



Citation: M. Innocenti, W. Giurlani, M. Passaponti, A. De Luca, E. Salvietti (2019) Electrodeposition and innovative characterization of precious metal alloys for the Galvanic and Jewel industry. *Substantia* 3(1) Suppl.: 29-37. doi: 10.13128/Substantia-602

Copyright: © 2019 M. Innocenti, W. Giurlani, M. Passaponti, A. De Luca, E. Salvietti. This is an open access, peer-reviewed article published by Firenze University Press (<http://www.fupress.com/substantia>) and distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Electrodeposition and innovative characterization of precious metal alloys for the Galvanic and Jewel industry

MASSIMO INNOCENTI, WALTER GIURLANI, MAURIZIO PASSAPONTI, ANTONIO DE LUCA, EMANUELE SALVIETTI

Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy

Abstract. In recent years the idea that metals, oil and, more generally, natural resources are not endless has been firm. Furthermore, people become aware that humanity must not only increase the production of customer-goods, but they also must produce them with respect for the environment, trying to limit either dangerous processing techniques and hazardous materials. The elimination of many metals from alloys has also reduced the possibility to modify or to produce a wide range of precious jewels and new materials. For such reasons it is essential to develop new techniques for manipulation and preparation of precious jewellery products. Nowadays this economic policy drives many companies and even the single craftsmen to a cultural innovation and technological growth. Many small and medium-sized companies ask the University for a technological support, otherwise impossible to achieve alone for high costs. The basic research of University has become an important point for the development of the goldsmith sector and for the increase in production and variety of new jewels. This important collaboration between universities and industries is called "the Third Mission for the University". This collaboration is important from a cultural, as well as from a productive point of view. Nowadays, the symbiosis "Research centre - Goldsmith company", allows the company to expand internationally its market, thus making the whole industrial sector competitive and innovative. This union is extremely important not only for the goldsmith sector but for the entire National economy.

Keywords. Electrodeposition, Surface Analysis, Galvanic, Jewel.

INTRODUCTION

Since several years, industrialists, politicians and scientists have become aware that the energy resources of our planet may sooner or later end since they are limited. Awareness contributed to move towards the development of numerous renewable energy sources. Alternative energies and new renewable sources supported by developing technologies are already a big market creating many, high quality jobs. National research on major societal challenges, such as renewable energies, synthesis of new materials or creation of technological poles, will have more impact if efforts would be combined at the

European level. Besides technological poles and Innovation Centres – widespread across European Union – must help to improve networking and dissemination of experience with entrepreneurs in the industry, universities and civil society organisations.

Some problems have emerged in recent years for all precious metals starting from gold, platinum, silver, copper and even zinc. Then, in 2010, the first official reports were published in Europe [1] and America [2]: these documents highlight the scarce availability of the elements mentioned above, which in a few years will become even rarer [3,4]. In addition to this problem, which is not easy to solve, a second one has been added: the banning of numerous metals regularly used in the jewellery and fashion sectors:

- elimination of lead from brass alloys
- elimination of Nickel from wearables
- the abolition of galvanic baths based on chromium (VI)
- the imminent elimination of cyanides from galvanic baths

These legislative provisions have limited or even eliminated certain galvanic or synthetic processes. For this reason, many techniques employed for decades in the jewellery sector, have been abandoned. It has become necessary to invest in real applied research to find out new ways to meet the market demands. To accomplish this highly qualified and onerous task, a collaboration between the University and Industry has arisen. At a local level as well as international one, this process of collaboration has exacerbated competition among companies: a scientific war has begun between those companies which have invested more or less in new technologies and the other which did not. The future industrial development will penalize countries in which this Industry-University synergy has not yet been created. This costly commercial war left many Italian companies unarmed. The few Italian researchers employed by Italian companies have often been forced to work in conditions of inferiority (in terms of financial resources): without appropriate structures and large-scale investment in research, it was impossible to face the fierce world competition. This led some companies to bankruptcy and has condemned others to remain at the edge of the global scene. The latter category of industries has undergone a much faster and more unexpected cultural aging than it could be imagined.

Some examples are the case of gold galvanic bath in which it is difficult to replace the cyanides with other less dangerous substances; sparing some metals as additives in castings is a major challenge; replacing nickel, with a fundamental metal preventing the diffusion in the solid

solution of easily oxidized metals such as silver and copper, is a conceptually and economically titanic undertaking. Not only that, but the scarce availability of gold has triggered the research to decrease the amount of this element in alloys. With low carat alloys of gold and the creation of alloys based on non-precious metals, a “precious-perceived” market has been created. If the economic problems can be limited in this way, the chemical and physical ones cannot be avoided at all, rather they are increased and new ones are added: the corrosion resistance worsens in alloys with a lower gold content. In addition to that also the evaluation of the colorimetric parameters needs some development as well as morphological characterization techniques and new techniques able to examine the composition of the new products.

