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Regal Electrochemistry: British 5 pence coins provide useful metallic macroelectrode substrates

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Abstract

The utilisation of British Currency (GBP) as an electrode substrate is demonstrated for the first time. Termed *Regal Electrochemistry,* a 5 pence (GBP) coin is electrically wired using a bespoke electrochemical cell and is electrochemically characterised using the outer-sphere redox probe hexammineruthenium (III) chloride. The electroanalytical utility of the 5p coin electrode is demonstrated towards the novel, proof-of-concept sensing of lead (II) ions using square-wave voltammetry in model buffer solutions over the linear range 5 – 2000 nM exhibiting a limit of detection (3σ) of 1.97nM. Interestingly, the actual cost of the electrode is 2.5 pence (GBP) since both sides of the coins can be utilised and provide a cheap yet reproducible and disposable metallic electrode substrate that is electrochemically useful.

Keywords: Novel electrode substrates; 5 pence electrode; 5 pence sensor; environmental electrochemistry; lead detection.

Introduction

Electroanalysts are always searching for new materials that are both economical and electroanalytically useful. To this end, a wide array of different materials are explored in the hope of finding the next low cost, reliable sensor that, if applicable, is useable in-the-field (disposable) and shows good sensitivity towards the target analyte.

One analyte that demands attention is the sensing of lead (II) ions which continues to be one of the most problematic toxic heavy metals which has caused environmental contamination and health problems around the world.[1-3] It acts as a cumulative toxicant that affects different body systems including the neurological, haematological, gastrointestinal, cardiovascular and renal systems. Children are particularly vulnerable to the neurotoxic effects of lead, even at even relatively low levels of exposure, potentially causing serious and irreversible neurological damage. [1, 3] As a result of its negative health affects, lead (II) ions are regulated by the World Health Organisation (WHO) to a maximum of 10 ppb (48.26 nM) within drinking water[4] mirrored by the United States Environmental Protection Agency (EPA) which states no higher than 15 ppb (72.39 nM) in drinking water.[5] There is a need for the on-site detection of lead (II) ions using portable, inexpensive and sensitive analytical methods with electrochemical techniques providing a potential solution. In the literature there are various attempts at the electrochemical quantification of lead (II) ions [2, 6-14] such as DNA electrodes,[6] carbon nanotubes,[8] carbon ionic liquid electrodes,[9] screen-printed sensors[12] and reduced graphene oxide modified screen-printed sensors..[14]

In this communication, it is demonstrated for the first time, that British coinage, namely a 5 pence (GBP) coin, can be used as a novel electrical substrate. For this new branch of electrochemistry the phrase '*'Regal Electrochemistry*'' has been coined. Through the use of information readily available from the Royal mint website,[15] the composition of the current coins in circulation is known and presented in Table 1.[15] The British 5 pence (GBP) coin offers the potential to produce a range of low cost electrochemical sensing platforms that are reproducible and particularly useful as they are two sided , placing their value at 2.5 pence per sensor. This is primarily useful when the electroanalytical protocol is intended to be implemented into third world countries where the realisation of low cost, reliable sensors is imperative to applications such as heavy metals testing nevertheless, there is no reason to suggest that '*Regal*' electrochemical sensors cannot be 'coined' for other analytical applications.

Results and Discussion

British coinage was obtained and treated as described in the experiment with which to test the theory that coins can be potentially utilised as novel electrode substrates; to the best of our knowledge, there are no reports using coins as electrochemical substrates. To test the coins electrochemical reactivity towards the detection of lead ions, two coins, held within a bespoke Polytetrafluoroethylene (PTFE) 'housing unit' (See ESI Figure 1), were subject to 'electrolysis' to allow the ions to deposit on the surface. To this end, the two coins were independently held at a suitably negative potentials (-1.2V) in an aqueous pH 4 acetate buffer solution containing 1000nM Pb(II) (lead (II) nitrite) to allow the deposition of lead, in the form of lead metal onto the coins surface to occur. As is visible in Figure 1i), scanning electron microscope (SEM) images following Scanning Electron Microscope Energy-Dispersive X-ray microanalysis (SEM-EDX). Note: EDX was employed as confirmatory analysis to see whether the coins contain no impurities and to show if lead is present on the surface following deposition. It was also utilised to confirm the sheet nickel metal used (see later) was pure Nickel. Discernible from Figure 1 is that the deposition of metallic lead shows a much higher affinity of adsorption on the 5p coin minted post-2012 (Figure 1ii)B) opposed to the surface of coins minted prior to 2012 (Figure 1ii)A). As previously mentioned, in information readily available from the United Kingdom's Royal Mint, the composition of a 5p coin since January 2012 has been nickel plated steel and prior to this date it was a copper-nickel alloy (cupro-nickel). This suggests, as it is present in both, lead (II) binds to the nickel present in the coins/upon the coins surface. A secondary result of this is as the lead is actively deposited on nickel this technique could be used for mapping nickel-based alloys in light of its selectivity towards nickel over other metals.

