

Investigations of Electrochemical deposition of Galfenol Thin Films and Nanowires

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□ Galfenol ($\text{Fe}_{1-x}\text{Ga}_x$ with $x \approx 18\text{-}28\%$) alloy in thin film and nanowire forms is an important material owing to its large magnetostriction and high ductility with immense potential as functional materials in biomimetic and microfluidic devices.

□ Electrochemical deposition of Galfenol (GF) thin films and nanowires was demonstrated earlier (Ref. [1]), but understanding of the electrochemical deposition processes occurring at the electrode-electrolyte interface is lacking.

□ The present study throws light on the role of various deposition parameters like overpotential, pH of the solution, concentration of ions and complexing agents in the electrochemical deposition of GF.

Common observations during GF electrochemistry

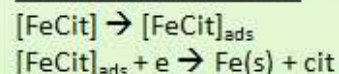
1. For GF depositions, concentration of $[\text{Fe}^{+2}]$ ions has to be kept lower than $[\text{Ga}^{+3}]$ ions.
2. Presence of Ga in the electrolyte shifts the deposition potential of Fe^{+2} ions to higher overpotentials.
3. High concentrations of citrate complexing agent or $[\text{H}^+]$ ions shift the H_2 evolution to lower potentials.
4. **Cyclic Voltammetry**: GF depositions occur at low reduction potentials, while the depositions occurring at large reduction potentials contain mixed Fe-Ga oxides.

Phenomenological Model explaining the GF Electrochemistry (see cartoon)

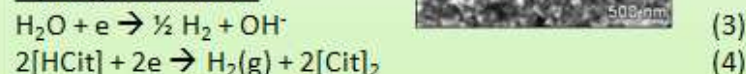
1. Fe^{+2} ions exhibit anomalous deposition (Ref. [2]) in two steps (Eq. 1, 2). Eq. (1) is fast, resulting in preferential adsorption of $[\text{FeCit}]_{\text{ads}}$ complex on the electrode, thus blocking the Ga ions. Hence $[\text{Fe}^{+2}]/[\text{Ga}^{+3}]$ ratio has to be kept low.
2. The deposition of Ga might involve Fe-Ga-citrate complexes (Eq. 5, 6). For reduction into metal phase, the equations (7), (8) and (2) might be occurring simultaneously: the electrode potentials of equations (2), (7) and (8) are tied.
3. H_2 evolution not only takes place by Eq. 3, but also by citrate dimerization (Eq. 4). Hence citrate content has to be kept low.
4. Evolution of H_2 causes local rise in pH. This might inhibiting reactions (7) and (8) while promoting reactions (9) and (10), thus forming the oxide phases.

Plausible Reactions at the Electrode-Electrolyte Interface

Reduction of Fe^{+3} to Fe



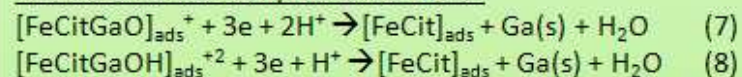
Hydrogen evolution



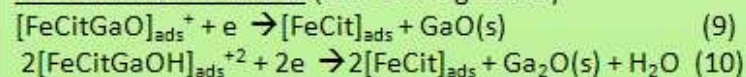
Complexation of Ga^{+3} ion



Reduction of Ga complex to Ga metal



Formation of Ga oxides (see SEM fig above)



Fe-Ga mixed oxide phase