HISTORY OF GALVANIC INDUSTRY

The history of electroplating begins in the early 18th century [5,6] when, in 1805, L. V. Brugnatelli used the Volta’s voltaic pile to plate silver with metallic gold from a gold solution. His discovery was not appreciated from the scientific community and only thirty years later the Russian scientist B. Jacobi devised a process similar to the Brugnatelli’s work. Jacobi used the more performing Daniell cell for electroplating copper on metal plates thus rediscovering electroplating [7] and electroforming [8]. The first patent to perform gold and silver deposition were submitted in Birmingham by Henry and George Elkington in 1840. Their use of potassium cyanide as electrolyte led to establish Birmingham as the industrial center for electroplating with the inauguration of the first large-scale plant in 1876. Later, the stability of gold plating bath was improved with the use of ferrocyanides, thus providing the capability of depositing gold alloys containing silver and copper. From then on, electroplating quickly spread throughout the rest of the world and became a common process for depositing precious and non-precious metals. Since then few improvements were made in the following decades, except for the large-scale electric power distribution; only after the Second World War, in 1946, A. Brenner and G. E. Riddell discovered the first autocatalytic metal deposition by adding sodium hypophosphite to a nickel bath giving birth to the “electroless” deposition [9]. Since the early 1950s some baths were implemented by replacing cyanides with acidic solutions obtaining a more manageable and sustainable working environment [10]. In recent years electrodeposition in non-aqueous solution was investigated leading to the development of electrodeposition in ionic liquids and electrophoretic deposition [11]. Ionic liquids are used to

deposit metals with a Nernst reduction potential more negative than the evolution of hydrogen in water, e.g. aluminum, [12]. In ionic liquids the electrolyte is composed of anionic and cationic organic species which are in the liquid phase at low temperature; this allows the salts of the metal precursor to solubilize by means of the electroreduction process. Ionic liquids are very sensitive to moisture and therefore they must be employed in a special closed environment with a controlled atmosphere. The electrophoretic deposition process involves the reaction of organic monomeric precursors driven by an external electric potential [13]. Differently from the aqueous-based electrodeposition, the organic molecules not only occur in a redox reaction, but they also form a network leading to the formation of a polymer. The resulting coatings are generally well-adhered and softer than the metal ones with fewer cracking issues. The final polymer could be either conducting or insulating materials. The organic-based coatings tend to be more degradable over time, another issue is the environmental toxicity in the production process due to their precursors. The impact of electroplating on our lives is huge: in 2015 electroplating represented 37 % of the total market share within the metal finishing sectors with applications in automotive, aerospace, building, jewelry and electronics [14,15]. The most commonly galvanically-deposited metals are zinc and zinc alloys (about 15 %), followed by nickel, copper, chromium, tin, and precious metals [16]. According to a recent study published by Future Market Insights the global electroplating market is expected to increase at a compound annual growth rate (CAGR) of 3.7% over the forecast period of 2016-2026, projecting revenues of over US \$21 billion by the end of 2026 [17]. The main limit to an even larger expansion of electroplating is the strict environmental regulations: many plating processes involves toxic metals and dangerous chemicals. Another issue facing industrial development is the price volatility of highly on-demand electroplated materials (e.g., gold, copper, and nickel). Although significant technological and processing advancements occurred in the past forty years, industrial firms are still struggling to provide viable solutions to energy conservation, reduction of costs and toxic wastes, as well as strategic challenges such as product durability and corrosion protection [18,19]. Today, a deeper knowledge of the electrochemical mechanisms and the research of new materials and emerging technologies are driving the traditional manufacturing process towards a more reliable, flexible and interconnected production [20]. By exploiting the natural affinity of some elements is possible to obtain a surface-limited reaction that spontaneously generates a single atomic layer. This behavior is very useful from a technological

point of view and, therefore, widely studied by the scientific community. Starting from this principle, many techniques have been developed during the last years: Electrochemical Atomic Layer Epitaxy (ECALE) [21,22], Electrochemical Atomic Layer Deposition (E-ALD) [23-25], Selective Electrodesorption-Based Atomic Layer Deposition (SEBALD) [26,27], Electrochemical Liquid-Liquid-Solid growth (ELLS) [28].

