FORMATION OF BIOMINERAL NANOFILM *VIA* ADSORBED SURFACTANT-DIRECTED PRECIPITATION CHARACTERIZED *IN-SITU* BY MEANS OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

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Agenda

- The Research Group
- Works on Interfacial Phenomena
- Prospective Collaboration

The Research Group

Ceramic/Carbonaceous Materials & Interfacial Phenomena Research Group – Major Aims :

- To understand deformation and flow properties of particulate green ceramic bodies including clays
- To understand interfacial interaction which leads to enhanced performance properties in composite materials
- To understand fundamentals of nucleation and growth of materials at the surfaces/interfaces
- To understand the underlying mechanisms of filming inhibition in the corrosion of metals

Current Research Interest(s) :

- Green State Properties of Ceramic Materials & Biocomposites
- Carbonaceous Materials & Agri-Based Fibre Composites
- Structure & Dynamics of Materials Surfaces/Interfaces
- Novel Concepts in Metallic Corrosion Inhibition

Research Works Involves the Application of :

- Fourier Transformed Infra Red Spectroscopy (FTIR)
- Scanning Electron Microscopy (SEM)
- Polarized Light Optical Microscopy (PLOM)
- Electrochemical Impedance Spectroscopy (EIS)
- Digital Mechanical Tester (Tensile/Compressive)
- Thermal Analyzer (DSC)

