Next Generation Processes for Carbonate Electrolytes for Battery Applications

Materials Modification Inc.
The Home of Futuristic Materials

Dr. Kausik Mukhopadhyay & Dr. Krishnaswamy K. Rangan

Materials Modification, Inc. 2809-K Merrilee Drive, Fairfax. VA 22031

U.S. DEPARTMENT OF ENERGY

ABSTRACT

❖ Dimethyl Carbonate (DMC) is a promising electrolyte solvent for lithium battery applications due to its inherent safety and robustness. Despite the enormous promise of its industrial use, this chemical is currently entirely imported from China. The global battery market is about US$ 50 billion, of which approximately $ 5.5 billion is captured by the rechargeable batteries for use in electric vehicles, laptops, consumer electronics, rechargeable batteries etc.

❖ Indigenous manufacture of DMC will enormously benefit not only the American lithium battery industry but also other industrial processes that use DMC as a methylating agent and fuel additive.

❖ Existing processes of DMC synthesis either use toxic materials or require improvements in terms of yield. Use of inexpensive raw materials and benign reaction conditions will enable easy manufacture of DMC within the country and *eliminate* reliance on imports. Catalytic conversion of carbon dioxide and methanol is being increasingly considered for the process, but yields have not been encouraging enough for industrial manufacturing.

MMI's APPROACH

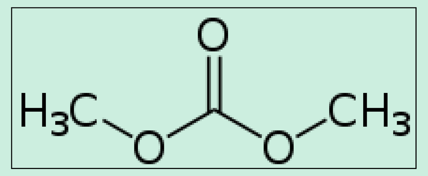
MMI proposes a three-pronged approach for DMC synthesis from CO_2 and CH_3OH by developing an efficient catalyst system and novel pervaporation membrane. Core-shell bimetallic catalysts on inorganic supports will be used as heterogeneous catalysts in a high pressure reactor for DMC reaction. Pervaporation membranes will be used to separate products and enhance the DMC yield (> 15%), thereby making the process economical.

DIMETHYL CARBONATE (DMC)

❖ **WORLD PRODUCTION**
- ❖ 1000 Barrels/ Day (1997)[a]
- ❖ 300,000 – 600,000 Ton/ Year (Future demand)

❖ **USES**
- ❖ Methylating and Carbonylating Agent (Biodegradable)
- ❖ Green Solvent (Non-VOC; Low toxicity) by US EPA, 2009
- ❖ Fuel Oxygenate Additive[§]
- ❖ Carbonate Electrolytes (Battery applications)

❖ **INDUSTRIAL/ DIFFERENT ROUTES**
- ❖ $2CH_3OH + COCl_2$ (Phosgene)
- ❖ Propylene Carbonate + CH_3OH (Transesterification)[b]
- ❖ $CO + O_2 + CH_3OH$ + Catalyst[c]
- ❖ Urea Methanolysis[*]



❖ **ISSUES**
- ❖ Phosgene's toxicity
- ❖ Low Yield and Conversion
- ❖ Product Separation
- ❖ DMC + H_2O → ACETONE

❖ **MMI APPROACH**
- ❖ $CH_3OH + CO_2$ + Heterogeneous Catalyst + Pervaporation

a) *Pacheco et al., Energy Fuels, 1997, 11, 2*
b) *Unnikrishnan et al. I&EC Research, 2012, 51, 6356*
c) *Xu et al., J. Am. Chem. Soc. 2011, 133, 20378*

BIMETALLIC NANOPARTICLES

❖ **MMI's SYNTHETIC ROUTE**
- ➢ Nickel and Copper salts
- ➢ Ligand Precursors
- ➢ Cu^0 on Ni^0 Core-Shell

❖ **CHARACTERIZATION**
- ➢ HRSEM, HRTEM, BET (Particle Size, Shape)
- ➢ XRD, SAED, EDS, XPS (Characteristics & Composition)

