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FASTER INTERFACIAL ELECTRON TRANSFER AND La(III) SQUARE-WAVE RESPONSE AT A NAPA-SOIL-DERIVED $NiAl_2O_4$/MWCNT PASTE ELECTRODE

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ABSTRACT

Alumina isolated from Napa soil was converted to $NiAl_2O_4$ and blended with a multiwalled carbon nanotube (MWCNT) paste to examine whether a mineral-derived spinel could accelerate electrode kinetics and generate a square-wave voltammetric signal for La(III). FTIR and XRD provided evidence for the nickel-aluminate spinel, while SEM showed rough agglomerates dispersed through the nanotube matrix. In the ferri/ferrocyanide test, incorporation of $NiAl_2O_4$ raised the anodic current from 6.117 to 8.246 µA and the cathodic current from 4.834 to 5.463 µA. The corresponding charge-transfer resistance fell from 38.0 to 2.0 kΩ, a 94.7% decrease, and the apparent heterogeneous electron-transfer rate constant rose from 8.75×10^{-5} to 1.66×10^{-3} cm s^{-1}, approximately nineteen times the control value. Screening of composition and operating variables identified 5% (w/w) $NiAl_2O_4$, 0.05 M KNO_3, pH 2.0, 90 Hz, a 2 mV step, an 80 mV pulse, and 15 s equilibration as the conditions producing the largest La(III) response. The signal varied with La(III) concentration between 1.0×10^{-7} and 1.0×10^{-2} M, although complete analytical validation remains necessary. Transforming a regional mineral resource into an electroactive modifier advances materials innovation consistent with Sustainable Development Goal-9, Industry, Innovation and Infrastructure.

Keywords: Lanthanum(III), Square-Wave Voltammetry, Nickel Aluminate, Multiwalled Carbon Nanotubes, Electron-Transfer Kinetics, Napa Soil.

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INTRODUCTION

Lanthanum-containing materials are important in catalysis, optics, ceramics, and several high-technology products. The wider circulation of these materials creates a practical need to measure La(III) in laboratory and environmental matrices. Highly sensitive instrumental techniques are available, yet routine use may be constrained by capital cost, operational demands, and sample treatment. Voltammetric analysis offers a more accessible route, and the square-wave waveform is particularly efficient because forward and reverse current sampling improves speed while limiting the contribution of charging current.[1–3] For an SWV measurement, the chemical and electrical properties of the electrode interface control the observed signal. MWCNTs can maintain conductive pathways and expose a large contact area, whereas a spinel oxide can supply additional surface sites for interfacial interaction. Electrochemical applications of $NiAl_2O_4$ have been reported, and recent work continues to demonstrate the value of voltammetric interfaces for trace-metal measurements.[4–6] However, most $NiAl_2O_4$-based sensors use commercial or high-purity aluminium reagents and focus on organic targets. Evidence is still lacking for an MWCNT paste containing $NiAl_2O_4$ produced from Napa soil alumina and evaluated against La(III). Napa soil, an aluminosilicate resource found in West Sumatra, can yield enriched silica and alumina fractions suitable for conversion into higher-value products.[7,8] Using its recovered alumina to prepare an electroactive oxide extends that valorisation pathway from bulk materials to electrode components. The approach also provides a concrete connection to Sustainable Development Goal-9 (Industry, Innovation and Infrastructure): a locally available feedstock is processed into a functional material for analytical

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technology. This work therefore converted Napa-soil alumina to $NiAl_2O_4$, incorporated it into an MWCNT paste, and assessed electron-transfer behaviour and the La(III) SWV response. It addresses an unreported combination of a Napa-soil precursor, a $NiAl_2O_4$/MWCNT paste, and a rare-earth target. The principal outcome was a 94.7% fall in charge-transfer resistance and an approximately nineteen-fold increase in the apparent heterogeneous electron-transfer rate constant.

