in batteries

Lithium-ion batteries (LIBs) are a promising energy storage technology due to their high energy density, low self-discharge property, near zero-memory effect, high open circuit voltage, and long lifespan. In Chemistry Group, BARC, research in lithium ion battery was initiated in the year 2012. Lithium iron phosphate (LiFePO_4) and carbon coated composite of LiFePO_4 were synthesized by soft chemical route. The loss of lithium in the composition which was ascertained by several techniques like ICP-OES, PIGE etc. during the synthesis procedure was adjusted by varying the stoichiometry of the lithium precursor. The poor electronic conductivity of pristine LiFePO_4 has been enhanced by composite formation using several carbon sources like glucose, lactic acid etc. The carbon coated LiFePO_4 has been found to have higher electronic conductivity. Half cells were fabricated using this cathode against lithium electrode and the cells could deliver capacity around 140 mAh/g after 100 cycles. At the same time $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode has been synthesized by sol-gel route followed by calcination at 700°C

The synthesis technology of cathode and anode has been documented and transferred to several private firms for commercialization. Further, the $\text{Li}(\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2})\text{O}_2$ has been synthesized and technology has been transferred to few private firms. Several developments have been made in the anode materials used in LIB. MoS_2 , Mo_2C , SnO_2 and chalcogenide-based anode has been developed. In order to improve the conductivity several coating agents like reduced graphene oxide, carbon nanotubes, conducting carbon etc. have been used. The additive added in MoS_2 not only increase the conductivity but also helps to entrap the polysulfides to slow down its migration.

Although Li-ion batteries have remarkable success in several electronic and portable appliances, the high cost and limited and unequally distributed lithium resources may obstruct its further usage in novel enhanced-scale electrochemical energy storages systems (EESs). Sodium ion batteries (SIBs) have been extensively studied as potential candidates for next-generation low-cost energy storage devices as sodium is readily available and abundant. Due to the large atomic radius of Na (0.97 \AA for Na^+ and only 0.68 \AA for Li^+), the practical applications of SIBs are hindered which is attributed to the sluggish sodium ion diffusion kinetics and large volume expansion of the electrode materials. Chemistry Group, BARC has an extensive research program on development of novel electrode materials for SIBs since 2017. Several biomass wastes have been identified as ideal precursor material for production of hard carbon and mesoporous carbon which are the standard anode materials for SIB. Sodium ion coin cell with energy density of $\sim 200 \text{ Wh kg}^{-1}$ has been fabricated using indigenously synthesized electrode material and has been used for lighting LED panels. Composites of biocarbon with $\text{Na}_2\text{Ti}_3\text{O}_7$ have been utilized as anodes for SIB which delivers reversible specific capacity of 135 mAh g^{-1} at 0.2 A g^{-1} after 250 cycles. The biocarbon

addition has enabled lower temperature monoclinic to triclinic phase transition in $\text{Na}_2\text{Ti}_3\text{O}_7$ where the latter phase supports faster sodium ion migration. Biowaste derived hard carbons with low tortuosity and high plateau capacity at low voltage has been obtained to develop the sodium ion pouch cell. These cells exhibited cyclic stability upto 1000 cycles in addition to reasonable anode electrode performance viz. a discharge capacity as high as $\sim 301 \text{ mAh g}^{-1}$ at 0.1C current rate. Subsequently, full cell was designed and developed with hard carbon anode and polyanionic sodium vanadium phosphate ($\text{Na}_3\text{V}_2(\text{PO}_4)_3$) as the cathode with a cyclic stability up to 450 cycles at a 0.1C current rate. Further, the single-layer pouch cell ($\sim 100 \text{ mAh}$ designed capacity) was fabricated and exhibited a cyclic performance up to 300 cycles and delivered $\sim 135.2 \text{ Wh kg}^{-1}$ of energy density at cell level with an average voltage of $\sim 3.0 \text{ V}$. Additionally, several novel cathode and anode materials based on polyanionic fluorophosphates and bimetallic chalcogenide composites, respectively, have been developed.

