Synthesis and Applications of N-Heterocyclic Carbene Based Ionomers in the Catalyst Layer of CO_2 Electrolysers

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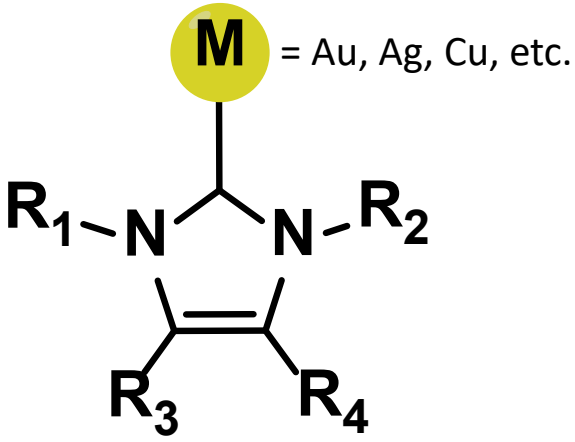
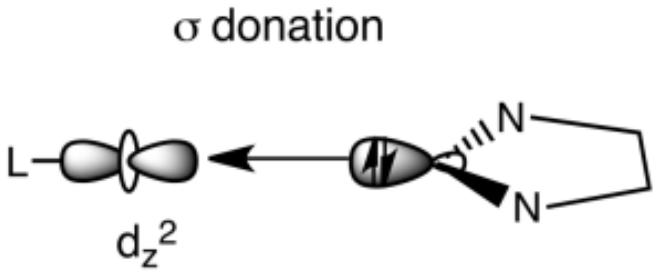
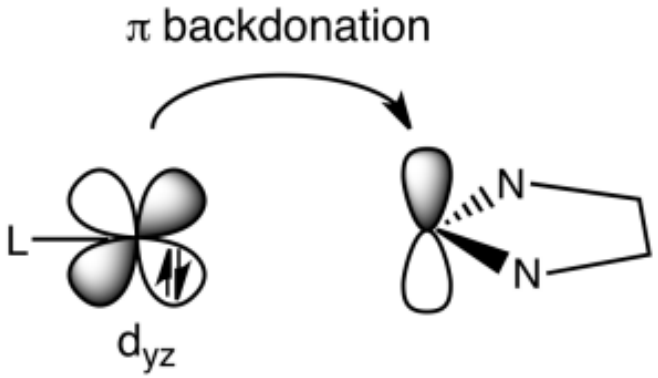
N-Heterocyclic Carbenes

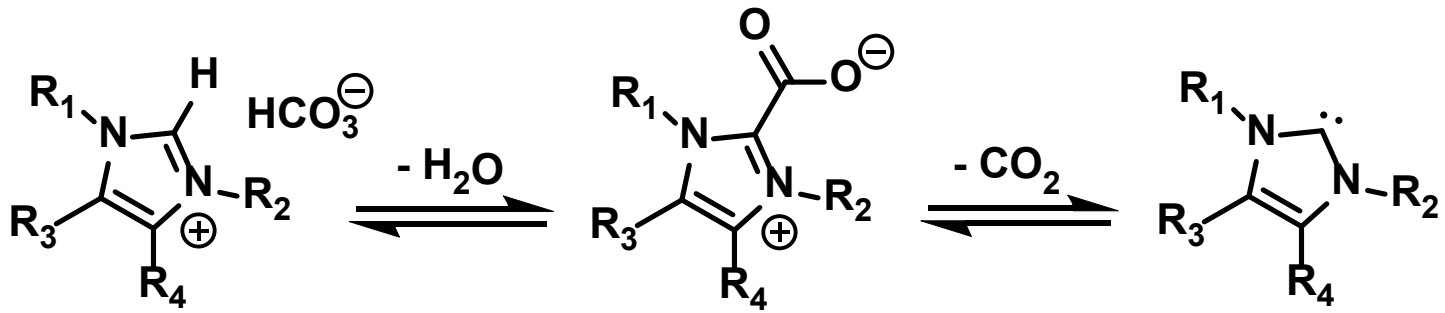


- NHCs have an unoccupied p-orbital, and a sp^2-hybridized lone pair at the C2 carbon
- σ-donor ligands with low π*-backdonating character