EXPERIMENTAL

West Sumatran Napa soil supplied the alumina. Recovery followed the published sequence of thermal treatment, hydrochloric-acid leaching, precipitation, drying, and final calcination.[7] Nickel nitrate hexahydrate, citric acid, HCl, NaOH, $K_3[Fe(CN)_6]$, KCl, KNO_3, $LaCl_3 \cdot 7H_2O$, MWCNTs, and paraffin oil were analytical-reagent grade and were used without further purification. $NiAl_2O_4$ was produced by a citrate-assisted sol-gel route from nickel nitrate and the recovered alumina, followed by gel drying and calcination. FTIR, XRD, and SEM examined bonding, crystalline phase, and morphology. Working pastes contained 100 mg MWCNTs, 5, 10, or 15% (w/w) $NiAl_2O_4$, and four drops of paraffin oil. After homogenisation, each paste was packed into a Teflon holder and contacted with a copper wire. The control paste contained no oxide. The paste electrode, Ag/AgCl, and platinum wire served as the working, reference, and counter electrodes. CV and EIS were recorded in 4.0 mM $K_3[Fe(CN)_6]$/0.1 M KCl. CV covered -1.0 to +1.0 V at 100 mV s^{-1}; EIS covered 1 Hz to 1 MHz with a 5 mV perturbation. La(III) was examined by SWV while the modifier fraction, electrolyte, pH, frequency, potential step, pulse amplitude, and equilibration time were varied. The selected conditions were then applied to 1.0×10^{-7} to 1.0×10^{-2} M La(III) solutions for a preliminary concentration-response assessment.

RESULTS AND DISCUSSION

Structural and Morphological Characterisation

The three characterisation techniques supplied complementary evidence for the material incorporated into the paste (Fig.-1). Absorptions at 414.58, 506.18, and 833.47 cm^{-1} fall in the metal-oxygen region expected for nickel aluminate. Diffraction maxima at 2θ = 37.17°, 43.36°, and 45.23° were consistent with the assigned spinel phase.[4,6,7] Electron micrographs showed rough, irregular agglomerates rather than a smooth compact solid. In the composite image, these particles occur among the nanotube features, indicating physical integration of the oxide with the conductive carbon matrix. Taken together, the spectra, diffraction pattern, and morphology justify using the recovered-soil product as the inorganic fraction of the electrode.

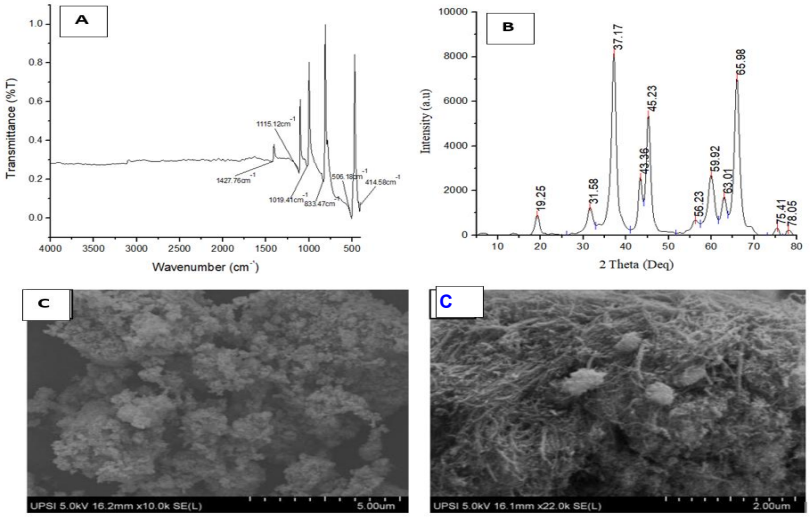


Fig.-1: Physicochemical Evidence for the Soil-Derived Modifier: (A) FTIR Spectrum, (B) XRD Pattern, and (C) SEM Micrographs of $NiAl_2O_4$ before Mixing (left) and after Incorporation into the MWCNT Paste (right)

Interfacial Electron-Transfer Enhancement

The ferri/ferrocyanide probe yielded two independent indicators of faster interfacial kinetics (Fig.-2). First, the modified paste produced larger peak currents: the anodic signal rose by 34.8% and the cathodic signal by 13.0%. Second, impedance fitting showed that charge-transfer resistance declined from 38.0 to 2.0 kΩ.