(Happy) members of the group

2002

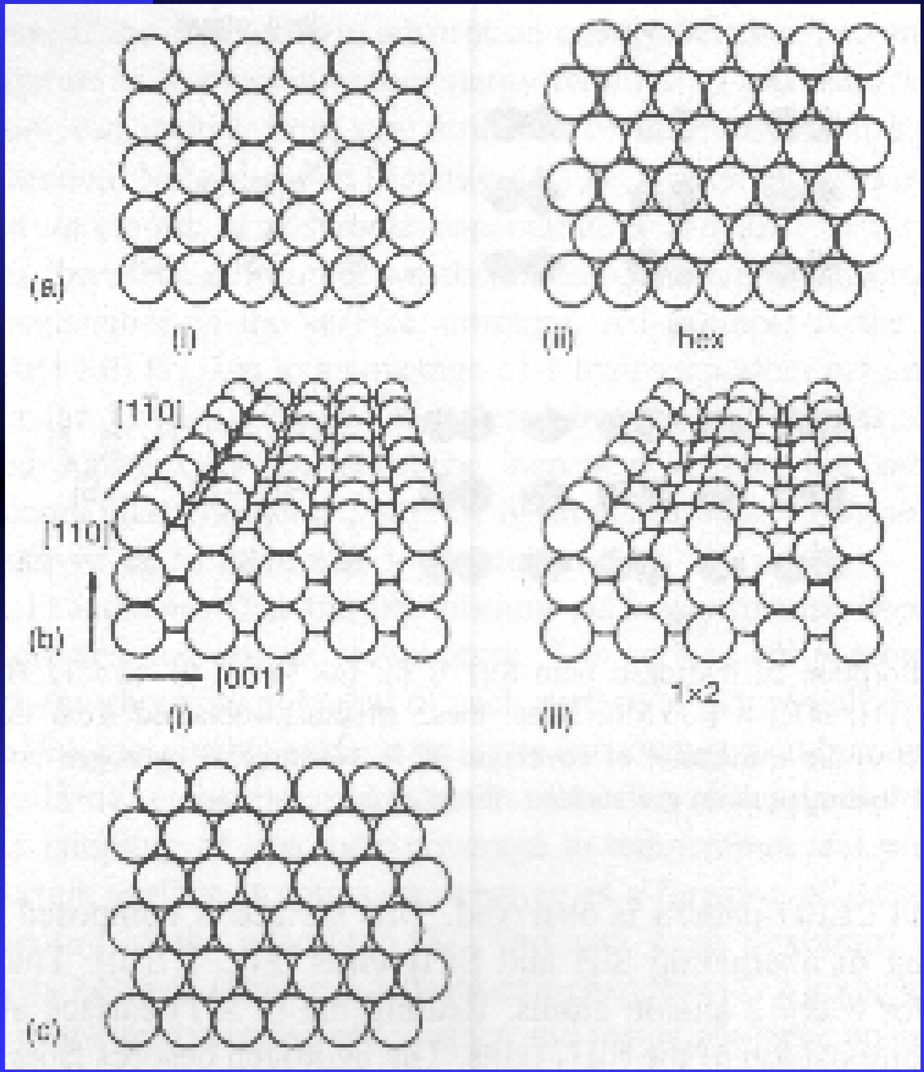
2004

2003

2005

Works on Interfacial Phenomena

Paramount Importance of Surface/Interface in Nanotechnology



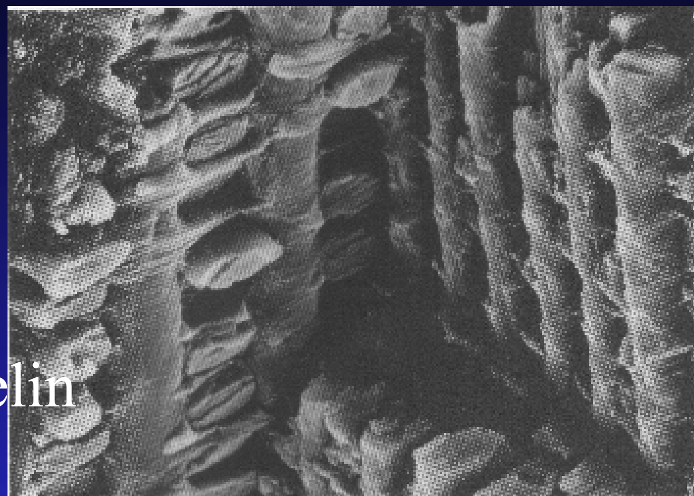
Interfacial Phenomena in Biomaterials

- Biomaterials → Biomimetic Processing → Biomineralization → Flat Precipitation
- Templated Nucleation & Growth → Molecular Recognition on the interface
- Solid / Liquid Interface → Electrode / Solution Interface → Charge Transfer Characteristics → AC Techniques → EIS