In light of its higher nickel content (and therefore higher affinity for lead deposition) the electrochemical performance of the post-2012 5 pence (5p) coin electrode (held in the custom-made PTFE 'housing unit'; see ESI Figure 1) was explored first using the outer-sphere redox probe 1mM Hexaammineruthenium (III) chloride/ 0.1M KCl over the scan rate range 5-200m Vs^{-1}. Figure 2 shows the obtained voltammetric response and clearly observable is the process of electron transfer with a reversible signal wherein the reduction occurs at approximately -0.25 V and the oxidation is at -0.1V: this is indicative of the potential use of a 5p coin as an electrochemical substrater. Note: a pre-2012 coin was also tested in 1mM Hexamineruthenium (III) chloride/ 0.1M KCL however yielded a poor electrochemical (ESI Figure 2). This is because the desired electrochemical reduction of lead (II), which will produce a measurable signal, is as follows:

$$Pb^{2+}_{(aq)} + 2e^{-}_{(m)} \rightleftharpoons Pb_{(s)}$$

However, on coins minted pre-2012, there is a large composition of copper (75%) that is, mostly likely, in the form of an oxide such as Cu_2O or CuO. In light of the composition, it is likely the following processes occur:

$$Cu^{2+}_{(aq)} + 2e^{-}_{(m)} \rightleftharpoons Cu_{(s)}$$

or

$$Cu^{+}_{(aq)} + e^{-}_{(m)} \rightleftharpoons Cu_{(s)}$$

This is confirmed through inspection of the pre-2012 coin's cyclic voltammetric profile in pH 4 acetate buffer (ESI Figure 2) which shows a reduction peak with very large current at 0.10V that is similar in both profile and value of copper reduction previously reported in the literature.[16] From this it can be deduced that the reduction of copper will dominate the electrochemical response as opposed to the desirable reduction of lead (II) on pre-2012 5 pence coins and as such, all experiments performed were with the use of a coin minted post-2012.

A control experiment was performed using a possible alternative to the potential coin electrodes. Visible in ESI Figure 3, confirmation of nickel's electroactivity towards lead (II) by using pure nickel sheet metal (contained within the PTFE 'housing unit') towards a 48.3 nM solution of lead (II). Whilst there is a measurable response, it comes with a much greater financial outlay (25mm x 25mm sheets can have costs in excess of £100[17]) and its availability is not as prevalent as the readily available 5 pence coin. Regal electrochemistry is also beneficial when compared to using nickel plated metal which have been used as electrode substrates [18] as the plating can be a long process and not everybody has access to the specialist equipment required to perform such techniques however, everybody in the United Kingdom has access to low denominations of its currency. Note that the use of coinage as an electrode material is attractive since everyone will have a coin in their pocket which can be readily utilised at low cost with minimal pretreatment.

Having determined that 5p coins minted post-2012 offered the best sensor apropos of lead determination its electroanalytical performance towards lead was explored. A series of additions were made over the analytical range 5 – 1000 nM into a pH 4 acetate buffer solution; the square wave voltammograms obtained utilizing the 5p-coin through the additions of lead are illustrated in Figure 3. Note that at high concentrations the electrode surface is likely saturated accounting for the plateau observed in the insert of figure 3 and the additional pre-peak. Analysis of the calibration curves (Figure 3 inset), constructed using the oxidation peak at approximately -0.40 V revealed a limit of detection (3σ) equal to 1.97nM which.is within the WHO guidelines of 10 ppb (48.26 nM) within drinking water.[1, 4] In light of this, the presented avant-garde, proof-of-concept ‘*Regal electrochemistry’* square-wave voltammetric approach is a much cheaper, facile method for the detection of lead as opposed to other key advancements within the area.[19-21] Note that faces on the coins have reliefs. In our experiments both sides of the coin are utilised; ESI figure 4 shows the two sides of the coinage used in this work. This potentially adds to the surface "roughness" however, this is negligible since on the timescale of the experiment the diffusion layer is larger than the “roughness”. Note that both sides of coins have been used and used to provide error bars presented in the insert of figure 3.