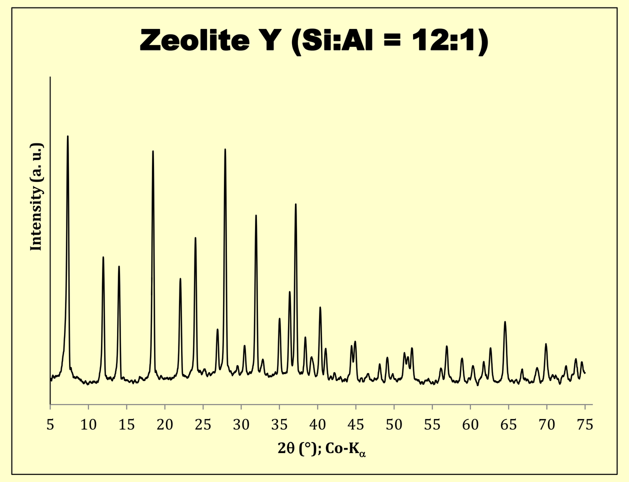
HETEROGENEOUS CATALYST

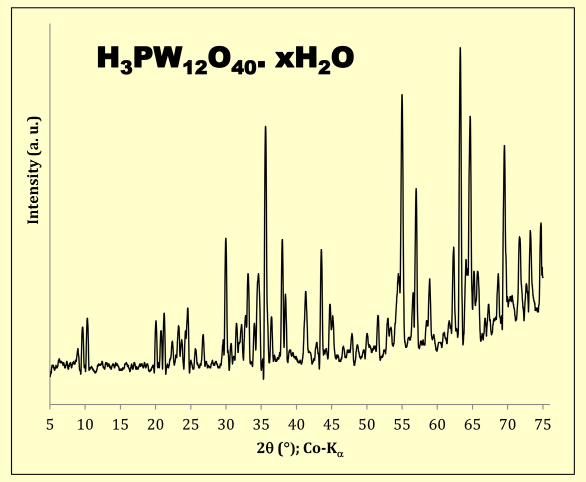
❖ **CATALYST MATRIX**
- ➢ SiO_2, Zeolite, Mesoporous Materials

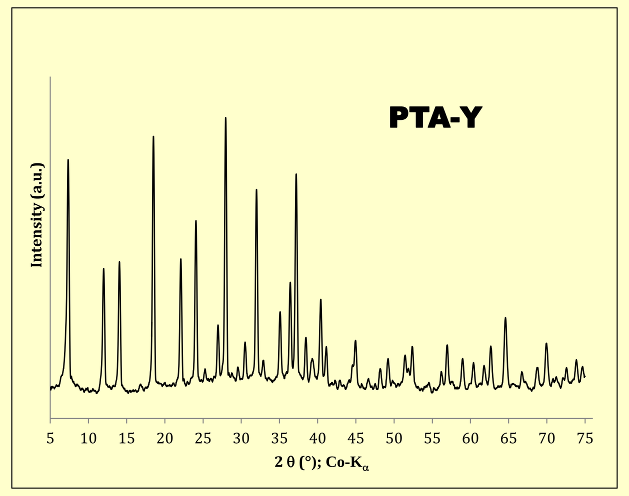
❖ **FUNCTIONALIZATION**
- ➢ APTS ($-NH_2$), PTA ($PW_{12}O_{40}^{3-}$)
- ➢ Incipient Wetness (Matrix, Salts, H_2)

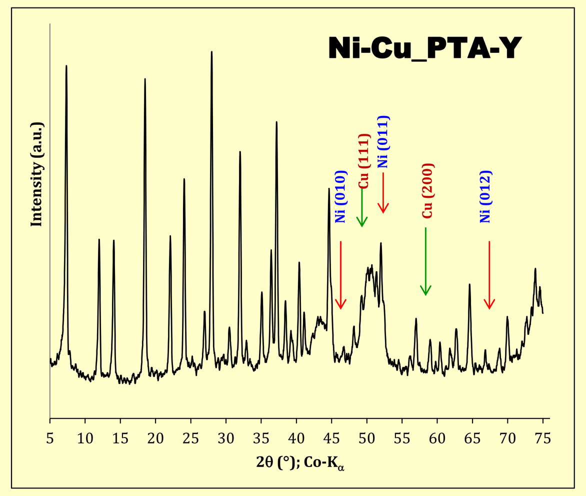
❖ **TETHERING**
- ➢ CuNi_NP-NH_2, CuNi_NP-$PW_{12}O_{40}$

