

Chemical Reactivity of Alkyl Thiolates Used in Electrochemical CO₂ Capture in Ionic Liquids

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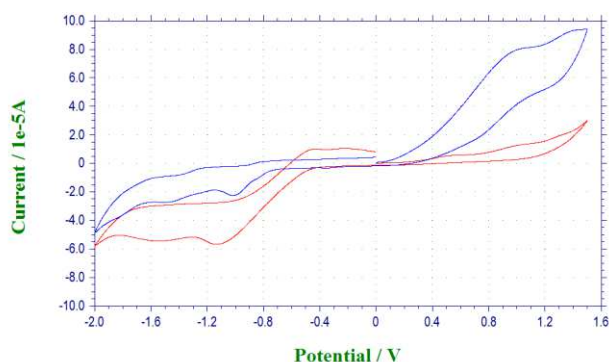
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Separating CO₂ from its mixture with other gases, such as flue gas and natural gas streams rich in CO₂, has been in practice for a long time. Carbamate formation using amines is the only commercially viable method for this purpose but the release process uses a large amount of thermal energy which makes it economically less favorable. A new electrochemical method for CO₂ capture and release, being developed in our lab, offers a more energy efficient way which uses electricity as the energy source, a room temperature ionic liquid (RTIL) as medium and thiolates as capture agents.

ILs are chosen as the capture medium because of high CO₂ solubility and their zero volatility, wide electrochemical stability window, acceptable electrical conductivity.

Alkyl thiolate ions which are used as capture agents are potentially capable of undergoing reactions other than the CO₂ reaction. Thiolates, especially at high temperatures are reactive species. High electron density on the sulfur atom and high polarizability of the atom's HOMO orbital make the thiolates both fairly easily oxidizable and very potent nucleophiles.

Cyclic Voltammetry is used to study the kinetics of thiolate reaction with molecular oxygen (O₂) dissolved in the ionic liquid. The method is used to quantitatively analyze a thiolate solution in IL in the presence of O₂ and measure the thiolate concentration as it reacts with oxygen over time as is shown in the figure below:



The reaction of thiolate with the solvent is also considered and studied by NMR spectroscopy. Nucleophilic substitution reaction of thiolate with quaternary ammonium cations and ether linkage at high temperatures is studied. Quaternary ammonium cations are present both in the ionic liquid and as the thiolate counter ion. Ether linkages of glymes, also sometimes used as solvent, are potentially susceptible to nucleophilic attack from thiolate ion too.