In summary we have demonstrated that coinage can be successful utilised as electrode sensor. Further work will see other coins explored electrochemically for their response to an array of analytes to advance the area of *Regal Electrochemistry*.

Conclusions

Proof-of-concept that British coinage can be successfully utilised as a useful electrode material has been shown with detection of lead in the nM range with model solutions. This has been compared to high quality (pure) nickel sheet and due to its significant cost has no advantages over the use of coinage as an electrode material - the use of a 5 pence incurs the cost of just 2.5 pence since both sides can be readily utilised. Note that the use of coinage as an electrode material is an attractive proposition since everyone will have a coin in his or her pocket, which can be readily utilised at low cost with minimal pretreatment and in light of its low cost - can be used as a one shot sensor. This is particularly useful in both developing countries and emergency cases such as those postured in militaristic applications. The concept of *Regal Electrochemistry* can be expanded to other coinage towards a range of target (electroactive) analytes; such work is currently underway.

References

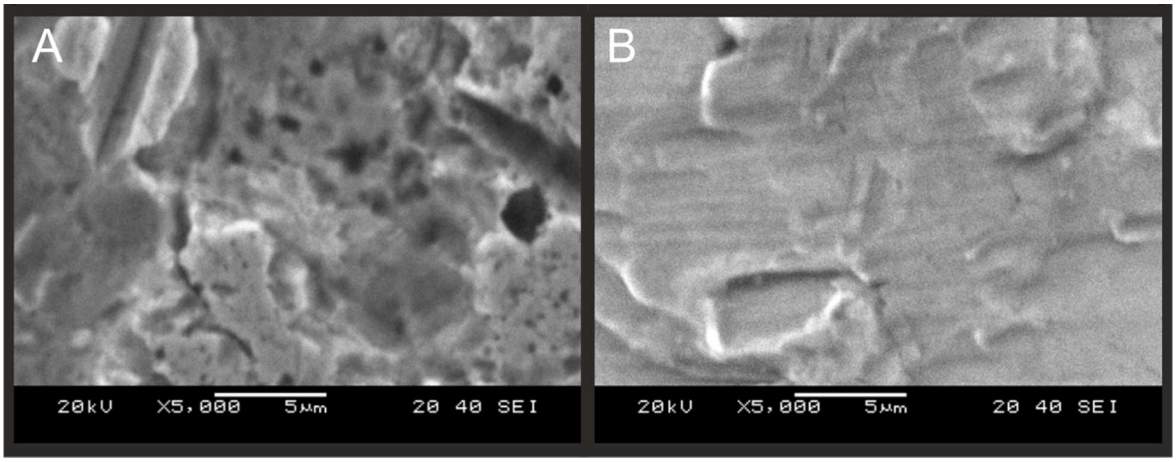
1. World Health Organization, International Programme on Chemical Safety: Lead, http://www.who.int/ipcs/assessment/public_health/lead/en/, Accessed April 2015.
2. W. Yantasee, Y. Lin, K. Hongsirikarn, G. E. Fryxell, R. Addleman and C. Timchalk, *Environmental health perspectives*, 2007, **115**, 1683-1690.
3. R. A. Goyer, *Toxicology of metals - biochemical aspects*, Springer-Verlag, New York, 1995.
4. WHO, Guidance for Drinking Water Quality, Recommendations, Geneva, 2nd edn., 1993, vol. 1.
5. United States Environmental Protection Agency, Safe Water Drinking Act: Levels of Copper and Lead, http://water.epa.gov/lawsregs/rulesregs/sdwa/lcr/index.cfm, Accessed June 2015.
6. Y. Xiao, A. A. Rowe and K. W. Plaxco, *Journal of the American Chemical Society*, 2007, **129**, 262-263.
7. G. Mai, L. Xia and W. Wang, *Russ J Electrochem*, 2013, **49**, 447-452.
8. Y. Zhu, G.-m. Zeng, Y. Zhang, L. Tang, J. Chen, M. Cheng, L.-h. Zhang, L. He, Y. Guo, X.-x. He, M.-y. Lai and Y.-b. He, *Analyst*, 2014, **139**, 5014-5020.
9. H.-J. Liu, L.-N. Qu, S. Hu, T.-R. Zhan, C.-Z. Zhao and W. Sun, *Journal of the Chinese Chemical Society*, 2010, **57**, 1367-1373.
10. A. Wanekaya and O. A. Sadik, *Journal of Electroanalytical Chemistry*, 2002, **537**, 135-143.
11. I. V. Anambiga, V. Suganthan, N. A. N. Raj and A. S. Kumar, Electrochemical sensor for the detection of lead ions, 2013.
12. A. Mandil, L. Idrissi and A. Amine, *Microchimica Acta*, 2010, **170**, 299-305.
13. A. P. Ruas, C. W. Foster, A. V. Kolliopoulos, M. Bertottib and C. E. Banks, *Analyst*, 2015, (In Press).
14. J.-M. Jian, Y.-Y. Liu, Y.-L. Zhang, X.-S. Guo and Q. Cai, *Sensors (Basel, Switzerland)*, 2013, **13**, 13063-13075.
15. The Royal Mint, Coin Design and Specifications: Five Pence Coin, http://www.royalmint.com/discover/uk-coins/coin-design-and-specifications/five-pence-coin, Accessed April 2015.
16. D. Stankovic, G. Roglic, J. Mutic, I. Andjelkovic, M. Markovic and D. Manojlovic, *International Journal of Electrochemical Science*, 2011, **6**, 5617.
17. Goodfellow Supplier of Materials for Research and Development, http://www.goodfellow.com/E/Nickel-Foil.html, Accessed July 2015.
18. P. Y. Chen, H. H. Yangi, J. M. Zen and Y. Shih, *Journal of AOAC International*, 2011, **94**, 1585-1591.
19. B. Chen, Z. Wang, D. Hu, Q. Ma, L. Huang, C. Xv, Z. Guo and X. Jiang, *Sensors and Actuators B: Chemical*, 2014, **200**, 310-316.
20. G. Lisak, J. Bobacka and A. Lewenstam, *Journal of Solid State Electrochemistry*, 2012, **16**, 2983-2991.
21. E. Kirowa-Eisner, M. Brand and D. Tzur, *Analytica Chimica Acta*, 1999, **385**, 325-335.