[1]



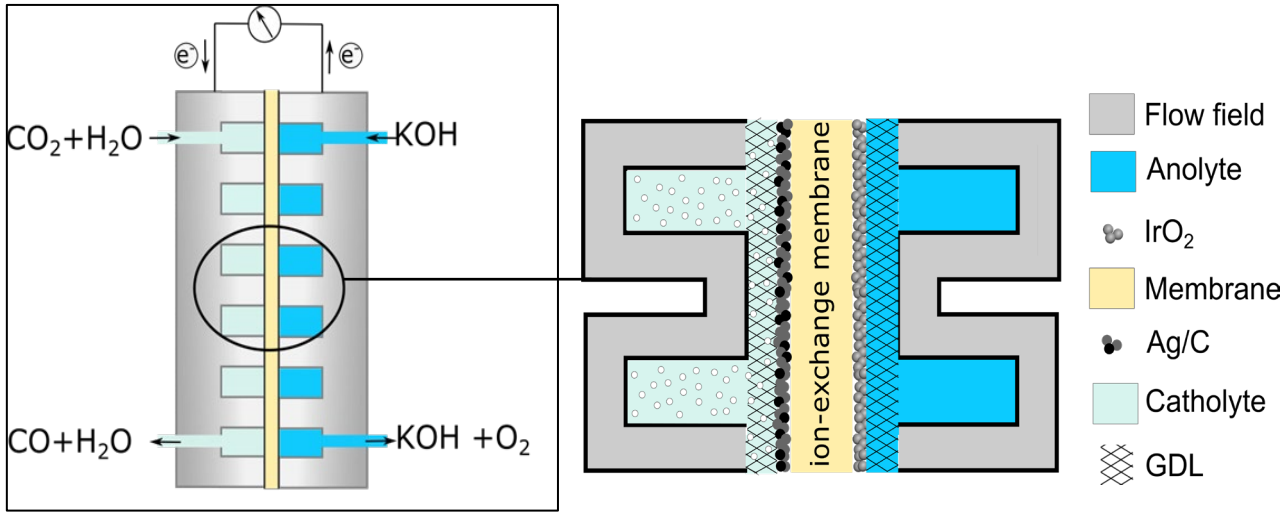


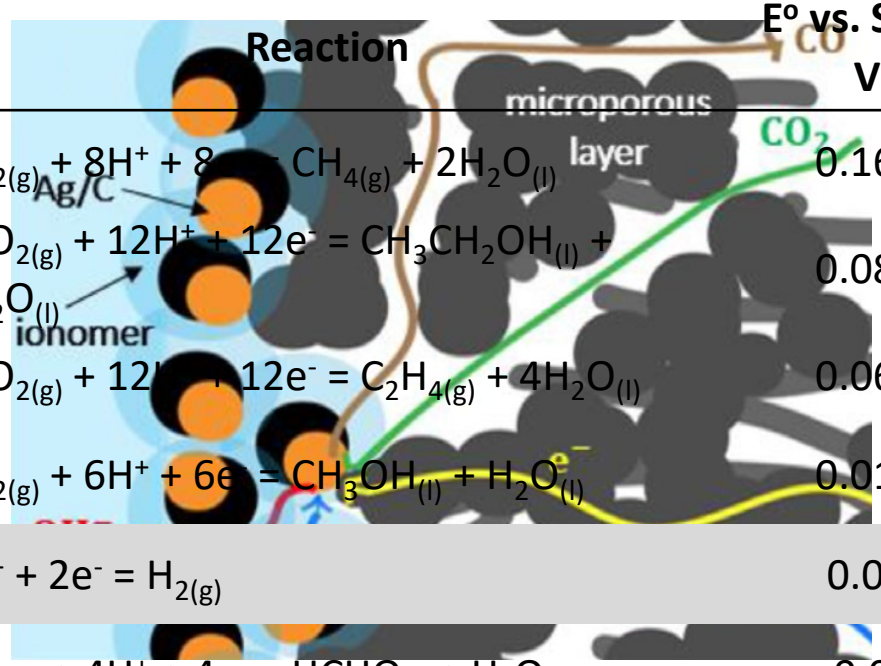


- Imidazolium bicarbonate salts are in equilibrium with free NHCs

[1] Rezabal, E.; Frison, G. *J. Comput. Chem*. **2015**, 36, 564–572.