HUBBERT PEAK OF PRECIOUS METALS

The World Gold Council estimated that about 190,000 tons of gold have already been mined from Earth [29]. Almost half (48 %) of the total was manufactured in jewellery; almost a quarter (21 %) was channelled into private investments; 17 % in official sector and the remaining 14 % assigned to other sectors such as technology. It is difficult to answer to question of how much gold remains to be extracted. It has been observed that two thirds of the gold already extracted until now occurred after 1950. One might think that if we follow this trend for in the next 100 years we can expect to achieve more hundreds of thousands of tons. Unfortunately, experts estimated that the current underground reserves amount to only 50,000 tons. It is understandable that this relatively modest picture is in contrast with the increasing production and use of gold in recent years.

The idea of peak oil pushed up the price of petroleum, but now another peak theory has emerged, this time involving gold and all the other precious metals. Hubbert's peak, called also Hubbert's curve, is a theory that approximates the production rate of a resource over a period of time. From a careful analysis of the Hubbert's curve we found that the initial production rate follows the increas-

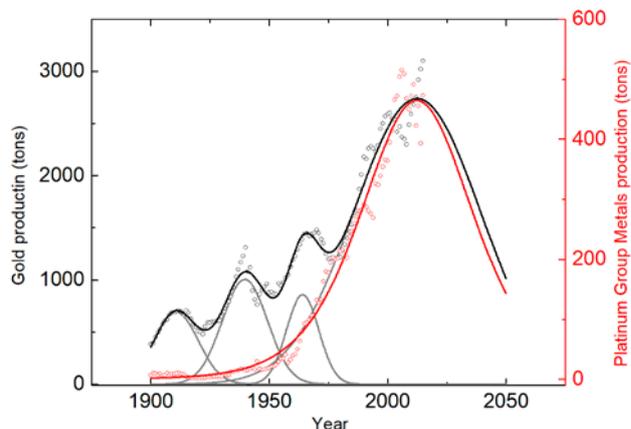


Figure 1. Hubbert peaks of Gold (black) and Platinum Group Metals (red): past production and future previsions.



Figure 2. Price of gold from 1970 to 2019.

ing demand for the new resource, but then it is predicted a loss of correlation and a decreasing in production while the demand still grows up. During this fall, there may be dramatic differences in production and demand as demand continues to rise, but production falls overall.

From the estimations of the remaining unmined gold and its increasing price, many analysts of precious metals and gold miners are taking a cue from the prediction of the Hubbert's theory, according to them the same concept can be applied equally well to the ingots, as well as to the oil, and can lead to outsized investment returns from the purchase of the yellow metal. In this context, the supporters of the golden peak claim that mining has a discrete number of similarities with oil extraction.

Just as the slowing of production and the diminishing reserves observed in the old oil wells, many of the best gold deposits exhibit the same kind of geriatric tendencies, with high quantities extracted long ago. However, after the peak, it was not observed a sustained decline as was the case of the model proposed by Hubbert. The reason could be the evolution of new technologies that provided us the tools to extract oil from unconventional resources. Then, a question arises: does the gold extraction follow this story? The answer is complex; the extraction of gold is connected to something more than just the technology. In fact, the price of the metal itself influences its extraction: it is observed that when gold becomes too cheap the extraction process stops. Furthermore, gold ores becoming increasingly more difficult to access compared to previous decades, and the likelihood of a discovery leading to mine development is very low (less than 0.1% of the proposed sites will lead to a production mine), according to the research of the World Gold Council, even if the 10 % of global gold deposits contain sufficient gold to justify further development, the exploration alone could take up to 10 years and

entail heavy costs in terms of geological investigations and chemical analysis.

ELECTRODEPOSITION OF LOW-CARATS GOLD

Galvanic baths containing considerable amount of toxic substances, such as cyanides, and heavy metals, which are also toxic and difficult to remove. For example, cadmium, in the matrix¹ have been used for decades to get one gold alloy containing less than 75% by weight of gold metal (corresponding to a gold alloy of 18 carats or less). These baths allow to get effectively gold deposits having the desired carat value e considerable thickness. However, the presence in them of highly poisonous substances makes them virtually unacceptable for practical use. The alternatives in use, however, exploit products that have only partially solved known problems met with the use of previous galvanic baths and, in addition, do not demonstrate the same suitability for practical use and the same quality of results. In fact, these are generally formulations that only partially eliminate toxic products used and which have limited periods of use or with which an alloy is obtained characteristics of the value of carats, thickness or appearance that do not meet the needs of the intended use. However, baths of this type also include solutions that use cyanide in the matrix or that, though they do not contain cyanide in the matrix, contain other elements or compounds of a certain toxicity. A recent study [30] has opened the possibility to satisfy the above needs due to galvanic alkaline baths containing: gold salts, copper and indium salts, salts of polycarboxylic organic acids, organic amines, and possibly complexing agents, surfactants and other metals in smaller quantities, as gloss additives and refiners of deposits. It is noted that, in contrast to the antecedent technique, cyanide is not present in the bath matrix and its content in the electroplating the solution is caused by its counterion function in the gold salts alone. Cyanide is therefore practically irrelevant, though necessary for the stability of gold in solution.

