Electrochemistry and Single Entity Plankton

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Phytoplankton are microscopic, photosynthetic plant cells which are too small to be seen with the naked eye.[1] Although they account for less than 1% of the planet's total biomass they are estimated to produce 50% of the atmospheric oxygen. Phytoplankton are remarkably diverse yet they all convert sunlight and dissolved carbon dioxide into particulate organic carbon (biomass). One specific group of phytoplankton, coccolithophores, additionally sequester dissolved carbon dioxide as calcium carbonate (calcite) forming a shell of inorganic ca micron-sized platelets ("coccoliths"). The shells ultimately find their way from surface water to the deep where they may remain for millions of years. It is estimated that more than 10^{15} tonnes of atmospheric CO_2 per year are sequestered in this way! This rate is similar to that of the anthropogenic release of carbon dioxide. For this reason, and because phytoplankton are the basis of the oceanic food chain they are an important sensing target for oceanic health. Moreover as they are not farmed but, as a result of their short lifetimes are quick to respond to local changes in the environment they have been referred to as a 'beacon of climate change".

The lecture will discuss the basis and application of two different electrochemical experiments for monitoring plankton. First electrochemistry in conjunction with optical microscopy[2-4] will show how the quantity of biomineralized CO_2 in the form of calcite can be measured at the single coccolithophore level by combining imaging of the cell as it is exposed to electrogenerated protons which chemically react with and remove the shell. Knowledge of the diffusion field around a wire electrode in a bespoke electrochemical cell coupled with a knowledge of the rate of proton induced calcite dissolution allows the determination of $CaCO_3$ masses spanning over three orders of magnitudes, ranging from tens of pico-grams to tens of nanograms.

Second electrochemical-fluorescence measurements allow the counting and identification of plankton.[5-7] By immobilizing phytoplankton cells on an electrode and applying a controlled potential step or galvanostatic sweep the chlorophyll fluorescence is monitored as a function of time to reveal a rapid species-specific decay of fluorescence with the different switch-off times and fluorescence transient shape reflecting differences in exoskeleton structure, cellular membranes and cellular biology allowing the development of a low-powered, automated fluoroelectrochemical based sensor so facilitating phytoplankton classification and identification within tens of seconds., the task being simplified by the use of a 1-D inception neural network[6] to analyze the fluoro-electrochemical transients of 500 unseen phytoplankton single cell transients spanning 29 phytoplankton strains, into their taxonomic orders with a better than 95% accuracy.The methods were validated against microscope taxonomy and flow cytometry and applied to field testing in the summer of 2023 allowing observation of phytoplankton blooms associated with the coccolithophore *E.huxleyi*.

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