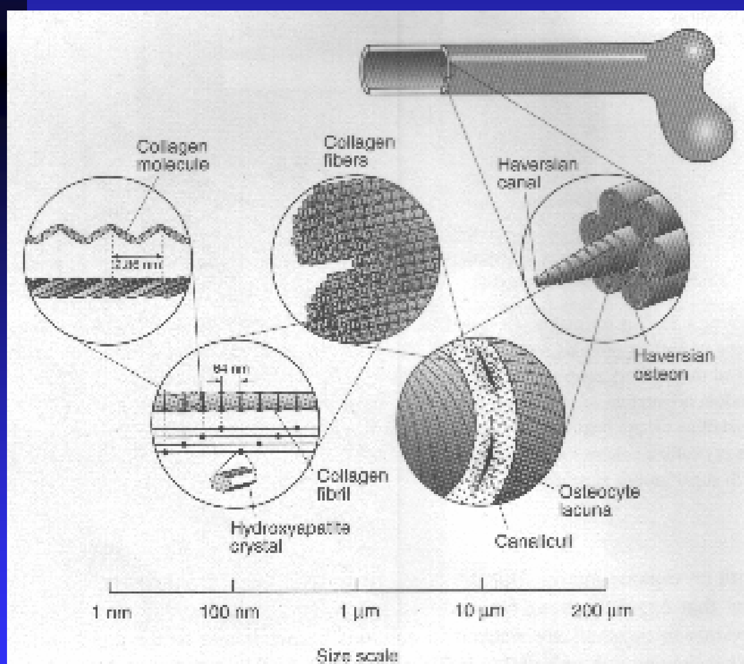
Biomaterials

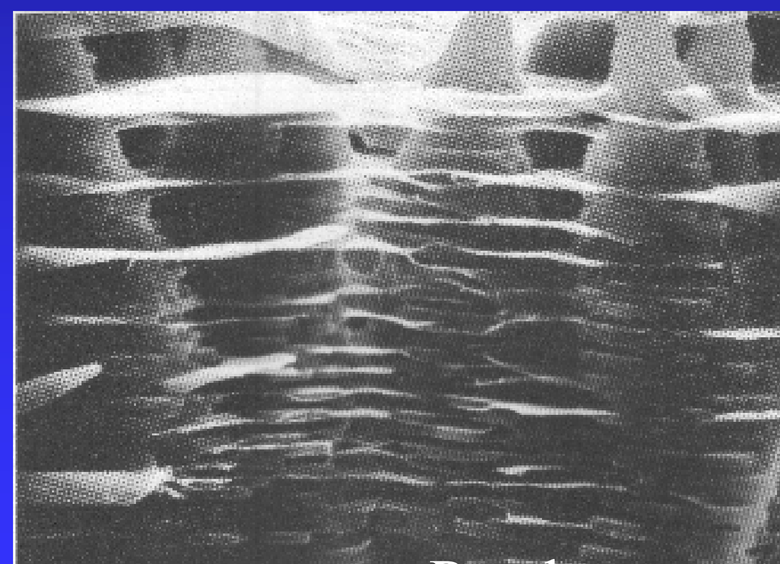
- The ultimate of advanced materials
- Sophisticated properties
- Ability to serve many functions simultaneously

Examples of (Natural) Biomaterials



Enamelin





Pearl

Constituents of Biomaterials

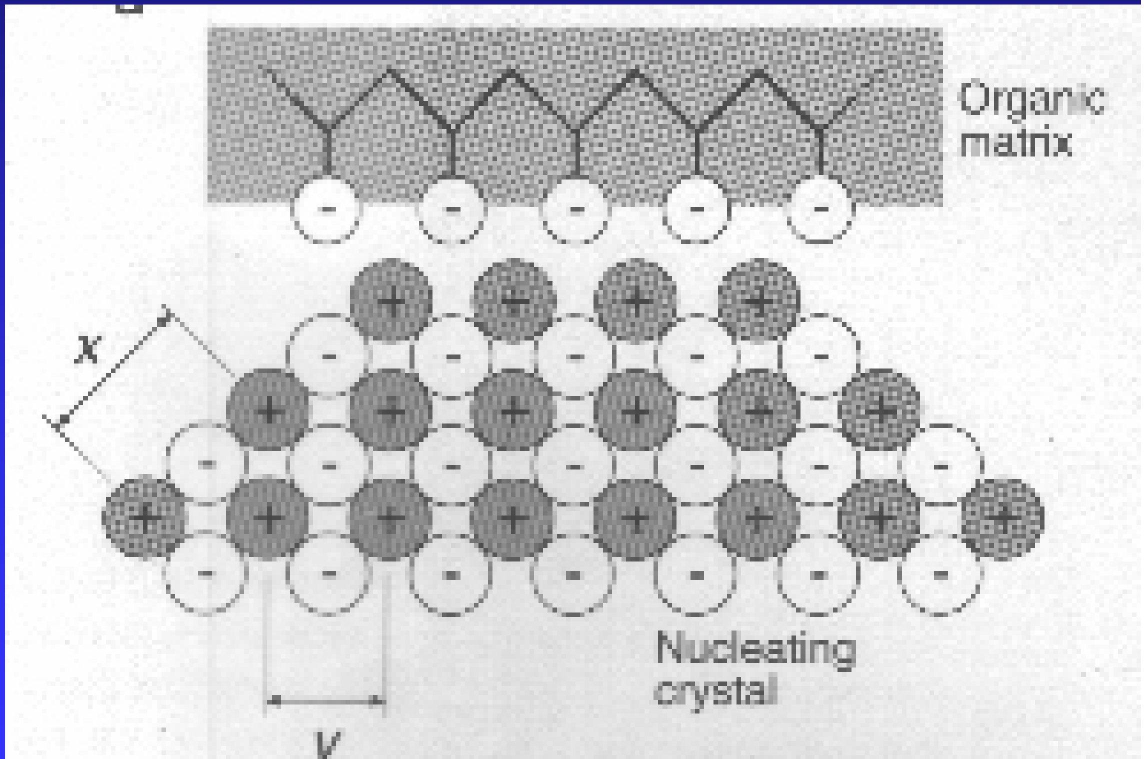
- Organic/polymeric → covalent bond → high tensile strength
- Inorganic/minerals → ionic bond → high compressive strength
- Both → Crack deflecting mechanisms → high fracture toughness
- Biomaterial high proportion of inorganic phase → biominerals