CHARACTERIZATION OF ELECTROPLATED COATINGS

Color measurements

The determination of the color has a central role in the quality control of electroplated deposits. The color

¹ Matrix is an aqueous solution of organic and inorganic acids and their salts.

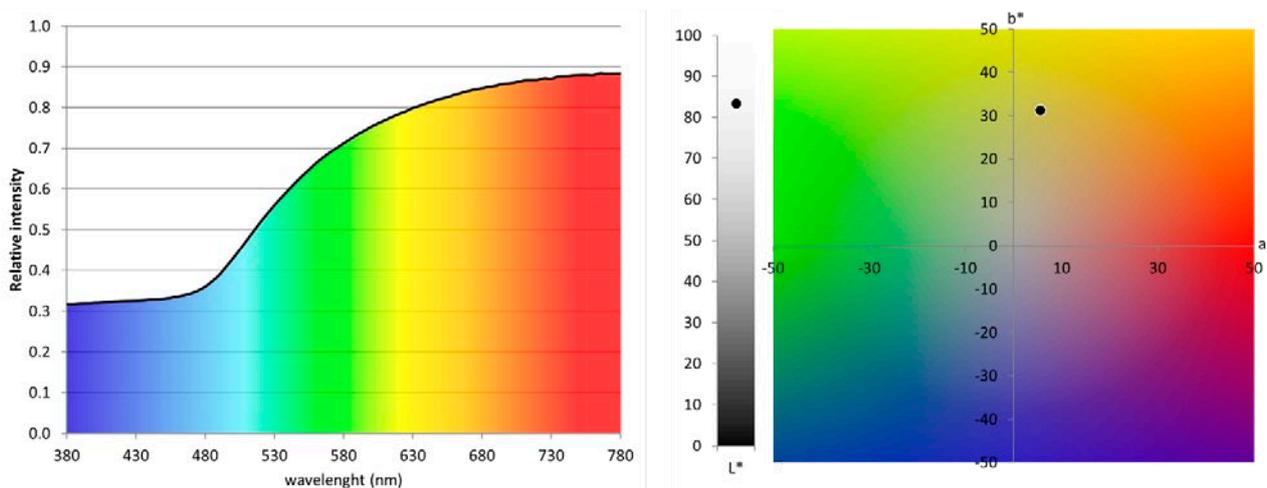


Figure 3. Measured reflectance spectrum (left) and the calculated colorimetric coordinates (right) of a gold sample.

measurement may seem a trivial task, but environmental factors and intrinsic properties of the objects might generate inconsistent data [31]. The formalism used for color assessment is the Lab color space [32] in which the three coordinates L^* , a^* , and b^* are considered. L^* identifies the brightness with values from 0 to 100, a^* the red-green component ($a^* > 0$ red, $a^* < 0$ green), and b^* the yellow-blue component ($b^* > 0$ yellow, $b^* < 0$ blue). The coordinates a^* and b^* do not have fixed limits but are generally in the range of ± 100 . The color coordinates $a^* = b^* = 0$ represents grays. The color of a sample can be compared with a target with several metrics [33]. The simplest and most commonly used approach defines color difference (ΔE^*) as the Euclidean distance between the coordinates of two different colors. It is generally accepted that two colors, placed one next to the other, are not distinguishable $\Delta E^* < 1$ [34]. In practice, companies generally tend to give an acceptable range for the single colorimetric coordinates ($L^* \pm dL$; $a^* \pm da$; $b^* \pm db$), whose values are defined by the customer. Colorimetric coordinates are obtained from the mathematical combination of the illuminant, sample reflectance spectra and the average of human eye sensitivity (tristimulus functions) [35]. The main problem in color determination is the inconsistency of the results, even from the same paint or metallic coating, due to instrumental differences (colorimeters are generally used instead of more expensive and accurate spectrophotometers) substrate polishing (reflective or matte), dimensions and irregular patterns and textures [36].