This 94.7% decrease was accompanied by an increase in the apparent heterogeneous electron-transfer rate constant from 8.75×10^{-5} to 1.66×10^{-3} cm s^{-1}. The simultaneous current enhancement, resistance decrease, and rate increase indicate that the response cannot be attributed solely to a change in apparent area. Instead, the composite creates a more permissive electron-transfer interface, plausibly through continuous MWCNT conduction coupled with accessible $NiAl_2O_4$ sites, as observed for related oxide-carbon systems.[4,6,9]

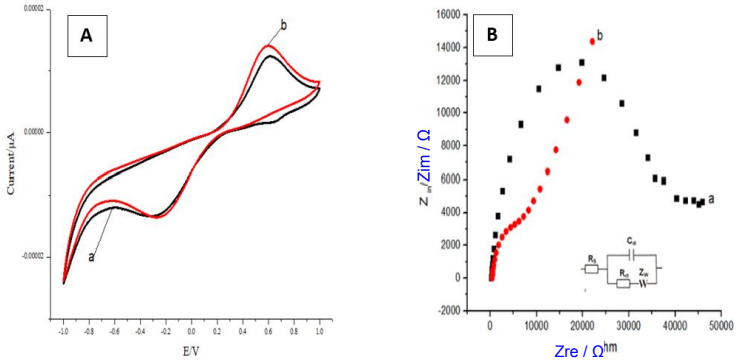


Fig.-2: Kinetic Comparison of the Control and Modified Pastes in 4.0 mM K_3 [$Fe(CN)_6$] plus 0.1 M KCl: (A) Cyclic Voltammograms and (B) Nyquist Responses; a Denotes the Unmodified MWCNT Paste and b Denotes the $NiAl_2O_4$/MWCNT Paste

Optimisation of Electrode Composition and Supporting Medium

Modifier content produced a non-linear response rather than a continual increase in current (Fig.-3A). Adding 5% (w/w) $NiAl_2O_4$ generated the sharpest and largest La(III) peak, whereas the 10 and 15% formulations gave lower, broader signals. Thus, the oxide is beneficial only while the conductive nanotube network remains sufficiently continuous. At higher fractions, replacement or separation of conductive carbon by the less-conductive oxide probably offsets the additional surface sites. Electrolyte screening also produced a pronounced matrix effect (Fig.-3B). Of the chloride, acetate, nitrate, and sulfate media examined, KNO_3 gave the most intense and clearly resolved peak. This observation indicates that the La(III) response depends not only on ionic strength but also on the specific ions present near the paste-solution boundary. Such dependence is consistent with the known influence of supporting electrolytes on migration suppression, background current, and voltammetric peak shape.[3,10] Subsequent experiments therefore used the 5% composite in KNO_3.

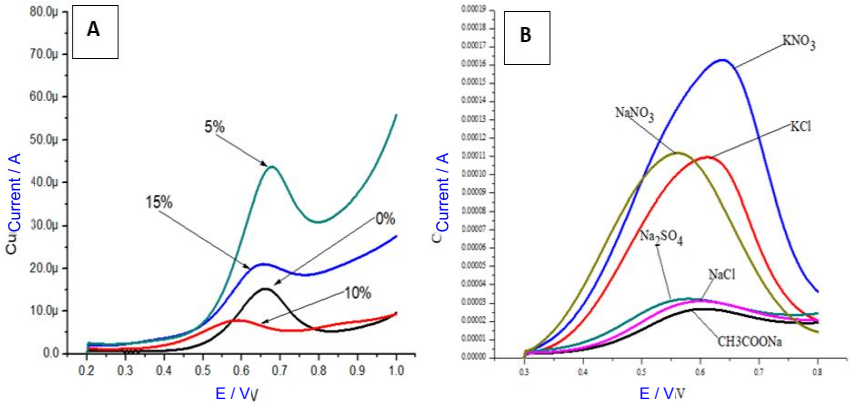


Fig.-3: Screening of Factors that Define the La(III) Signal: (A) $NiAl_2O_4$ Fraction in the Paste and (B) Supporting-Electrolyte Composition

Optimisation of Solution and SWV Parameters

Salt concentration, acidity, and waveform settings each altered the observed current (Fig.-4). The response reached its maximum in 0.05 M KNO_3 at pH 2.0 and declined when the solution became less acidic. Within the tested waveform range, 90 Hz produced the strongest useful response, while a 2 mV potential increment preserved peak definition. Increasing pulse amplitude raised the current up to 80 mV. The equilibration study selected 15 s. Combining these findings gave the operational set used for the

concentration experiment: 5% $NiAl_2O_4$, 0.05 M KNO_3, pH 2.0, frequency 90 Hz, step size 2 mV, pulse size 80 mV, and equilibration time 15 s.