Biomineralization

- Control exerted by organic matrix on mineral crystal nucleation and growth during biomineral formation
- Organic matrix govern: orientation, shape and size of mineral crystals

Biomineralization Principles

- Complementarity of electrical charge
- Disposition/distance and geometry of binding sites



Biomimetics

- The art of mimicking biology
- Materials Science → learns from nature, in an attempt to mimic and adapt nature's materials, to develop new synthetic materials with such a sophisticated properties → biomimetic materials

Dominant Guide Themes in Biomimetic Materials Research

- Composites
- Hierarchical Structure & Organization in many scales

Elements of Biomimetic Materials Processing

- Self Assembly
- Control of Nucleation and Growth
- The Usage of Templates

Electrochemical Techniques :

- DC Signal Techniques : large perturbation (curr/pot sweeps/steps), drive electrodes far from equilibrium, unsteady/transient responses
- AC Signal Techniques : small amplitudes, varying frequencies, steady state responses

→ Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) - Applications

- Corrosion and corrosion control
- (Electrical) energy storage, batteries, & fuel cells
- Semiconductors & solid electrolytes
- Electronic & ionic conducting polymers
- Charge transfer dynamics and electrochemical reaction mechanisms

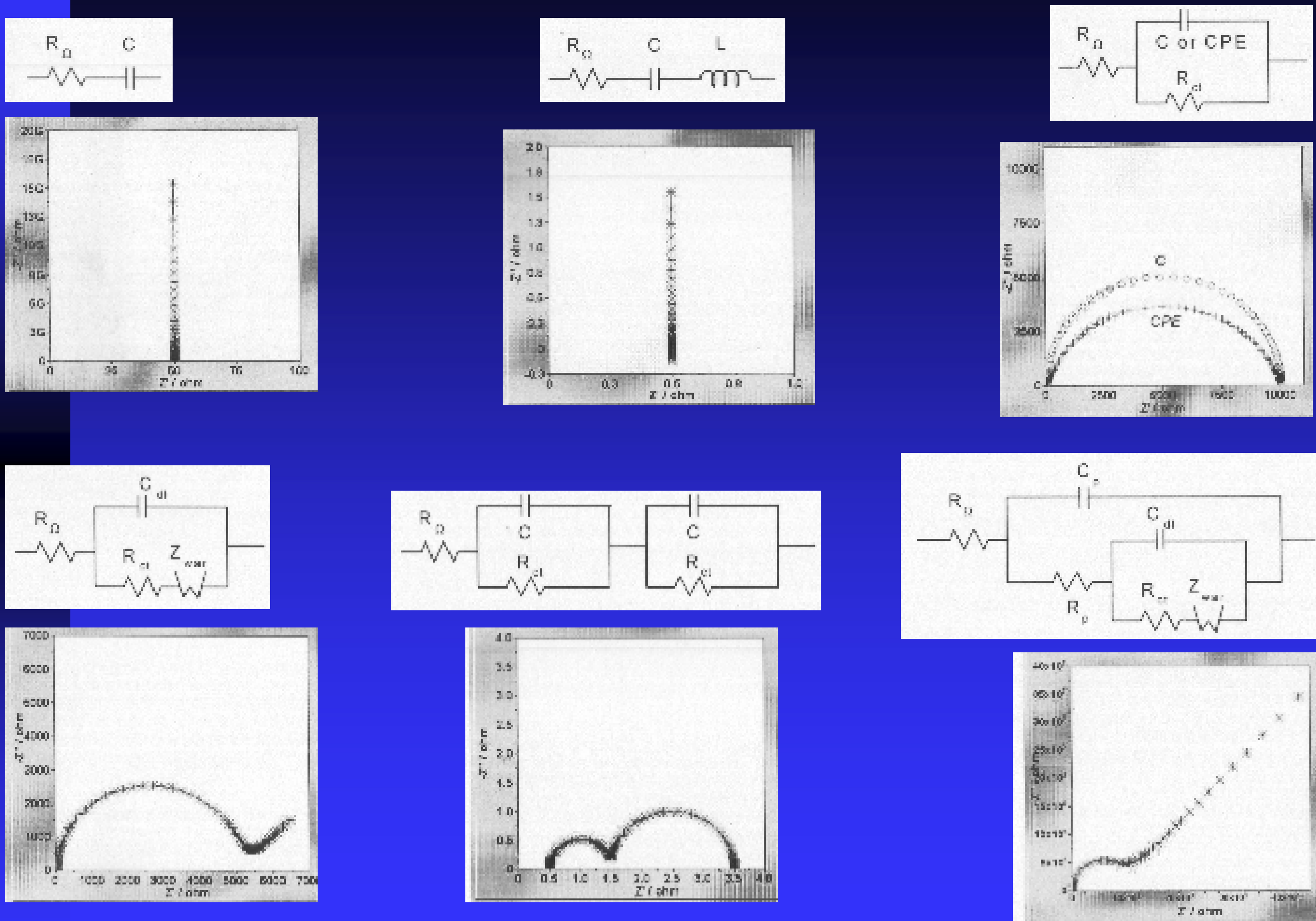
Electrochemical Impedance Spectroscopy (EIS) - Advantages

