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Further advances in lead carboxylate coatings: coating unprimed heritage lead

Rosie A. Grayburn^{1,2,3}, Mark G. Dowsett^{1,2*} and Annemie Adriaens²**Abstract**

Further to the previously published work in this journal “Towards a new coating for heritage lead”, a coating has been trialled with samples replicating aged lead artefacts. Lead was corroded in an oak environment to simulate storage or display in a wooden case then coated with ethanolic solutions of tetradecanoic and octadecanoic acid. X-ray diffraction and electrochemical impedance data suggests a better-quality coating is formed leading to improved corrosion resistance.

Keywords: XRD, EIS, Coatings, Conservation, Heritage lead

Findings

Heritage metals are often coated as part of a conservation treatment to protect the metal surface from atmospheric deteriorogens [1–5]. The coating of lead by long chain carboxylates by immersion has been studied extensively [6–12]. In this journal, a relatively simple deposition process has previously been shown to produce layers of lead carboxylate on polished lead which are protective against a range of environments [10]. However, heritage lead is often not polished prior to coating [13]. Therefore, this work aims to show the effectiveness of the same ethanolic-deposited coatings on a more apt sample for the context of conservation practice-corroded lead.

The samples were prepared in such a way as to simulate the corrosion of lead due to oak-emitted volatile organic compounds (VOCs) when displayed or stored in an oak display cabinet. The creation of an oak environment has been described elsewhere [11]. Polished lead coupons were enclosed within the oak environment at 50 % RH for 9 months in order to develop a measurable layer of corrosion products [14]. After corrosion, coupons were coated in the same manner as previously described [10]. XRD and EIS measurements were performed using the same conditions as described in Ref. [10].

X-ray diffraction

In Fig. 1a–c, crystalline corrosion products are detected, namely lead formate (ICDD No. 014-0825) and hydrocerussite (ICDD No. 13-0131). Lead formate, a product of formic acid [15] reacting directly with surface lead oxide, is an important intermediate to the formation of lead carbonates such as hydrocerussite. The presence of both species shows that the lead surface is still corroding actively after 9 months [11, 14].

Comparing Fig. 1c to a and b we can see that the height of the lead and hydrocerussite peaks increases by one order of magnitude on coating. This could be due to the coating formation reaction: amorphous corrosion products lead formate and lead acetate dissolve in ethanol [16] and lead carboxylates form simultaneously (as described in [10]); the atomic density of lead in formates/acetates is much higher than in the longer chain carboxylates, so the removal of the former accompanied by the growth of the latter leaves a surface layer more transparent to x-rays even if it is thicker. In addition, the general increase in peak to background ratio across the whole of Fig. 1a and b compared to c suggests that a transfer from amorphous to crystalline corrosion products [17] occurs at the same time due to recrystallization.

Electrochemical impedance spectroscopy of corroded and polished coated samples

Figure 2a shows the Bode plots from the polished and corroded coated samples. The difference in impedance

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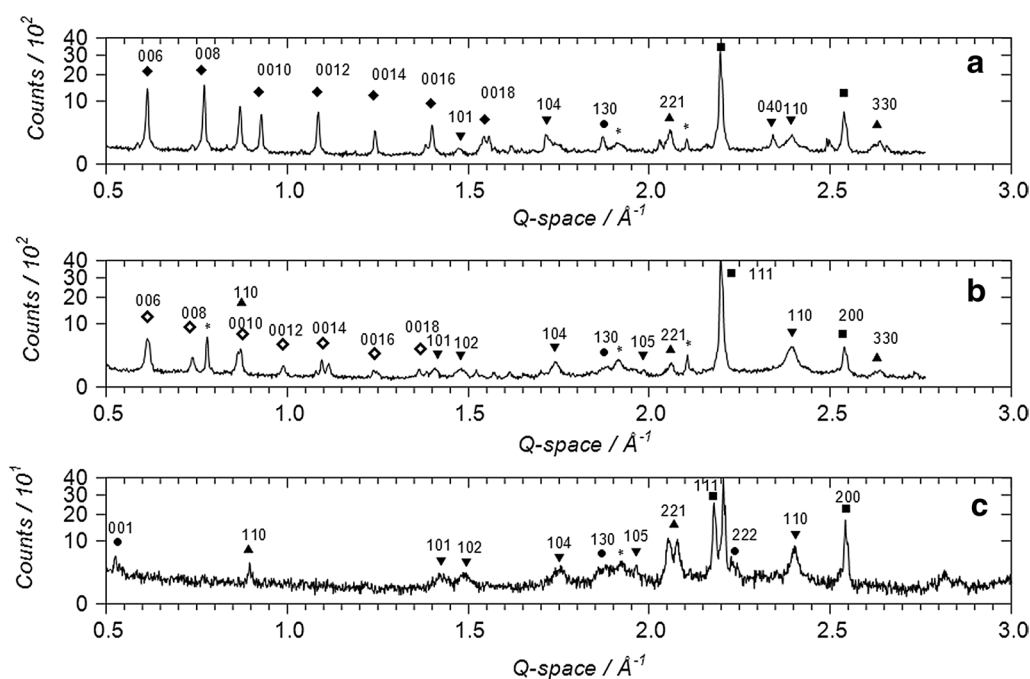