CO_2 Electrolysis and the Cathode Surface

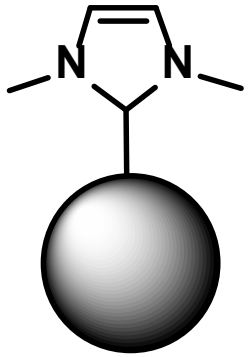




[1] Reaction	E° vs. SHE / V
$CO_{2(g)} + 8H^+ + 8e^- = CH_{4(g)} + 2H_2O_{(l)}$	0.169
$2CO_{2(g)} + 12H^+ + 12e^- = CH_3CH_2OH_{(l)} + 3H_2O_{(l)}$	0.084
$2CO_{2(g)} + 12H^+ + 12e^- = C_2H_{4(g)} + 4H_2O_{(l)}$	0.064
$CO_{2(g)} + 6H^+ + 6e^- = CH_3OH_{(l)} + H_2O_{(l)}$	0.016
$2H^+ + 2e^- = H_{2(g)}$	0.00
$CO_{2(g)} + 4H^+ + 4e^- = HCHO_{(l)} + H_2O_{(l)}$	-0.07
$CO_{2(g)} + 2H^+ + 2e^- = CO_{(g)} + H_2O_{(l)}$	-0.106
$CO_{2(g)} + 4H^+ + 4e^- = C_{(s)} + 2H_2O_{(l)}$	-0.210
$CO_{2(g)} + 2H^+ + 2e^- = HCOOH_{(l)}$	-0.250
$2CO_{2(g)} + 2H^+ + 2e^- = (COOH)_{2(aq)}$	-0.500

Possible effects of using NHC as a binder:

- Reaction environment changes (hydrophilicity)
- Physical blockage (of pores)
- Coordination of CO_2 intermediates



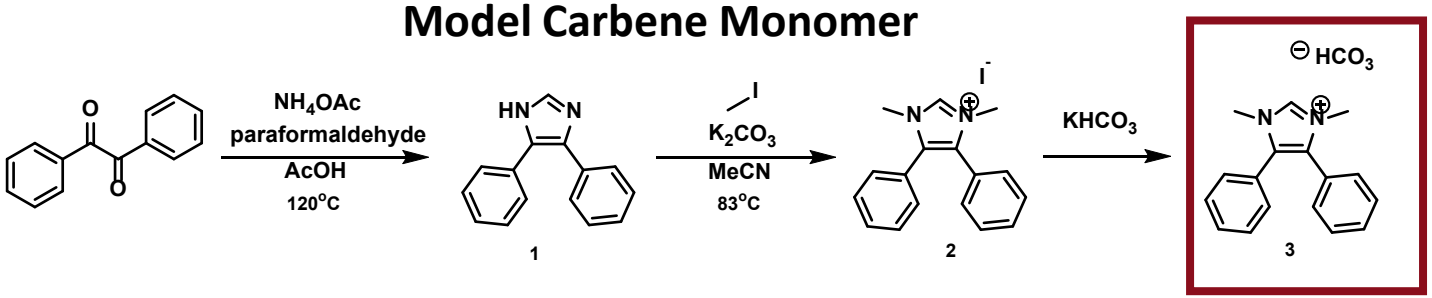
NHC on Au surface

- gaseous phase (CO_2)
- ion conducting phase (electrolyte)
- electron conducting phase (cathode)