Thickness evaluation

The precise determination of the electrodeposited thickness is a fundamental parameter to characterize a galvanic coating. Mechanical properties are influenced by the thickness, beyond the type of alloy and the succession of the underlying layers. A thick deposit can have very high tensile stress and low adhesion. On the other hand, if the layer is too thin, gloss, diffusion, color, and corrosion problems might occur. The most common methods for measuring the thickness are through scanning electron microscopy (SEM) of metallographic cross-sections or using X-ray fluorescence (XRF). Cross-sectional analysis allows acquiring a direct image of the layers' sequence and then measure the thickness. Therefore, quantification is very simple, for thick deposit the cross section can be also measured with an optical microscope. The main disadvantages of this approach are the high cost of the instrument (60,000-200,000 €) and the slow and destructive sample preparation. On the other hand, XRF allows for non-destructive and fast measurements, with an instrumental price of around 40,000-60,000 €. Knowing the composition and sequence of the metallic layers an appropriate calibration curve is made, then the thickness of all the layers can be measured, with a typical 10% standard deviation. The researchers should be knowledgeable *about* the sample under investigation and the impossibility of measuring layers in which a certain element is repeated: for example, in a typical deposition bronze/copper/brass, the copper layer cannot be measured because it is present in both the deposits and brass, while bronze can be evaluated by analyzing the tin and correcting the result based on its percentage in the alloy.

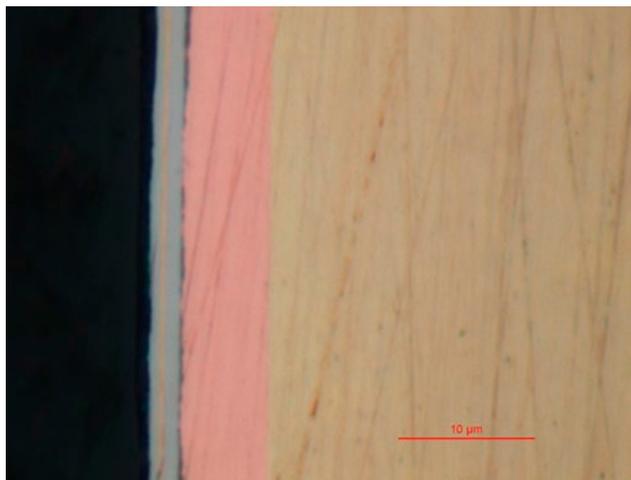


Figure 4. Cross section of typical galvanic deposition analyzed with optical microscope. From left to right it is possible to distinguish: brass substrate, copper, nickel and gold finishing. Before the cut of the sample an additional layer of nickel was deposited on gold to preserve its integrity and sharp edge during the lapping process.

A new methodology based on Energy Dispersive X-ray (EDX) spectroscopy for the determination of the thickness and the composition of electrodeposited thin films was developed in the last year [37]. The proposed method employed a combination of EDX spectra acquisition and Monte Carlo simulation. This method has better lateral resolution than the XRF technique and allows reliable measurement of the thickness on thin metal films, with the capability to determine also the composition of the film in the 1% concentration range. The approach was validated by the analysis of electrodeposited plates with known metal thickness using various approaches and custom-made software. The results were compared with other techniques showing an uncertainty of 9%, which is consistent with the literature data obtained using real standards [38]. The method has been validated on copper-based substrates covered by a layer of nickel, palladium and gold.

CORROSION AND MECHANICAL STRAIN

Product durability is a fundamental aspect which a producer must deal with, therefore mechanical and corrosion test must also be evaluated. The methods for examining the coatings' adhesion are describe by international standards by the qualitative examinations with thermal shock ASTM B571-97:2008, the network of cuts method ISO 2819:2017 and ISO 11644:2009, and the tape test under ISO 11644:2009. The formation of blisters or exfoliations indicates weak adhesion. The effects



Figure 5. Corrosion test of a gold-plated sample, before (left) and after (right) 12 hours under syntenic sweat test.

of time and environment on a sample is simulated with accelerated aging. The corrosion test can be carried out on a new sample or after mechanical tests in order to obtain a more pronounced effect. The most common international corrosion tests are: the effects of exposure to damp heat with or without leather ISO 4611:2010 and ISO 17228:2015, resistance to synthetic sweat ISO 3160-2:2015, salt spray test ISO 9227:2017, and tests with chemicals derived from atmospheric pollution, such as thioacetamide ISO 4538:1978, sulfur dioxide, and nitric acid ISO 4524:2000. Corrosion test generally takes long time (hours to days) to obtain a result and are intrinsically destructive. For these reasons, efforts have recently been made to find faster and non-destructive, or micro/semi-destructive, systems. A probable evolution in this sense could come from electrochemical measurements of Open Circuit Potential (OCP) and Electrochemical Impedance Spectroscopy (EIS).

FLORENTINE APPLIED ELECTROCHEMISTRY LABORATORY

In the Florentine Laboratory of Applied Electrochemistry, 20 people (professors, researchers, technicians and PhD students) are working. All of them are specialized in the various fields of chemistry and electrochemistry, engineering and materials science. The laboratory is affiliated with the Chemistry Department of the University of Florence. The academic research sectors in which the attention has been focused mainly concern:

- 1) Study of electrified interfaces with particular attention to the adsorption of electroactive organic substances and inorganic ions on different metals.
- 2) Study of nanomaterials obtained electrochemically.
- 3) Morphological and compositional characterization exploiting many technique: Scanning Electron Microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), X-ray Photoemission Spectroscopy (XPS), Scanning Probe Microscopy (SPM) with par-

ticular regard to Atomic Force Microscopy (AFM). In this field the attention has turned to the morphological characterization of substrates of Technological, Environmental and Biological interest.