POWDER XRD: CATALYST SYNTHESIS

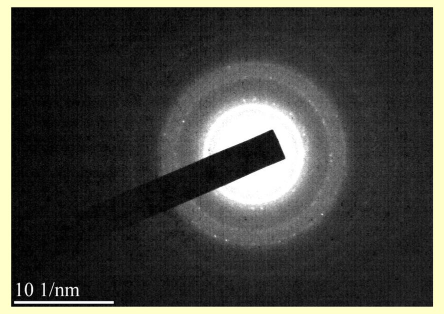






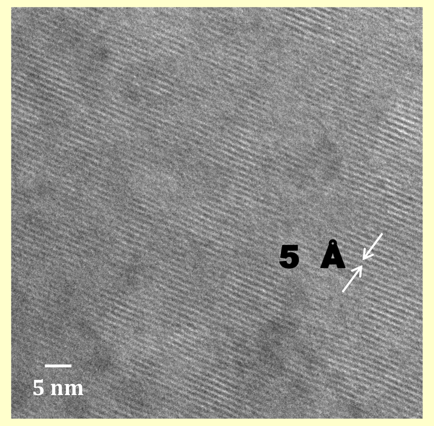


SAED



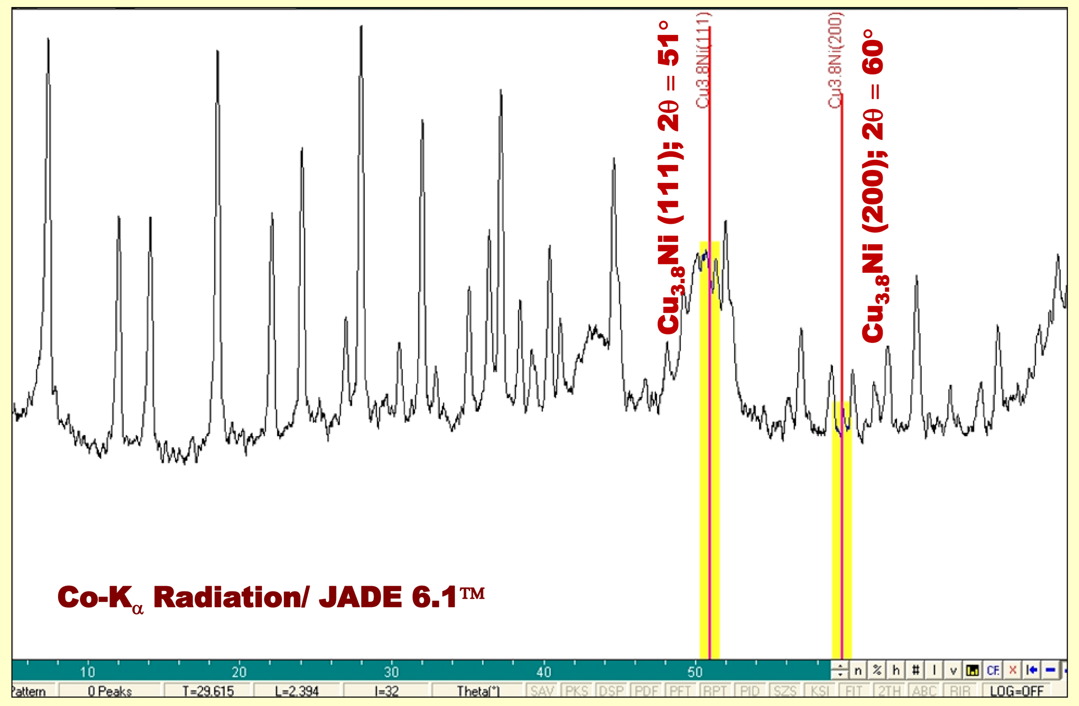
Cu-Ni CSNP

HRTEM