- Higher precision measurement, steady response could be long-term averaged
- Theoretical treatments by linearized response
- Simplified kinetic/diffusional treatments
- Works for less conductive systems (*eg*. polymer coated, oily media, etc)

Main Idea Behind EIS Technique

- Analogies between the electrochemical cell under study with networks of resistors and capacitors which thought to behave like the cell

Examples of Typical Equivalent Circuit Models



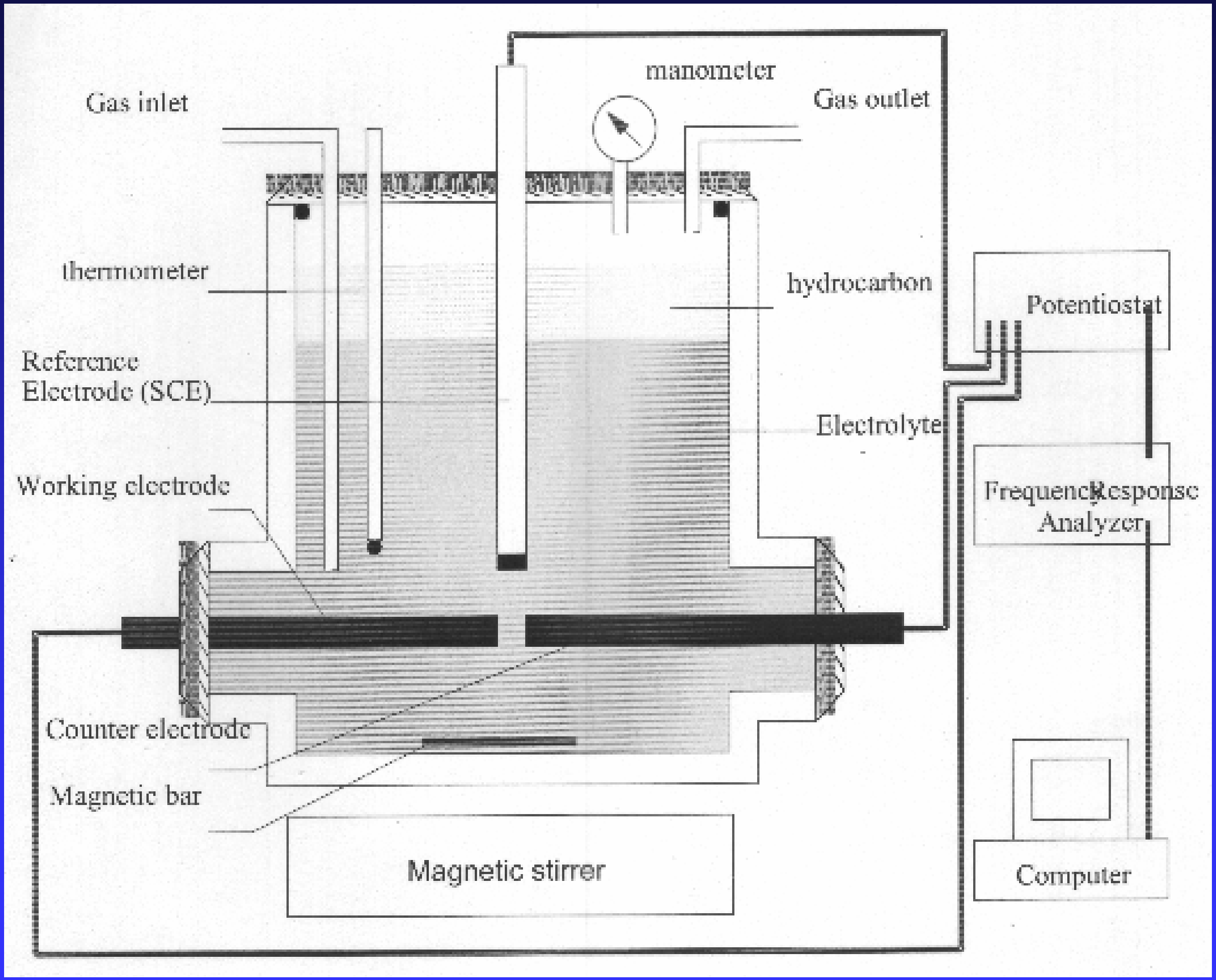
EIS Instrumentation

- Voltalab-40 from Radiometer
- Freq. Range : 1 mHz – 100 kHz
- Sampling rate up to : 20 Freqs/decade
- Sine wave amplitude range : 1 mV – 1 V
- Over potential range : 50 – 1000 mV
- Resolution : 12.5 µV