- 4) Microcontact printing and electrodeposition on a nanometric scale.
- 5) Preparation of modified surfaces of catalytic or technological interest by confined metal electrodeposition.
- 6) Electrodeposition of ternary or quaternary sulfides for the preparation of surfaces of technological interest in the field of solar cells.
- 7) Design and implementation of devices in the energy sector with natural materials with low environmental impact and with low energy consumption preparation techniques.

In recent years the laboratory has also been involved in applied research in the industrial field, for the development of sensors in medical use, low-cost instrumentation for oil and wine analysis, absorbent materials for acid spills courses of Basic Microscopy and Galvanic Baths. As previously reported, the Florentine applied electrochemistry laboratory shared the project of the university's third mission activity. The "third mission" of the University addresses the growing societal economic challenges. In reality the term "third mission" is ambiguous because it is used to indicate a multiplicity of activities that relate university research and society. A first fundamental typology is that of technological transfer activities aimed at the evaluation, protection, marketing and marketing of technologies developed in the field of research projects conducted by the academic world and, more generally, for the management of intellectual property in relation with the same projects. In this context laboratory's research activity has been carried out in a very important way, placing the Applied Electrochemistry Laboratory directed by Prof. Innocenti Massimo to a central role in the transfer of knowledge from the University to the industry and vice versa. In addition, the numerous contracts obtained have allowed an exponential growth of this group acquiring high-level instruments, of great impact in the regional production sector. Thanks to the various research activities, the applied electrochemistry laboratory has been able to boast numerous research funds and above all to play a central role for high-level training and the introduction into the working world of numerous graduates and post-doctoral graduates in Chemistry.

MIUR projects financed:

- 1) PRIN 2004 project financed by the title "Integrated study on the national territory for the characteriza-

tion and control of atmospheric pollutants (SITE-COS)" of which Professor Innocenti was responsible of the Operative Unit of Florence

- 2) PRIN 2008 project financed by the title "Platinum-free electrocatalytic materials for direct fuel-based fuel cells" of which Professor Innocenti was deputy manager

Projects funded:

Monte dei Paschi di Siena Foundation

- 1) Monte dei Paschi di Siena Foundation - 2006-2007
He financed the project entitled "Design Synthesis and Characterization of nano-structured composite materials with pre-selected Functional characteristics"

Tuscany region:

- 1) Gabbrielli 2013 Regional Project 1.3b of the POR CREO 2007-2013 "ECO-SOL".

Research Project "Eco-sustainable and low-cost production of sulphides for photovoltaic applications"

- 2) ESA 2016, Participant Project Tuscany Region, POR ERDF 2014-2020 Call 2: Research and development projects of SMEs, "New electrolytes for electroforming of yellow gold alloys with low environmental impact" Present and Research Manager of the subcontractor.
- 3) Regione Toscana Spettrox Project, POR ERDF 2014-2020 Call 2: Research and development projects for SMEs, Present as Researcher INSTM.
- 4) GADGET Project Call for POR CREO 2014-2020 - DD 3048 of 21/02/18, Call for proposals 2: Research and development projects for SMEs, "Silver, Galvanic, Ecological and Technological Jewelry"
- 5) EL4ALL Project Bando POR CREO 2014-2020 - DD 3048 of 21/02/18, Call 2: Research and Development Projects of SMEs, "New Aluminum Electrodeposition process on fashion accessories through the development of DES and next coloring "
- 6) THIN FASHION Project Bando POR CREO 2014-2020 - DD 3048 of 21/02/18, Call 2: Research and development projects for SMEs, "Plasma technologies for the luxury industry: 4.0 approach to additive manufacturing". INSTM . Appropriation 1.995.704,55 Euro (Classified 61, Head of Industry, TEXTS)
- 7) GALVATRON Project Call for POR CREO 2014-2020 - DD 3048 of 21/02/18, Call 2: Research and Development Projects for SMEs, My Research Group is present as a Subcontractor. Project Approved but Admitted to the Funding with Resource Reserve (probable



Figure 6. Applied Electrochemistry Laboratory group, headed by Professor Innocenti. Department of Chemistry of the University of Florence.

project start by 2018) Budget 469.302,45 Euro (Classified 108, Head of Industry ECO-TECH FINISH)

