Cobalt Phthalocyanine Active Site Tuning via Atomic Linker Immobilisation for CO$_2$ Electroreduction

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The journey to discover an efficient, stable, and high performing catalysts for CO$_2$ electroreduction reaction (CO$_2$ERR) has taken many roads from surface catalysts to metal-organic frameworks to molecular catalysts. Recent studies have demonstrated enhanced CO$_2$ERR performance for axially immobilised cobalt centred-phthalocyanine (CoPc) via pyridine linker, forming an N5-complex [1,2]. This study focuses on molecular catalysts, in-particular CoPc tuned at its cobalt active site via different atomic linker species (9 species and 10 unique linkers are considered) when covalently immobilised on single-walled carbon nanotubes (SWCNTs). Our investigation is carried out using density functional theory (DFT) calculations at the generalised gradient approximation (GGA) level of theory with D3(BJ) dispersion correction. DFT calculations are done using the Vienna Ab initio Software Package (VASP) plane-wave code. Reaction pathways have been calculated using the computational hydrogen electrode (CHE) method with solvation corrected entropy [3,4]. It is found NH and PH 'atomic' linkers show the best improvement in reaction pathway performance relative to the isolated CoPc catalyst. These linkers are hydrogen terminated, indicating there is an important role played by hydrogen termination of the linker in directly influencing active site properties. Linkers with strong CO$_2$ adsorption, and consequently good CO$_2$ERR, performance are found to have a large number of *d*-orbital states at, or just above, the Fermi level. Transition state, geometries, and corresponding activation energy barriers are calculated to provide more detailed insight into the reaction pathways of both the isolated and linker-immobilised CoPc systems.

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