Studies on CO_2 capture, storage and utilisation:

Photocatalysis is considered to be a promising method for CO_2 conversion into valuable products, such as methanol, methane, formaldehyde, and higher hydrocarbons. Research in this direction was initiated in Chemistry Group with the exploration of Cu-doped TiO_2 materials as a potential photocatalyst to convert CO_2 to methane under visible irradiation in absence of any sacrificial agent. The role of the cation Cu dopant was to significantly reduce the optical band gap of UV-active TiO_2 to the visible region. The photocatalytic performance of the Cu-doped TiO_2 materials were even better than anatase TiO_2 for the photoreduction of carbon dioxide to methane. A doping of 1% Cu in TiO_2 lattice exhibited a methane production rate of $\sim 1081 \mu\text{L/h/g}$. The photocatalytic activity for CO_2 reduction decreased with increasing Cu content in the TiO_2 lattice. The rate of photocatalytic reduction of carbon dioxide to methane is found to be dependent on surface Cu^+ species along with O-vacancies.

Ultrafast pump-probe spectroscopic studies were performed to understand the mechanism of the photocatalytic CO_2 reduction to useful chemicals using different classes of heterogeneous photocatalysts. $[\text{Ru}(\text{bpy})_2]^{2+}$ grafted Ce-based metal organic framework (MOF) photocatalyst, where the ruthenium complex photosensitizer (PS) was used to harvest the visible light, shows the formation of C2 product (acetic acid) by the photoreduction of CO_2 . Femtosecond transient absorption studies showed that upon photoexcitation the ruthenium complex transfers its electron to Ce clusters of MOF with a time constant of 2.7 ps. The extremely slow charge recombination process observed from our studies further indicates that the photo-excited electron from the PS is available for the photocatalytic reaction for a reasonably long time. Such ultrafast electron transfer and extremely slow charge recombination process are mainly responsible for the higher catalytic activity of the ruthenium complex when embedded in the Ce-MOF system. A charge transfer complex, consisting of 1-pyrenebutyric acid (PBA) and methyl viologen (MV), embedded in the Zr-based MOF (MOF-808) was used for efficient conversion of CO_2 to methane with $>99\%$ selectivity. Time-resolved spectroscopy was used to understand the role of the charge transfer complex in the photocatalytic activity. Upon exposure to the light, the PBA unit of the photocatalyst absorbs the light. Due to its strong charge transfer interaction with the MV unit, the electron from photoexcited PBA gets transferred to the MV very fast. The absence of the electron transfer process in a homogeneous solution of PBA and MV suggests the importance

of confinement in the electron transfer process. The extremely fast decay of reduced MV moiety inside the MOF suggests a very efficient transfer of electron from the reduced MV unit to the Zr cluster of MOF, which is the catalytic site for the reduction of CO₂. Ultrafast spectroscopy was also used to understand the electron transfer dynamics in tetrathiafulvalene (TTF) and terpyridine (TPY) based organogels (OG). It was shown that the incorporation of metal nanoparticles in the OG leads to the faster electron transfer from OG to metal nanoparticle which leads to efficient production of methane from CO₂. Our ultrafast spectroscopic studies provide the detailed path of electrons from the photosensitizer to the photocatalytic center. Such information leads to the development of better photocatalysts for the reduction of CO₂.

Way forward:

Chemistry Group has been actively involved in the development of materials towards achieving the net zero goal aligned with the Government of India. The R&D efforts in Chemistry Group involved both the basic and the applied aspects (mostly related to departmental program) and the trend is still continuing. At present, chemistry group is engaged with (i) the development of catalysts/electrocatalysts/membrane electrode assemblies for thermochemical hydrogen generation via Sulphur-Iodine, Hybrid-Sulfur and Copper-Chlorine processes at engineering scale (ii) development of visible light active photocatalysts for hydrogen generation (iii) development of materials for hydrogen storage in engineering scale (iv) research on varied materials for hydrogen storage (v) development of electrodes/electrolytes for Li-ion batteries and Na-ion batteries (vi) development of next generation materials for carbon capture, storage and utilization. The extensive R&D efforts have led to publications in high impact journals, patents, technology transfer to private industries and also deployment in engineering scale processes in BARC. The futuristic activities include the development of catalysts/electrocatalysts for enhanced scale hydrogen generation by thermochemical cycles, scale up of photocatalytic hydrogen generation process under direct sunlight. Devices will be fabricated with full cell operational conditions and sustainable generation of hydrogen through the PEC route. Mechanistic understanding of hydrolysis of boron-based hydrides in the presence of metal nanocomposites will be undertaken. Photocatalytic CO₂ reduction process will be carried out on novel materials to delineate the underlying processes that improve the performance of the photocatalyst.