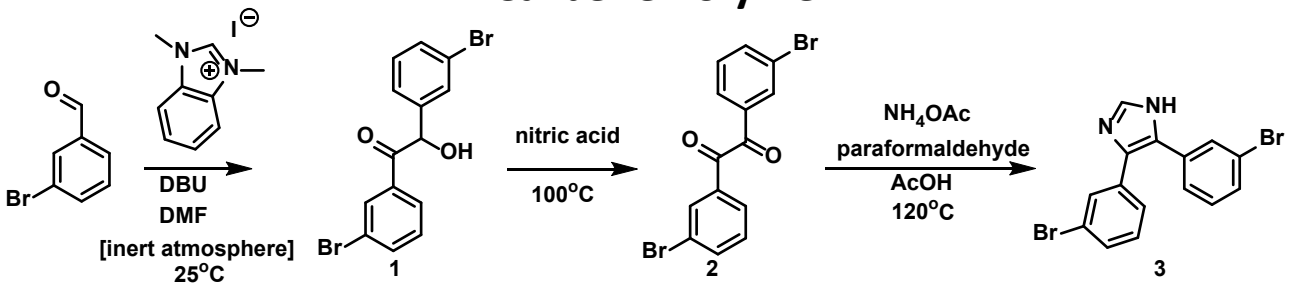
[1] Mardle, P.; Cassegrain, S.; Holdcroft, S *et al., J. Phys. Chem. C,* **2021**, *125* (46), 25446–25454.