Fig. 1 XRD diffraction patterns for C14 (a) and C18 (b) coated corroded lead compared with the corroded lead precursor (c). All peaks are indexed apart from unidentified peaks (asterisk): lead acetate (filled circle), lead formate (filled triangle), hydrocerussite (filled inverted triangle), lead (filled square), lead ditetradecanoate (filled diamond) and lead dioctadecanoate (diamond)

between the corroded and polished coated samples is considerable. The data at low frequencies show an 83 % increase in coating impedance for lead dioctadecanoate [$\text{Pb}(\text{C}_{18})_2$] and 79 % increase for $\text{Pb}(\text{C}_{14})_2$ corroded samples compared to polished samples.

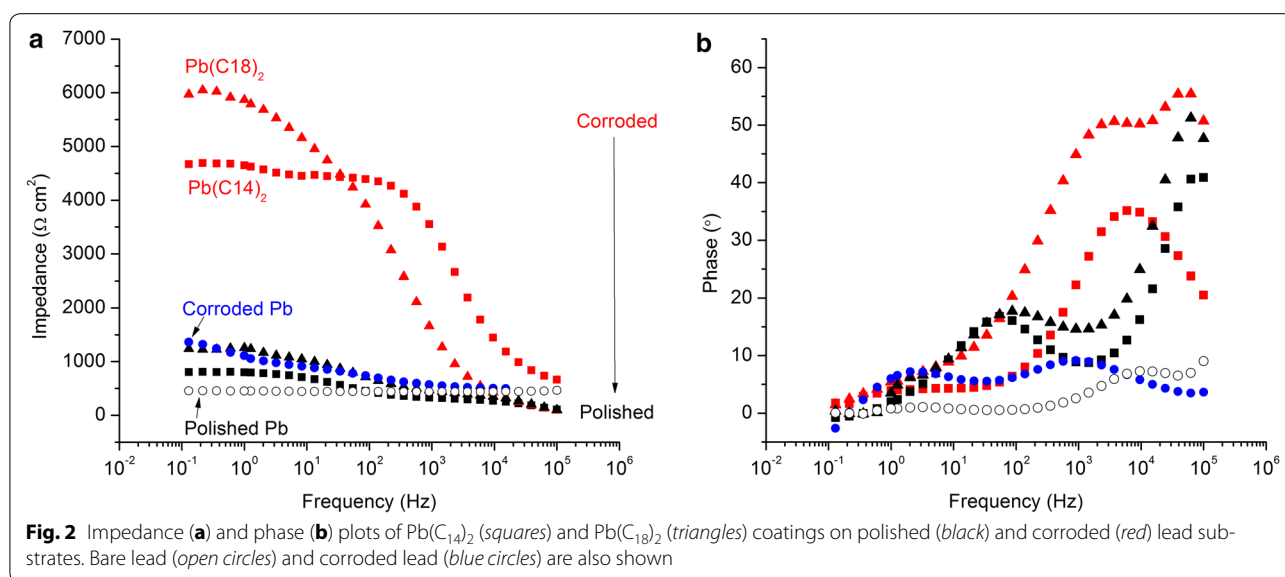
The impedance of the polished coated samples is larger than bare lead, but not larger than corroded lead. As shown in the XRD results, there is a significant layer of corrosion products on the surface of the corroded coupon which provides a protective layer against the electrolyte compared to bare lead. However by coating the samples, the improved impedance effect is not simply additive (polished coated sample plus corroded sample). This implies a significant improvement of the coating properties by forming the coating on a corroded sample. That said, the low coating resistance ($5 \text{ k}\Omega \text{ cm}^2$) does not represent a reasonably protective coating [1]; lead carboxylates deposited in this way merely passivate the surface and provide porous or patchy coverage.

Figure 2b shows the corresponding Bode phase plots. For polished, corroded and bare samples, two maxima (time constants) are shown showing the freely corroding nature of the metal substrate by the corrosive electrolyte. For the polished samples, the first maximum at $\sim 70 \text{ Hz}$ is the same for both samples. This maximum corresponds to the double layer and surface oxide and demonstrates

the reproducibility of the polishing technique. The second maximum at $\sim 10,000 \text{ Hz}$ corresponds to the coating. For the $\text{Pb}(\text{C}_{18})_2$ coating this maximum is approximately 10° higher due to the improved corrosion resistance provided by the longer carbon chain. The corroded coated samples show a time-constant (C18 shows a double maximum) at $\sim 10,000 \text{ Hz}$. This is due to the combined corrosion and coating layer providing greater corrosion resistance from the electrolyte. However, the improved capacitive properties compared to the polished sample could be due to coating deposition on the corroded surface, as observed in the impedance plots.