Table 1 Composition of coins currently in circulation in the United Kingdom,[15] text in bold indicates the coinage used in this work.

Coin	Composition
1p	Bronze (97% copper, 2.5% zinc, 0.5% tin) - until September 1992 Copper-plated steel - since September 1992
2p	Bronze (97% copper, 2.5% zinc, 0.5% tin) - until September 1992 Copper-plated steel - since September 1992
5p	**Pre-2012 copper-nickel (Cupro-nickel alloy) 75% copper, 25% nickel** **Post-2012 Nickel-plated steel - since January 2012**
20p	Pre-2012 copper-nickel (Cupro-nickel alloy) 75% copper, 25% nickel Nickel-plated steel - since January 2012
50p	Cupro-nickel (84% copper,16% nickel)
£1	Cupro-nickel (75% copper, 25% nickel)
£2	Outer: Nickel-Brass (76% copper, 4% nickel, 20% zinc) Inner: Cupro-nickel (75% copper, 25% nickel)

Figure 1 i) SEM micrographs of British 5 pence coins minted A: Pre-2012 (Cupro-nickel alloy 75% copper, 25% nickel) and B: post-2012 (Nickel-plated steel). ii) SEM micrographs following the desposition of lead(II) on British 5 pence coins minted A: Pre-2012 (Cupro-nickel alloy 75% copper, 25% nickel) and B: post-2012. (Nickel-plated steel).

i)



ii)

