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IMMOBILISATION OF NI-CROWN POM FOR THE Electrocatalysis of bromate and chlorate in water

Bushra Ali and Timothy McCormac

Dundalk Institute of Technology, Ireland

Polyoxometalates (POM) are versatile and attractive compounds due to their molecular and structural diversity which have a broad range of applications in different fields, such as, electronics, electrocatalysis, sensors and nanotechnology. The aim of the present research work is the immobilisation of POMs onto the surface of glassy carbon electrode (GCE) to investigate their potential applications towards the electrocatalysis. A successful immobilisation of the POMs is important for their applications; two immobilisation methods are employed in this study: the layer-by-layer and incorporation into polymeric matrixes. These methods were investigated to immobilise Ni₄ ($P_8W_{48}O_{148}$)(WO₂)]²⁶⁻) POM by using glassy carbon electrode and it's electrocatalytic applications towards the chlorate and bromate. For the LBL method to build the cationic layer, a polyethylenimine (PEI) modified silver nanoparticles (AgNP's) were selected. It was found that the presence of AgNP's within the multilayer assemblies enhanced the electrocatalytic activities of immobilized POM on glassy carbon electrode (GCE) in aqueous solutions. Films were further characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) was employed to determine their elemental composition and surface morphology. The possibility of the fabrication of polypyrrole films doped with Ni-substituted crown-type POMs Ni₄ ($P_8W_{48}O_{148}$)(WO₂)]²⁸⁻ was investigated on glassy carbon electrode by chronocoulometry in aqueous buffer. Amperometric sensors for the detection of bromate based on the Ni-substituted crown type POM Ni₄ ($P_8W_{48}O_{148}$)(WO₂)]²⁸⁻ was investigated with high sensitivity in a linear range of 0.1-5 mM bromate.

Bushra.ali@dkit.ie



Figure1: (a) CV of a multilayer film comprised of 4-bilayers of AgNP's/[Ni₄(P₈W₄₈O₁₄₈)(WO₂)] ²⁸⁻ in pH 2.0 buffer at a scan rate of 10mVs⁻¹. (b) Typical amperometric response of the bare glassy carbon electrode (BGCE) (A= 0.0707 cm²) with in comparison of a chloride dopped polypyrrole (PPY-Cl) and a Ni₄ (P₈W₄₈O₁₄₈) (WO₂)]²⁸⁻ POM+ PPY in pH 2.0 buffer up to 2 mM