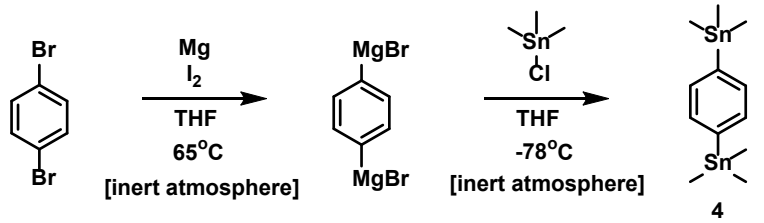
Synthetic Scheme

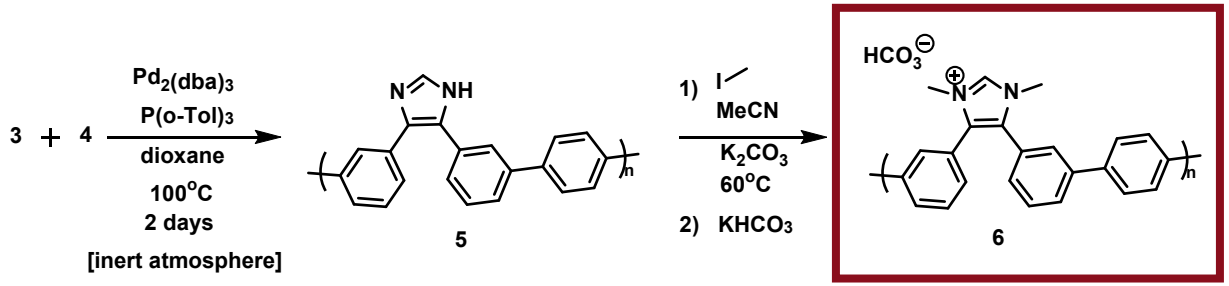
Model Carbene Monomer



Carbene Polymer



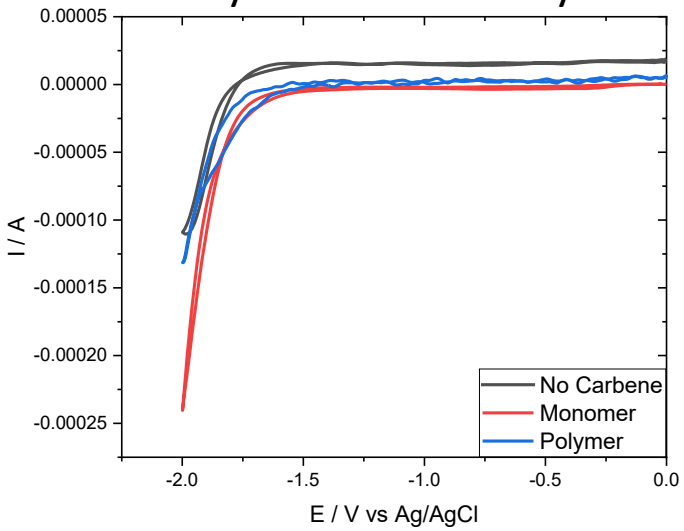




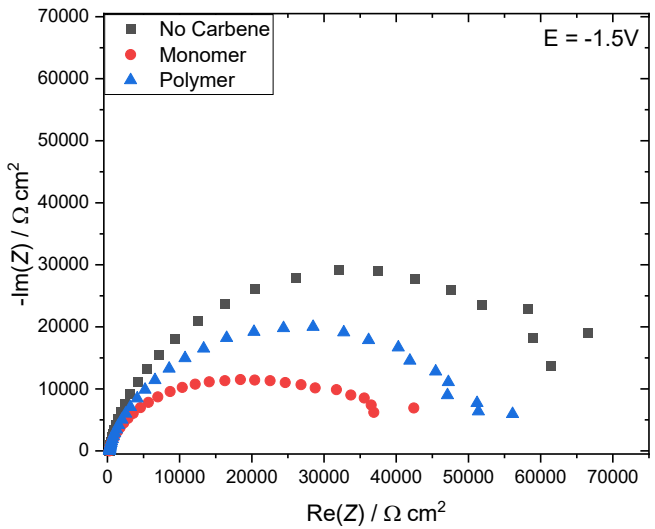
Ex-Situ Studies – Determining Ag-Carbene Binding Effects

