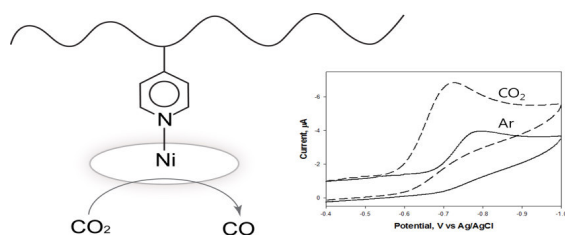


CO₂ Reduction at Low Overvoltage in Neutral Aqueous Solution by Ni-cyclam Attached Polyallylamine Polymer

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Artificial photosynthesis comprise of a light-driven water oxidation reaction and an electrochemical CO₂ reduction in dark. To achieve the efficient CO₂ reduction by the excited electron from the light-driven anodic reaction, the lowering the overvoltage of CO₂ reduction is an essential component. [Ni(cyclam)]²⁺ (cyclam=1,4,8,11-tetraazacyclotetradecane) and its derivatives are known to be efficient in CO₂ to CO conversion and the macrocyclic ligand, cyclam is known to stabilize Ni(I) state. However, those compounds still have ca. 0.6 V of overvoltages and the use of mercury electrode is essential to suppress hydrogen evolution on the electrode at such a negative potential. We found that the incorporation of the Ni(cyclam) unit into polyallylamine (PALA) backbone by Schiff's base condensation via axial coordination of 4-pyridine carboxaldehyde is effective in lowering overvoltage and it enables the catalyst to be used with carbon electrode material in neutral aqueous solution. The resulting redox polymer, Ni(cyclam)-PALA converts CO₂ to CO near its thermodynamic potential, -0.78 V vs. Ag/AgCl in pH 8, 50 mM tris buffer on glassy carbon electrode with current efficiency of over 90%. The axial coordination of 4-pyridine unit is mainly responsible for lowering the overpotential and the attached polyallylamine partly helps.



References

1. Saravanakumar, D.; Song, J.; Jung, N.; Jirimali, H.; Shin, W. *ChemSusChem* 2012 5, 634.