Conclusions

By coating a corroded sample instead of a polished surface, the effects of real artefact conservation by immersion in ethanolic carboxylate solution were observed. This improved coating was demonstrated in impedance and phase plots, where the effectiveness of the coating on corroded coupons was approximately 80 % higher than polished and corroded coupons. These results are encouraging for future trials with real lead artefacts as we have demonstrated the benefit of protecting unpolished, corroded lead using lead carboxylates. However, it must be stressed that lead carboxylates are merely passivating agents for the metallic surface and comparison



of the impedance data with earlier work [12] shows that a considerable increase in coverage for the non-conducting carboxylate should be possible. Nevertheless, their user-friendliness makes them accessible to conservators as a low-cost method for short-term protection of lead artefacts.

Authors' contributions

RG wrote the manuscript revised by MGD and AA. RG made the samples and performed EIS measurements. All authors read and approved the final manuscript.

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Acknowledgements

We would like to thank the Physics Department at Warwick University and the Special Research fund at Ghent University for the studentship of RG. We would also like to thank Tom Plankaert (UGent) for the XRD analyses.

Competing interests

The authors declare that they have no competing interests.

Received: 26 October 2015 Accepted: 29 February 2016

Published online: 29 March 2016

References

- Cano E, Lafuente D, Bastidas DM. Use of EIS for the evaluation of the protective properties of coatings for metallic cultural heritage: a review. *J Solid State Electrochem.* 2010;14:381–91.
- Letardi P. Laboratory and field tests on patinas and protective coating systems for outdoor bronze monuments. In: *Metal 2004: proceedings of the interim meeting of the ICOM-CC Metal Working Group.* 2004:379–387.
- Tétreault J. Sustainable use of coatings in museums and archives—some critical observations. *E-preservation Sci.* 2011;8:39–48.
- Rocca E. Inhibition treatment of the corrosion of lead artefacts in atmospheric conditions and by acetic acid vapour: use of sodium decanoate. *Corros Sci.* 2004;46:653–65.
- Watkinson D. Preservation of metallic cultural heritage. In: *Shreir's Corrosion.* 2010.
- De Keersmaecker M, Depla D, Verbeken K, Adriaens A. Electrochemical and surface study of neutralized dodecanoic acid on a lead substrate. *J Electrochem Soc.* 2014;161:C126–37.
- De Wael K, Keersmaecker M, Dowsett M, Walker D, Thomas PA, Adriaens A. Electrochemical deposition of dodecanoate on lead in view of an environmentally safe corrosion inhibition. *J Solid State Electrochem.* 2009;14:407–13.
- Dowsett M, Adriaens A. EC188 final report: time-resolved XRD and XAS for the conservation/protection of heritage and other metals using XMaS. 2011.
- Elia A, Dowsett M, Adriaens A. On the use of alcoholic carboxylic acid solutions for the deposition of protective coatings on copper. In: *Mardikian P, Chemello C, Watters C, Hull P, editors. Metal 10: proceedings of the interim meeting of the ICOM-CC Metal Working Group.* Clemson: Clemson University; 2010. p. 144–50.
- Grayburn RA, Dowsett M, De Keersmaecker M, Banerjee D, Brown S, Adriaens A. Towards a new method for coating heritage lead. *Herit Sci.* 2014;2:14.
- Grayburn R, Dowsett M, De Keersmaecker M, Westenbrink E, Covington JA, Crawford JB, Hand M, Walker D, Thomas PA, Banerjee D, Adriaens A. Time-lapse synchrotron X-ray diffraction to monitor conservation coatings for heritage lead in atmospheres polluted with oak-emitted volatile organic compounds. *Corros Sci.* 2014;82:280–9.
- Schotte B. A study of the electrolytic reduction of corroded lead objects and the application, characterization and testing of a protective lead carboxylate coating. PhD Thesis, Universiteit Gent, Belgium; 2007.
- Crawford J. Personal communication.
- Tétreault J, Sirois J, Stamatopoulou E. Studies of lead corrosion in acetic acid environments. *Stud Conserv.* 1998;43:17–32.
- Roffael E. Volatile organic compounds and formaldehyde in nature, wood and wood based panels. *Holz als Roh- und Werkstoff.* 2006;64:144–9.
- US Department of Health and Human Services: lead and lead compounds. NTP (National Toxicology Program), 13th Report on Carcinogens (RoC). 2014.
- Niklasson A, Johansson L-G, Svensson J-E. The influence of relative humidity and temperature on the acetic acid vapour-induced atmospheric corrosion of lead. *Corros Sci.* 2008;50:3031–7.