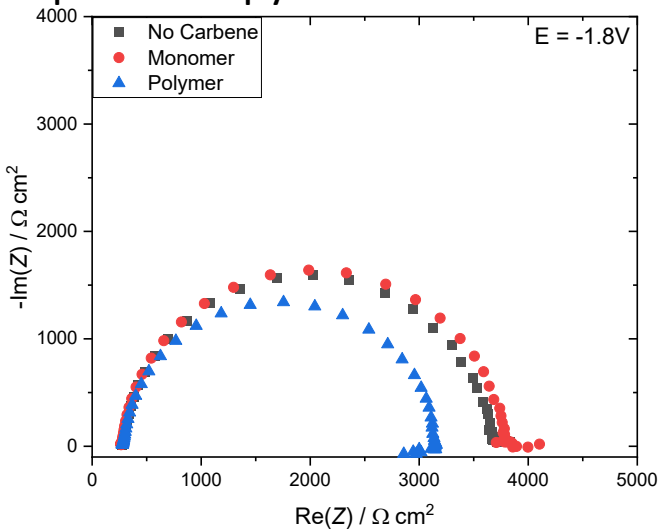
SFU

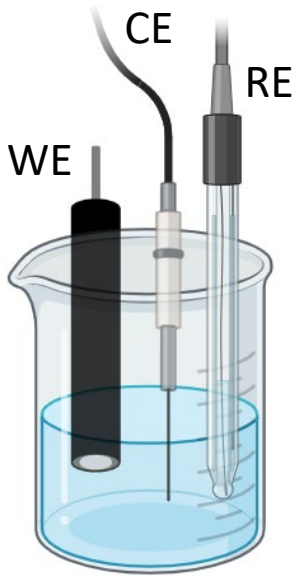
Cyclic Voltammetry



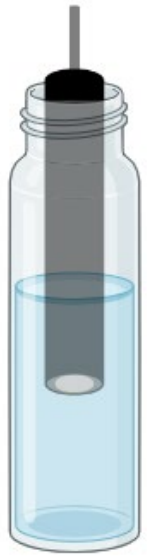
Electrochemical Impedance Spectroscopy







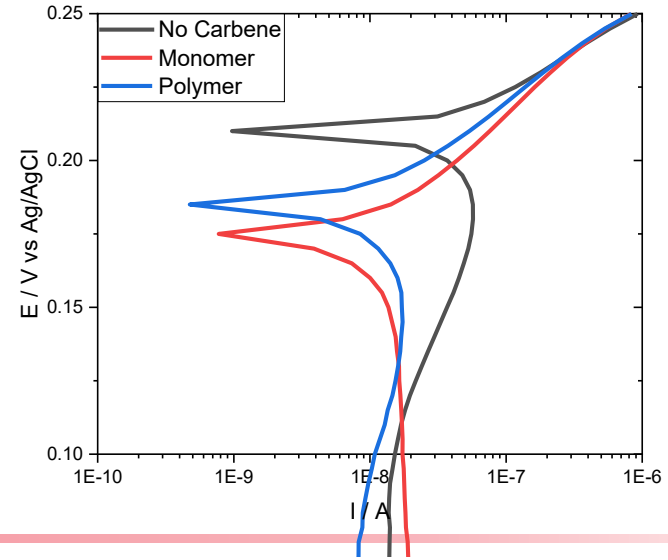
Working Electrode: Silver
Counter Electrode: Platinum
Reference Electrode: Ag/AgCl
10mM $KHCO_3$ electrolyte



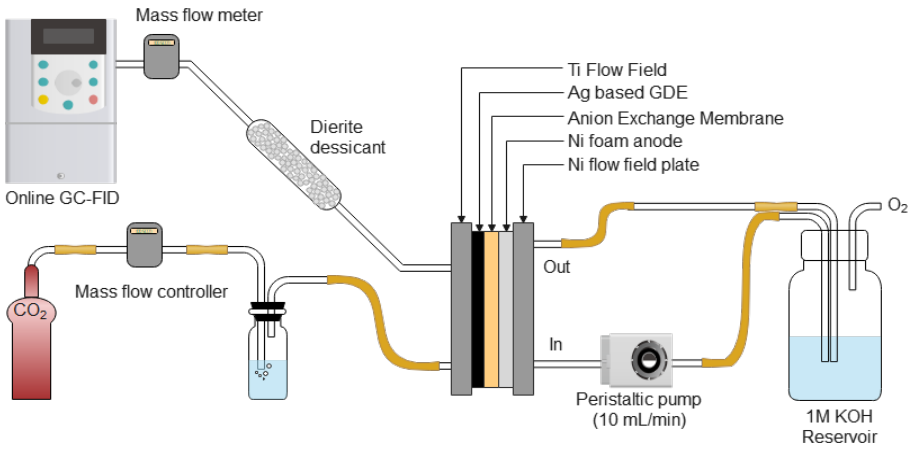
Deposition Method:

- Soak in 10mM solution of carbene in methanol
- Rinse thoroughly before testing

Potentiodynamic Polarization



In-Situ Testing – Preliminary Work

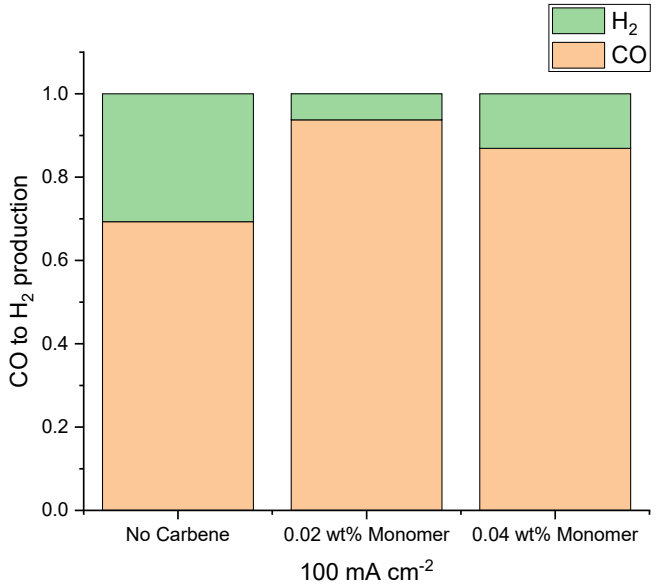


$$A: 2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$$

$$C: CO_2 + H_2O + 2e^- \longrightarrow CO + 2OH^-$$

Anolyte: 10mM $KHCO_3$
Anode: Dioxide (Ir+PFSA)
Membrane: Aemion+ 15µm
Cathode:
0.4 mg_{Ag}/cm^2
80% Ag/C and 20% Ionomer of 1wt% solid

GC results during a 100mA/cm² hold



IV Curve