REFERENCES

- Commission of the European Communities (EC) Tackling the challenges in commodity markets and on raw materials. *Brussels Eur. Comm.* **2011**, 1–22, doi:COM(2011) 25 final.
- Bauer, D.; Diamond, D.; Li, J.; Sandalow, D.; Telleen, P.; Wanner, B. US Department of Energy: Critical Materials Strategy, December 2010. *Agenda* **2010**, 1–166, doi:10.2172/1000846.
- Commission, E. Comm. from the Commission to the European Parliament, The Council, The European Economic and Social Committee and The Committee of the Regions: On the review of the list of CRMs for the EU and the implementation of the Raw Materials Initiative. **2014**.
- European Commission COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS on the 2017 list of Critical Raw Materials for the EU. **2017**, 8.
- Greene, J. E. Tracing the 5000-year recorded history of inorganic thin films from ~3000 BC to the early 1900s AD. *Appl. Phys. Rev.* **2014**, 1, 41302, doi:10.1063/1.4902760.
- Hunt, L. B. The early history of gold plating. *Gold Bull.* **1973**, 6, 16–27, doi:10.1007/BF03215178.
- Daniell, J. F. *On voltaic combinations*; Richard Taylor: London, **1840**;
- Jacobi, M. H. *Die Galvanoplastik, Oder das Verfahren coharentes Kupfer in Flatten Oder nach sonst gegebenen Formen unmittelbar aus Kupferauflosungen auf galvanischem Wege zu produciren*; Eggers und Co.: St. Petersburg, 1840;
- Abner, B.; Riddell, G. E. Nickel plating by chemical reduction **1947**.
- Landolt, D. Electrodeposition Science and Technology in the Last Quarter of the Twentieth Century. **2002**, 149, 1–8.
- Brett, C. M. A. Deep eutectic solvents and applications in electrochemical sensing. *Curr. Opin. Electrochem.* **2018**, doi:https://doi.org/10.1016/j.coelec.2018.05.016.
- Zhang, Q.; Wang, Q.; Zhang, S.; Lu, X.; Zhang, X. Electrodeposition in Ionic Liquids. *ChemPhysChem* **2016**, 17, 335–351.
- Yoshida, T.; Zhang, J.; Komatsu, D.; Sawatani, S.; Minoura, H.; Pauporté, T.; Lincot, D.; Oekermann, T.; Schlettwein, D.; Tada, H.; Wöhrle, D.; Funabiki, K.; Matsui, M.; Miura, H.; Yanagi, H. Electrodeposition of inorganic/organic hybrid thin films. *Adv. Funct. Mater.* **2009**, 19, 17–43, doi:10.1002/adfm.200700188.
- Pushpavana, M. Critical review on alloy plating: A viable alternative to conventional plating. *Bull. Electrochem.* **2000**, 16, 559–566.
- Raykhtsaum, G. PGM Highlights: Platinum Alloys: A Selective Review of the Available Literature - Johnson Matthey Technology Review. **2013**, 202–213.
- Th., L.; H., S.; M., Z.; S., S.; B., W. Status quo und Trends der Galvanotechnik. *Materwiss. Werksttech.* **2016**, 39, 52–57, doi:10.1002/mawe.200700241.
- Future Market Insights Electroplating Market: Global Industry Analysis and Opportunity Assessment, 2016–2026 Available online: <https://www.futuremarketinsights.com/reports/electroplating-market>.
- Valdez, B. Corrosion Control in Industry. In *Environmental and Industrial Corrosion*; Schorr, M., Ed.; InTech: Rijeka, **2012**.
- Giurlani, W.; Zangari, G.; Gambinossi, F.; Passaponti, M.; Salvietti, E.; Di Benedetto, F.; Caporali, S.; Innocenti, M. Electroplating for Decorative Applications: Recent Trends in Research and Development. *Coatings* **2018**, 8, 260, doi:10.3390/coatings8080260.
- Kang, H. S.; Lee, J. Y.; Choi, S.; Kim, H.; Park, J. H.; Son, J. Y.; Kim, B. H.; Noh, S. Do Smart manufacturing: Past research, present findings, and future directions. *Int. J. Precis. Eng. Manuf. Technol.* **2016**, 3, 111–128, doi:10.1007/s40684-016-0015-5.