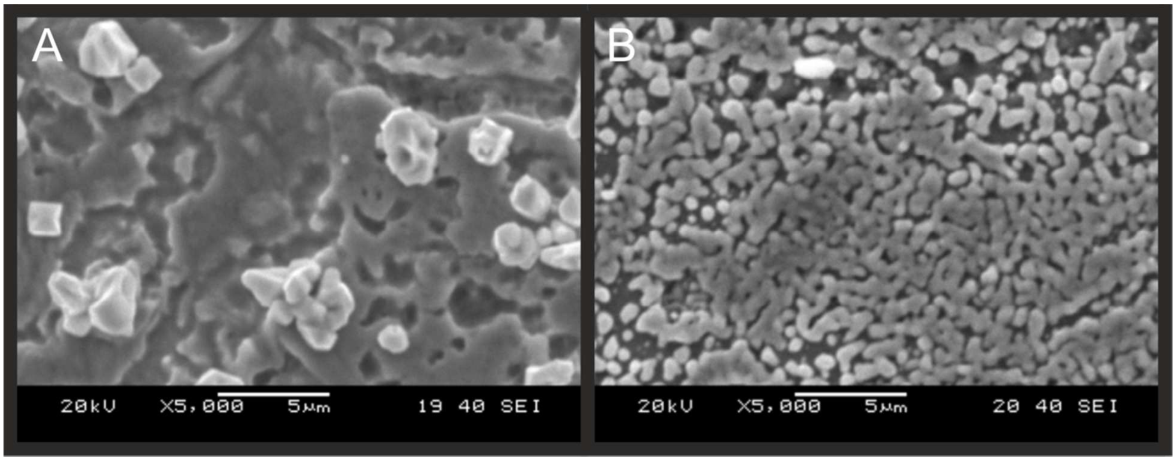


Figure 2 Cyclic voltammetry scan rate study recorded at 5, 10, 25, 50, 75, 100 and 200 mVs^{-1} (vs. SCE) using 5p british coin (2012) in 1mM Hexamineruthenium (III) Chloride in 0.1M potassium chloride.

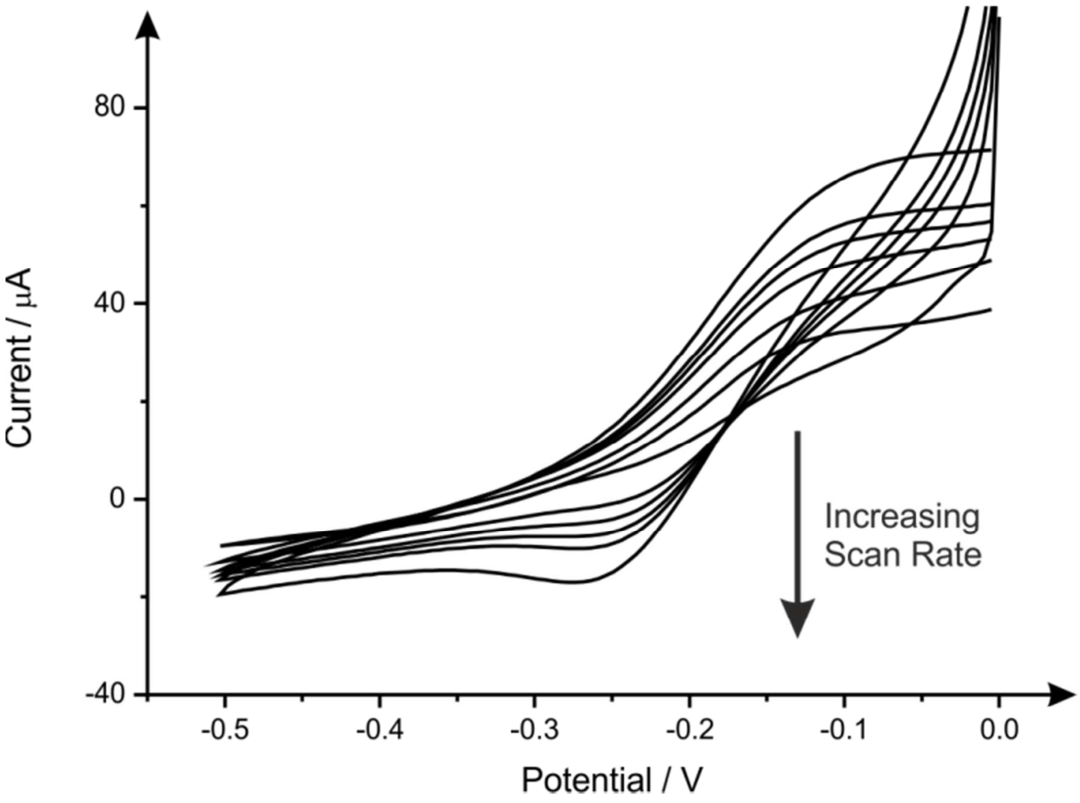


Figure 3 Square-wave voltammetry showing the response resulting from the additions of 5nM-1000nM lead (II) in a pH 4 acetate buffer solution. Dotted line represents blank pH 4 acetate buffer solution. Note: Visible peak in the blank is likely due to contamination of lead (II), a common issue associated with trace analysis. Inset: A typical calibration plot corresponding to addition of lead over the range 0nM-1000nM using 5p British (2012). The responses shown are an average response with corresponding errors bars (*N* = 3).