"Pulsed-Electrochemical Deposition of Fe-based nanoparticles from non-aqueous media: effect of different additives on morphology development"

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Abstract

Iron based-nanoparticles have a range of technologically-important applications which encompass diverse areas such as battery materials, photo- and electro-catalysis, environmental remediation, and as catalysts for the growth of nanostructured carbons.[1] The performance of iron-based nanoparticles on all of these applications depends strongly on their morphology (size, shape, distribution and orientation of particles), and their chemical composition. Therefore, developing synthetic methods that allow for the systematic control of these properties is a subject of intense scrutiny.

In this study we investigate the effects of additives during pulsed-electrochemical deposition (ECD) of iron-based nanoparticles from formamide/$FeCl_2$ solutions. ECD is a useful method to produce inorganic materials because it is a soft-solution synthesis in which the plating media can be easily adjusted to obtain electrodeposits with systematically-controlled morphologies.[2] Electrodeposition of Fe-based materials has been widely studied previously, however, most of the experiments done so far had been performed in aqueous media.[3] Non-aqueous plating media, like the one described in this work, offers wider potential and temperature windows for ECD, together with more complex and richer chemistry. This translates into more opportunities to tune the morphology and composition of inorganic nanoparticles.

To study the impact of additives on the morphology and composition of iron particles, we have chosen two general categories of additives, classified according to: (i) chemical interaction with the active cation, Fe^{2+}, (coordinating or chelating additives) or (b) surface interactions with growing iron nuclei (surfactants and polymers). Carboxylic acids such as citric acid had been demonstrated to quench the oxidation of ferrous (Fe^{2+}) ions in aqueous media, although their role in non-aqueous media had not been deeply studied yet.[3] Figure 1 shows an example of our own experiments using (a) $FeCl_2$/formamide solution, and (b) $FeCl_2$/formamide with citric acid additive, during pulsed-ECD. The corresponding current profiles are shown in (c) and (d), respectively. This figure shows a clear change in the particle size and distribution when using citric acid, which is also reflected in the shape of the current profiles and the variation of current densities.

Finally, the effects of various additives and the correlation between the chemistry of the plating media and the morphology of the electrodeposits will be discussed. The plating media and the electrodeposited nanoparticles had been characterized, by ultraviolet-visible (UV-vis), and Fourier Transform-Infrared-Attenuated Total Reflectance (FTIR-ATR) spectroscopy, Scanning Electron (SEM) and Optical Microscopies, by the analysis of current profiles, and voltammetric methods.

References

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Figures

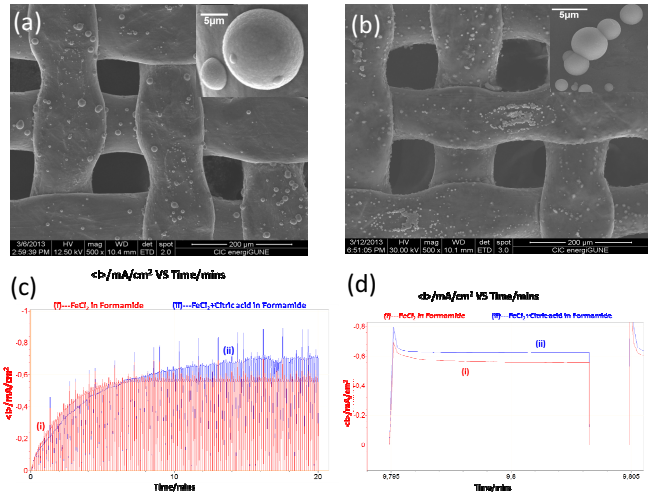

Figure 1: The relationship between morphology and current profile of pulsed-electrodeposited iron-based nanoparticles. SEM images of electrodeposits from: (a) 0.03M $FeCl_2$/formamide solution, (b) 0.03M $FeCl_2$/formamide with citric acid additive; the inserts in each panel show typical average particle size and aggregation patterns. Current profiles of the plating solutions used, (c) full profile and (d) amplification of a single pulse: (d-i) without additive (red line) and, (d-ii) with additive (blue line).