21. Gregory, B. W.; Stickney, J. L. Electrochemical atomic layer epitaxy (ECALE). *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *300*, 543–561, doi:[https://doi.org/10.1016/0022-0728\(91\)85415-L](https://doi.org/10.1016/0022-0728(91)85415-L).
22. Innocenti, M.; Forni, F.; Pezzatini, G.; Raiteri, R.; Loglio, F.; Foresti, M. L. Electrochemical behavior of As on silver single crystals and experimental conditions for InAs growth by ECALE. *J. Electroanal. Chem.* **2001**, *514*, 75–82, doi:10.1016/S0022-0728(01)00620-9.
23. Sharan, T. T.; Maarit, K. Atomic Layer Deposition of p-Type Semiconducting Thin Films: a Review. *Adv. Mater. Interfaces* **2017**, *4*, 1700300, doi:10.1002/admi.201700300.
24. Innocenti, M.; Bencistà, I.; Bellandi, S.; Bianchini, C.; Di Benedetto, F.; Lavacchi, A.; Vizza, F.; Foresti, M. L. Electrochemical layer by layer growth and characterization of copper sulfur thin films on Ag(1 1 1). *Electrochim. Acta* **2011**, *58*, 599–605, doi:10.1016/j.electacta.2011.10.004.
25. Bencista, I.; Di Benedetto, F.; Innocenti, M.; De Luca, A.; Fornaciai, G.; Lavacchi, A.; Montegrossi, G.; Oberhauser, W.; Pardi, L. A.; Romanelli, M.; Vizza, F.; Foresti, M. L. Phase composition of CuxS thin films: spectroscopic evidence of covellite formation. *Eur. J. Mineral.* **2012**, *24*, 879–884, doi:10.1127/0935-1221/2012/0024-2229.
26. Innocenti, M.; Bellandi, S.; Lastraioli, E.; Loglio, F.; Foresti, M. L. Selective electrodesorption based atomic layer deposition (SEBALD): A novel electrochemical route to deposit metal clusters on Ag(111). *Langmuir* **2011**, *27*, 11704–11709, doi:10.1021/la202174j.
27. Giurlani, W.; Giaccherini, A.; Salvietti, E.; Passaponti, M.; Comparini, A.; Morandi, V.; Liscio, F.; Cavallini, M.; Innocenti, M. Selective Electrodesorption Based Atomic Layer Deposition (SEBALD) of Bismuth under morphological control. *Electrochem. Soc. Interface* **2018**, 77–81, doi:10.1149/2.F08182if.
28. Fahrenkrug, E.; Maldonado, S. Electrochemical Liquid-Liquid-Solid (ec-LLS) Crystal Growth: A Low-Temperature Strategy for Covalent Semiconductor Crystal Growth. *Acc. Chem. Res.* **2015**, *48*, 1881–1890, doi:10.1021/acs.accounts.5b00158.
29. World Gold Council How much gold has been mined Available online: <https://www.gold.org/about-gold/gold-supply/gold-mining/how-much-gold-has-been-mined> (accessed on Sep 23, 2018).
30. Cavaciocchi, L.; Banchelli, E.; Canelli, V. D.; Innocenti, M. Galvanic baths for obtaining a low-carat gold alloy, and galvanic process that uses said baths 2013.
31. Cie CIE technical report. *Color. 3rd Ed.* **2004**, 552, 24, doi:ISBN 3 901 906 33 9.
32. CIE *Colorimetry - Part 4: CIE 1976 L*a*b* COLOUR SPACE*; **2007**;
33. Ronnier, L. M. The quality of light sources. *Color. Technol.* **2011**, *127*, 75–87, doi:10.1111/j.1478-4408.2011.00282.x.
34. Mahy, M.; Van Eycken, L.; Oosterlinck, A. Evaluation of Uniform Color Spaces Developed after the Adoption of CIELAB and CIELUV. *Color Res. Appl.* **1994**, *19*, 105–121, doi:10.1111/j.1520-6378.1994.tb00070.x.
35. Capitán-Vallvey, L. F.; López-Ruiz, N.; Martínez-Olmos, A.; Erenas, M. M.; Palma, A. J. Recent developments in computer vision-based analytical chemistry: A tutorial review. *Anal. Chim. Acta* **2015**, *899*, 23–56, doi:<https://doi.org/10.1016/j.aca.2015.10.009>.
36. Giurlani, W.; Gambinossi, F.; Salvietti, E.; Passaponti, M.; Innocenti, M. Color Measurements In Electroplating Industry: Implications For Product Quality Control. *ECS Trans.* **2017**, *80*, 757–766, doi:10.1149/08010.0757ecst.
37. Giurlani, W.; Innocenti, M.; Lavacchi, A. X-ray Microanalysis of Precious Metal Thin Films: Thickness and Composition Determination. *Coatings* **2018**, *8*, 84, doi:10.3390/coatings8020084.
38. Zhuang, L.; Bao, S.; Wang, R.; Li, S.; Ma, L.; Lv, D. Thin film thickness measurement using electron probe microanalyzer. *2009 Int. Conf. Appl. Supercond. Electromagn. Devices* **2009**, 142–144, doi:10.1109/ASEMD.2009.5306671.