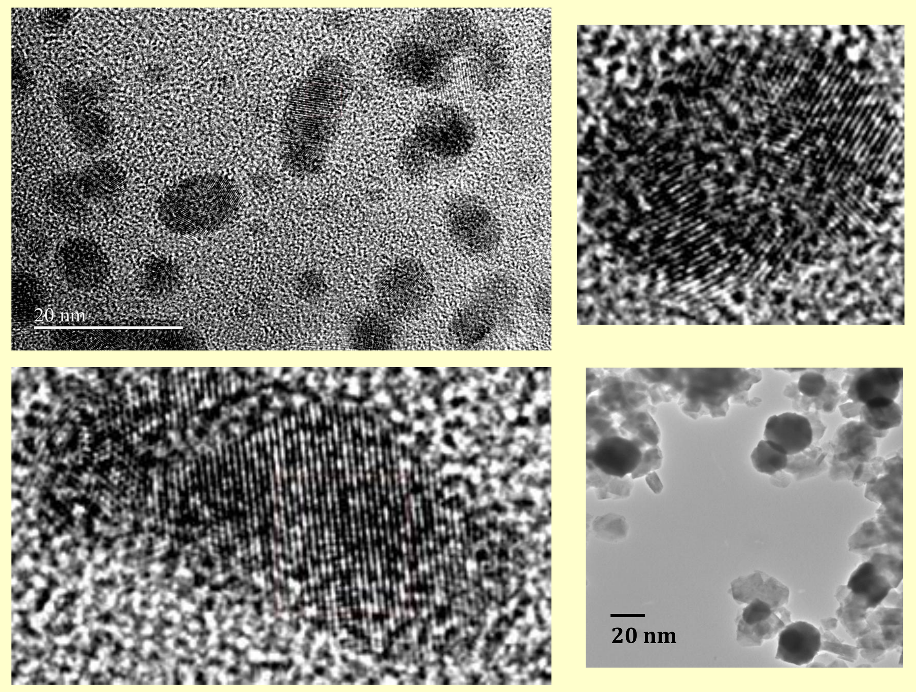


Zeolite Y matrix

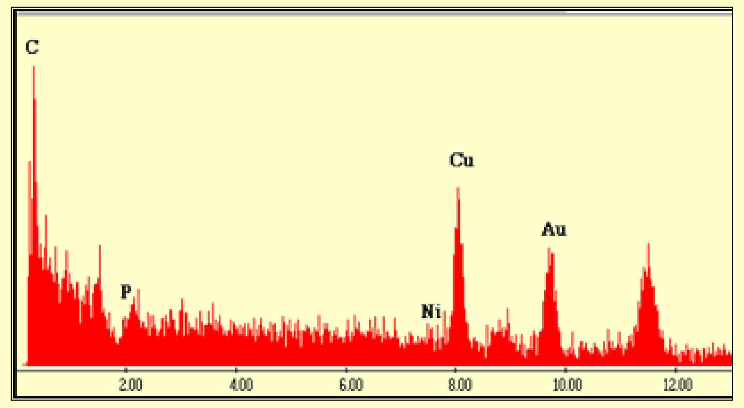
POWDER XRD: Cu-Ni Catalyst

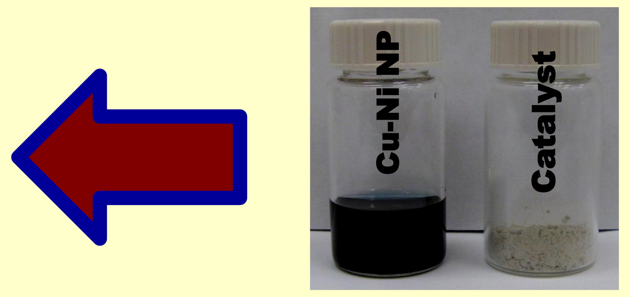


HRTEM

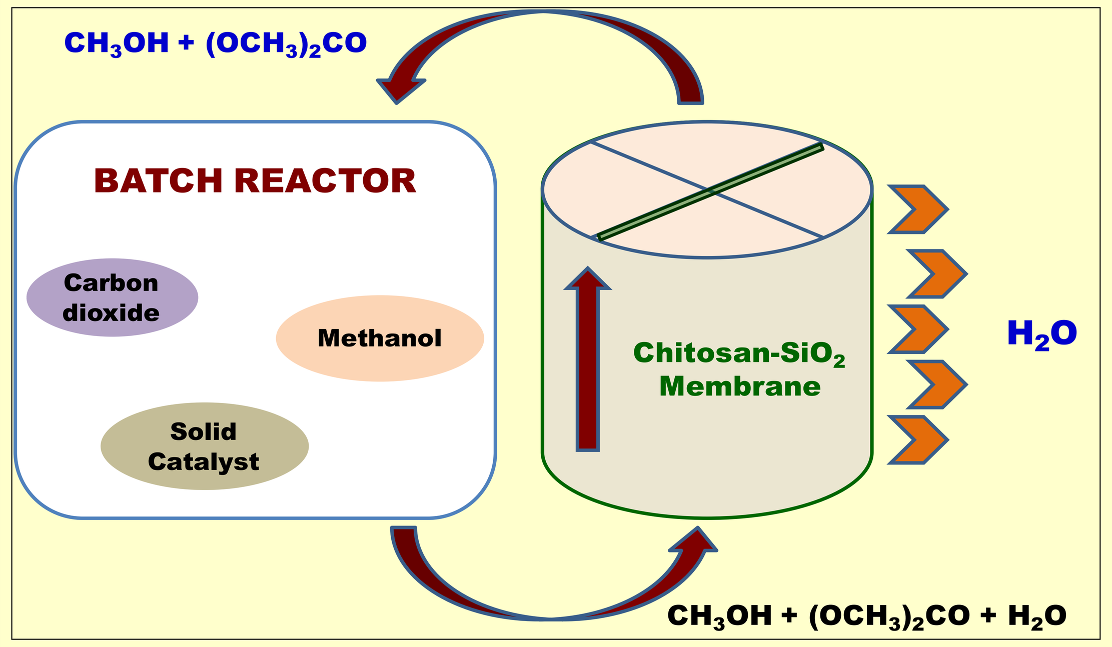


