Chapter-7

CONCLUSIONS

Work started on this thesis with the intention to address contemporary interests in materials chemistry such as (i) Synthesis of thin/thick films and coatings, (ii) Control over morphology, (iii) Oriented crystallization and (iv) Measurement of physical constants using electrochemical techniques.

Most of the materials synthesized are thick films and coatings. An attempt was made to synthesize thin films of nickel hydroxide by using EQCM. Morphology of many hydroxides and oxides has been studied. Oriented crystallization has been carried out in ZnO, calcium phosphate and copper iodide systems. Physical constant measurements have been done by measuring the interlayer basicity and anion exchange potentials of layered double hydroxides of Mg and Al. We could not extend this to other LDHs because of the difficulty in getting adherent coatings of other LDHs.

Summary of the results

Several hydroxides and their respective oxides have been synthesized on stainless steel substrates by using electrogeneration of base method. All the hydroxides and oxides synthesized have porous morphology. The porosity is not structural and arises due to the large amount of hydrogen gas evolution during deposition. We conclude that electrochemistry is a general method to synthesize coatings of inorganic materials with porous morphology.

An attempt was made to synthesize thin films of inorganic materials by taking nickel hydroxide as an example. The thickness of the films has been controlled by using an electrochemical quartz crystal microbalance. Films of 5-12 nms were synthesized and enabled the study of the effect of weak interactions on the electronic structure of nickel hydroxide.

In an attempt to demonstrate the use of electrochemistry in the measurement of physical constants we have taken layered double hydroxide as a model system. We measured the interlayer basicity using electroactive species such as hexacyanoferrate as a probe by using cyclic voltammetric technique to measure the redox potential. In order to determine the thermodynamic stability of LDHs, anion exchange potential for self-self
and self-not-self exchange reactions were measured. Using these potentials, we calculated the free energy of the anion exchange reactions.

Oriented crystallization of several technologically important inorganic materials on stainless steel substrate was studied. Oriented crystallization of ZnO is done using aqueous Zn salt solutions. Direction of orientation and extent of orientation can be changed by changing the bath concentration, deposition temperature and duration of deposition. When the ZnO deposition was done at a low temperature, the X-ray profile shows Scherer broadening. The crystallite size of these coatings was determined by employing Brass 2 Suite of programs. Oriented crystallization of ZnO is also done using isopropanol in the bath. In case of dicalcium phosphate dihydrate, orientation changes when the deposition current was changed. DCPD to hydroxyapatite transformation of differently oriented coatings was carried out by ageing studies. Differently oriented coatings show different kinetics of transformation. Hydroxyapatite could be deposited on stainless steel substrate in a one-step synthesis in the presence of complexing agents. When EDTA was used as a complexing agent the 002 orientation was observed at 85°C deposition temperature. When lactic acid was used oriented crystallization was observed at 65°C itself. In case of CuI the orientation switches when the deposition potential and temperature were changed.

Limitations and major failures of the work

Synthesis of many other unary hydroxides such as Al(OH)$_3$, Ce(OH)$_3$ and many rare earth hydroxides and their corresponding oxides on stainless steel substrate could not be achieved successfully.

We are unable to completely characterize phase purity of the very thin nickel hydroxide films made on the Pt coated on quartz crystal. Thickness of the coatings obtained were calculated using frequency change during the deposition, it is an indirect method. We could not get the thickness of the coatings using techniques such as AFM because of the nonavailability of the facility.

We are not successful in the measurement of interlayer basicity and thermodynamic stability of layered double hydroxides containing cations other than Mg and Al. This is because of the poor adherence of other LDHs on Pt substrate. In the
interlayer basicity measurement, the redox change is observed only at very high
ccentration of OH ion, where the activity is ill defined and it is very difficult to find
the thermodynamic basis for the observed variation and the obtained results are purely
empirical.

Oriented crystallization has been studied in several systems and the extent of
orientation has been quantified using Rietveld refinement. In case of ZnO use of lower
concentration and higher deposition temperature yields a c-axis oriented coating. We are
successful in finding conditions which yield other orientations. Oriented crystallization of
ZnO using low concentration of zinc nitrate has been done by making water-isopropanol
mixed baths. We have not extended this methodology to study the oriented crystallization
of other systems.

In the CuO system an attempt was made to selectively redissolve the high surface
energy faces by pulsing the potential and thereby obtain oriented coatings but we did not
succeed. Instead we observed indiscriminate redissolution of the coatings during the
anodic cycle, which reduced the number density of crystallites on the substrate. This
work is not described in the thesis.

There are some weaknesses of these studies:
(1) The observed orientations are only out plane orientations. There is no in-plane
orientation as the stainless steel substrate is polycrystalline. For specific applications, the
requirement is of single crystalline films with both in-plane and out-of-plane orientation.
Electrochemical synthesis is therefore unlikely to replace techniques which promote
epitaxial growth.
(2) In this work, there is great dependence on X-ray diffraction for characterization. This
is a semi-quantitative technique based on long range order. Minor quantities of impurity
phases as well as X-ray amorphous products are not observed in diffraction studies.
Thereby phase purity of the coatings reported in this thesis is not assured.
(3) We report nanosized ZnO, based on a rigorous estimation of crystallite size based on
XRD profile refinement techniques. Although the crystallite size is in the sub-100-
nanometer range, nevertheless, the observed size is much larger than the excitonic radius
of ZnO. The reported coatings are not expected to exhibit any size dependent
optoelectronic properties.
(4) Wherever possible we have tried to relate the observed morphology to the underlying crystal structure. Morphology is observed over the micrometer length scale, whereas crystal structure is described within a single unit cell at sub-nanometer length scales. Although the forces responsible for assembly and accretion of atoms over these vastly different length scales are the same, there is no necessary correlation between crystal structure and morphology. So any correlation found could be incidental rather than being conceptual.

Scope for future work

Since oxides with large surface area find great importance in catalysis, electrosynthesis can be employed to synthesize many other oxides on various substrates. Theses coatings can be employed to perform electrocatalysis.

In our study, electrosynthesis from aqueous baths yielded metal hydroxides and oxides coatings with porous morphology. One can attempt electrosynthesis of these materials from water-organic solvent mixed baths or from non-aqueous baths.

We could make coatings of layered double hydroxide of Mg and Al on Pt substrates to measure the physical constants but we did not succeed in making LDHs of other metal ions on Pt substrates. One can make an attempt to synthesize LDHs of other metal ions either by changing deposition conditions or by using any other substrate such as gold and one can measure the interlayer basicity and thermodynamic stability of given LDH with different anions in the interlayer and LDHs of different cations.

In case of ZnO orientation was switched by making water-isopropanol mixed baths. This methodology can be extended to study the oriented crystallization of various other inorganic materials. One can attempt to study the oriented crystallization from non aqueous baths.