SYNOPSIS

Scientific Background and Objectives of *the Project*

Vast literature show that the intercalation polymerisation is a promising strategy to study the confinement of polymer chains in the nanometre size inorganic galleries. The strategy may be extended to synthesise electronically conductive polymer intercalated inorganic layered materials. Electronically conducting conjugated polymers usually have high electric conductivities contributing to many potential technological applications. The electrical responses of the resulting clay-conducting polymers have been investigated for thin films fabricated on 15 urn interdigitated arrays. These nanocomposite materials may be highly suitable for chemical sensors for a variety of important gases and vapours. They also have uses as antistatitic coatings, electrochromic films, humidity sensors and as reversible cathodes for lithium batteries. Consequently, the introduction of organic guests into inorganic host materials by intercalation techniques has resulted in fabrication of nanocomposite materials with high potential for electronic, magnetic, optical, photonic and chemical sensor applications. This project work is concerned with the synthesis of electronically conductive polymer intercalated expandable clays, their characterisation and applications in gas sensing devices. The major characterisation techniques employed include Powder X-ray Diffraction (XRD), Electrochemical Impedance Spectroscopy (EIS) and AC Impedance methods and FTIR spectroscopy.

The work described in this report represent four-year long research studies in the area of clay-electronically conductive polymer nanocomposites. The work has resulted in a one Ph.D. being awarded to the research student and 7 publications in highly reputed international journals (3 in J. Composite Materials, Sage Publications, Impact Factor 4.000 I in Electrochimica Acta, and I in Solid State Ionic already published and two more manuscripts are in the refereeing stage). The work has also contributed to 2 publications in refereed local journals (Cey. J. Sci. Phys. Sci. 2 publications) and several communications. The work has also opened a way to further study and develop clay-polymer nanocomposites for their applications in Electrical, Mechanical and Thermal Devices and in

Green Catalytic Organic Synthesis and Green Catalytic Biochemistry. A major grant has recently been awarded to investigate such aspects (RGI2005/FR/04).

Procedure 1

1. Purification of montmorilionite (MMT).
2. Intercalation of di-valent and tri-valent cations in montmorillonite.
3. Intercalation of anilinium ions within the interlayer spaces of MMT (An$^+$-MMT).(washed with distilled water)
4. Polymerisation of anilinium ions within the interlayer spacing of MMT to prepare polyaniline (Emeraldine salt, EMS) once loaded in MMT (EMS1-MMT). (washed with distilled water)
5. Neutralisation EMSI-MMT suspension
6. Further incorporation of anilinium ions and polymerization within the once loaded MMT to obtain polyaniline twice loaded in MMT (EMS2-MMT). Similarprocedure was followed with fuller's earth clay.
7. Characterisation with XRD, FTIR, EIS and AC impedance analyses.
8. Excluding washing steps, similar procedure was followed to prepare ES-MMT members (ESI-MMT, ES2-MMT and ES3-MMT) where polyaniline is in the *insitu* and *exsitu* of clay.

Procedure 2

I. Preparation of cation-exchanged MMT as above
2. Intercalation of pyrolium ions within the interlayer spacing of MMT
3. Polymerisation ofpyrrolium ions within the interlayer spacing ofMMT
4. Characterisation with XRD, FTIR, EIS and AC impedance analyses

Procedure 3

I. Preparation of cupric ion exchanged MMT
2. Polymerisation of pyrolium ions within the interlayer spacing of MMT (spontaneously)
3. Fabrication a battery using cuprous Ion containing polypyrrole/MMT nanocomposite.

Results Obtained:

The XRD analysis reveals that the d-spacing of montmorillonite (MMT) varies with the interlayer water content. However, similar results were not observed in organically modified MMT clay. A procedure for the successive introduction of PANI chains within the inter-layer galleries of MMT was developed. The monomer introduced into the layer space of MMT was polymerised with ammonium peroxydisulphate. The d-spacing of the resulting materials, measured after heat treatment at various temperatures, serves as a measure of the amount of polymer inserted in the clay inter-galleries. FTIR spectroscopy reveals the presence of 'host-guest interactions of a hydrogen-bonded nature. The DC conductivities were found to increase with the amount of PANI intercalated. The samples prepared with the washing procedure developed to remove any externally bound anilinium ions, show lower electrical conductivities than that of samples prepared by excluding the washing procedure. For the MMT-polyaniline nanocomposite an FTIR band appearing around 1140 ern", which is assigned to B- NH+ = Q, is a measure of the electronic conductivity of the sample. AC impedance analysis shows that ES-MMT system possesses an electronic conduction which increases with successive loading of polyaniline. Ratio of the number of moles of anilinim ions to the mass of the MMT clay has a great influence on the conducting form of polyaniline present within the interlayers of the nanocomposites. The EIS studies reveal that the ES-MMT members have both electronic and ionic conductivities with similar transport numbers even when the polymer is in its fully electronically conducting state.

In addition to this, polypyrrole/montmorillonite (PPY-MMT) nanocomposites were also studied to understand the variation of chemical and physical properties of MMT upon polymer intercalation. The ionic conductivity of polypyrrole/MMT prepared by excluding the washing procedure has arisen from the motion of the lithium ions and it is higher than that of lithium ion exchanged MMT. In addition to that, it possesses high electronic conductivity. In order to polymerise the pyrrolium ions only within the intergallary spaces of MMT, Cu(ll)-exchanged montmorillonite was used. These pyrrolium ions undergo spontaneous polymerisation by the Cu(lI) ions present within the intergalleries to form Cu(l)-poly(pyrrole)-MMT nanocomposite. However, the polymerisation of pyrrole can not be achived by Cu(II) in the aqueous medium. The material possesses mixed electrical conductivity and is unusually high. The conjugation length and hence the electronic conductivity decrease as the temperature is increased as confirmed by the FTIR spectroscopy.

Conclusions:

The overall results are indicative of electrically conductive nature of polyaniline/montmorillonite nanocomposites developed in this project work. The conductivity of these materials can be tuned by changing the amount of polyanline within the later space of MMT. However, polypyrole/MMT nanocomposites show both electronic and ionic conductivities. The electrical properties of these material can be utilised in the design and development of gas sensors. The materials are also highly suited (PPY/MMT) to fabricate electrochemical cell.