EDS ANALYSIS





DMC CATALYSIS: MMI's APPROACH



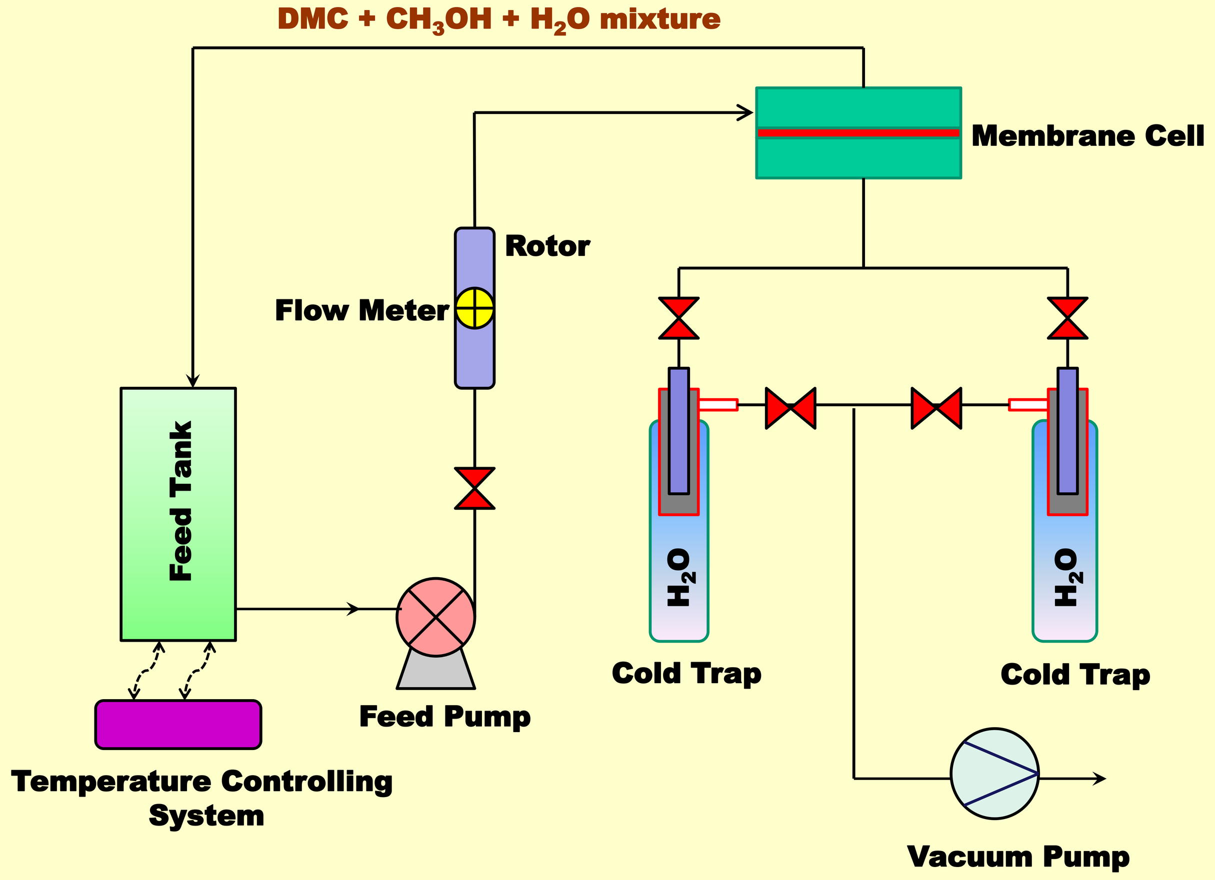
❖ $CO_2 + 2CH_3OH \rightarrow (OCH_3)_2CO + H_2O$
- ➢ GAS-LIQUID-SOLID
- ➢ STIRRED HIGH PRESSURE REACTOR