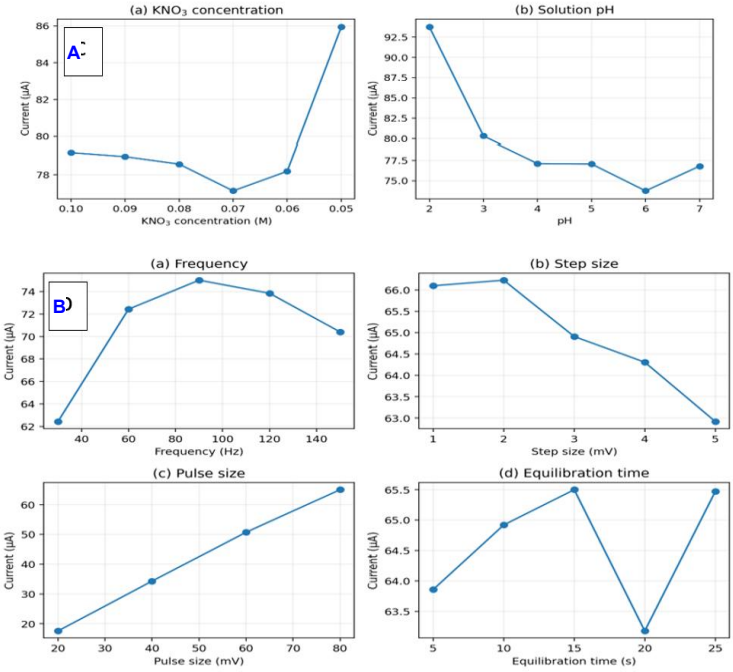


Fig.-4: Optimisation Profiles for the Selected Composite: (A) Effects of KNO_3 Concentration and pH and (B) Effects of Frequency, Potential Step, Pulse Amplitude, and Equilibration Period

Analytical Significance, Limitation, and SDG Relevance

When the optimised settings were applied, the SWV signal varied across La(III) solutions from 1.0×10^{-7} to 1.0×10^{-2} M. This experiment demonstrates concentration responsiveness, but it should be interpreted as proof of concept rather than as complete method validation. Alongside the CV and EIS evidence, it shows that $NiAl_2O_4$ made from recovered Napa-soil alumina functions within an MWCNT paste and modifies both kinetic and target-ion response. The combination of a regional mineral precursor, a nanotube matrix, and a rare-earth analyte differentiates this platform from earlier nickel-aluminate sensors prepared from conventional reagents.[4,6,7] From an SDG-9 perspective, the study illustrates how local mineral processing can feed directly into the development of an analytical-material prototype. Several analytical questions remain outside the present dataset. A subsequent validation study should determine the linear portion of the calibration, regression statistics, sensitivity, limits of detection and quantification, repeatability, electrode-to-electrode reproducibility, tolerance to competing ions, recovery, and accuracy in real matrices. Reporting the current work as an interface-enhancement and preliminary response study keeps the claims proportional to the available evidence and defines the experiments needed before routine measurement can be proposed.

CONCLUSION

Converting alumina recovered from Napa soil into $NiAl_2O_4$ produced an effective modifier for an MWCNT paste electrode. Relative to the control paste, the composite increased both ferri/ferrocyanide peak currents, lowered charge-transfer resistance by 94.7%, and raised the apparent heterogeneous electron-transfer rate constant approximately nineteen-fold, demonstrating substantially easier interfacial electron transfer. The largest La(III) square-wave signal occurred with 5% $NiAl_2O_4$ in 0.05 M KNO_3 at pH 2.0, using 90 Hz, a 2 mV step, an 80 mV pulse, and 15 s equilibration. The work therefore establishes a proof-of-concept route from a local aluminosilicate resource to an electroactive component and aligns with SDG-9. Calibration performance, detection capability, precision, selectivity, recovery, and real-sample accuracy should be established in the next stage.

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CONFLICT OF INTEREST

The authors report no financial or non-financial interests that could have influenced this study.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-9: Industry, Innovation and Infrastructure*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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