❖ **PARAMETERS**
- ➢ HETEROGENEOUS CATALYSTS (Solid)
- ➢ SOLVENT (CH_3OH) + REACTANT (CO_2)
- ➢ CONCENTRATION (CH_3OH : CO_2)
- ➢ PRESSURE (~ 1.0 – 1.6 MPa)
- ➢ TEMPERATURE (~ 80 – 130°C)
- ➢ STIRRING FREQUENCY (600 rpm)

❖ **CHARACTERIZATION**
- ➢ GC, GC-MS, HPLC (Products)

❖ **ESSENTIAL STUDIES**
- ❑ SELECTIVITY (Goal: ≥ 15%)
- ❑ ACTIVITY (Conversion & TOF)
- ❑ YIELD (DMC)
- ❑ RECYCLABILITY (Catalyst)
- ❑ CONCENTRATION vs. TIME PROFILE (Reaction Kinetics)

PERVAPORATION SET UP



COMMERCIALIZATION SIGNIFICANCE

Industrial processes using CO_2 as raw material	World capacity per year	Amount of fixed CO_2
Urea	143 Mton	105 Mton
Salicylic acid	70 kton	25 kton
Methanol	20 Mton	2 Mton
Cyclic carbonates	80 kton	~ 40 kton
Poly(propylene carbonate)	70 kton	~ 40 kton

FUTURE PLANS

- ❖ CATALYSIS AND KINETIC STUDY
- ❖ DEVELOP OTHER EFFECTIVE CATALYSTS
- ❖ INCREASE DMC YIELD > 15%
- ❖ DEVELOP NOVEL PERVAPORATION MEMBRANES
- ❖ STUDY COMMERCIALIZATION POTENTIAL

Tasks	Description Months	1	2	3	4	5	6	7	8	9
1	Materials Procurement									
2	Synthesis of Supported Nanocatalysts									
3	Synthesis of Pervaporation Membrane									
4	Design of Reactor									
5	Study of Catalytic Efficiency									
6	Reporting, Planning for Phase II									

SUMMARY OF TASKS PERFORMED

- ❖ SYNTHESIS OF NANO-CATALYSTS
- ❖ DEVELOPED PERVAPORATION MEMBRANE
- ❖ DESIGNED REACTOR SYSTEM
- ❖ CHARACTERIZATION OF CATALYSTS

ACKNOWLEDGEMENTS

♦ Funding: DOE SBIR Phase I Contract # DE-SC0008278 (2012)