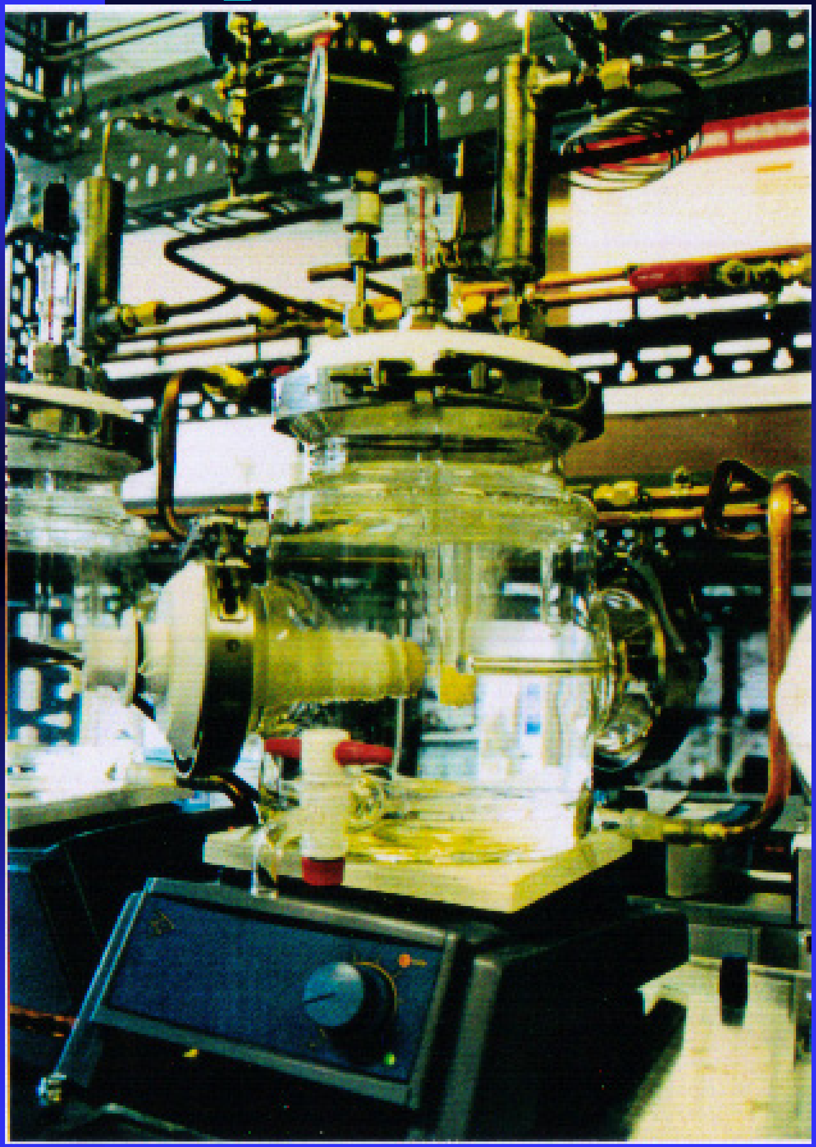
Methodology

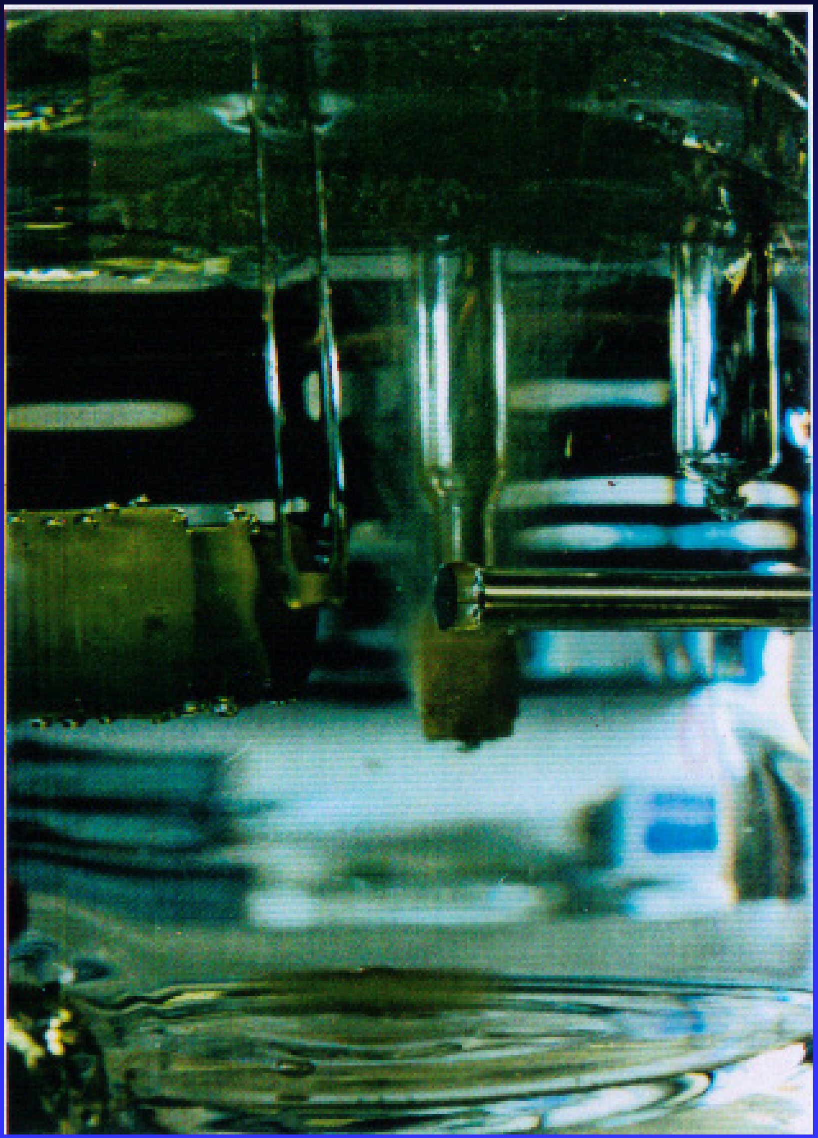
- Electrolysis of H_2O takes place on pair of Pt electrode surface
- Supersaturation of aqueous solution is maintained with $Ca(OH)_2$ crystals
- Slow $CaCO_3$ precipitation is enabled by CO_2 bubbling (±10 mbar above ambient)
- Precipitate (templated or not) on electrode surface, affects electrolysis rate *ie*. charge transfer resistance → R_P
- R_P are measured as a function of time from the commence of CO_2 bubbling

Experimental Set Up

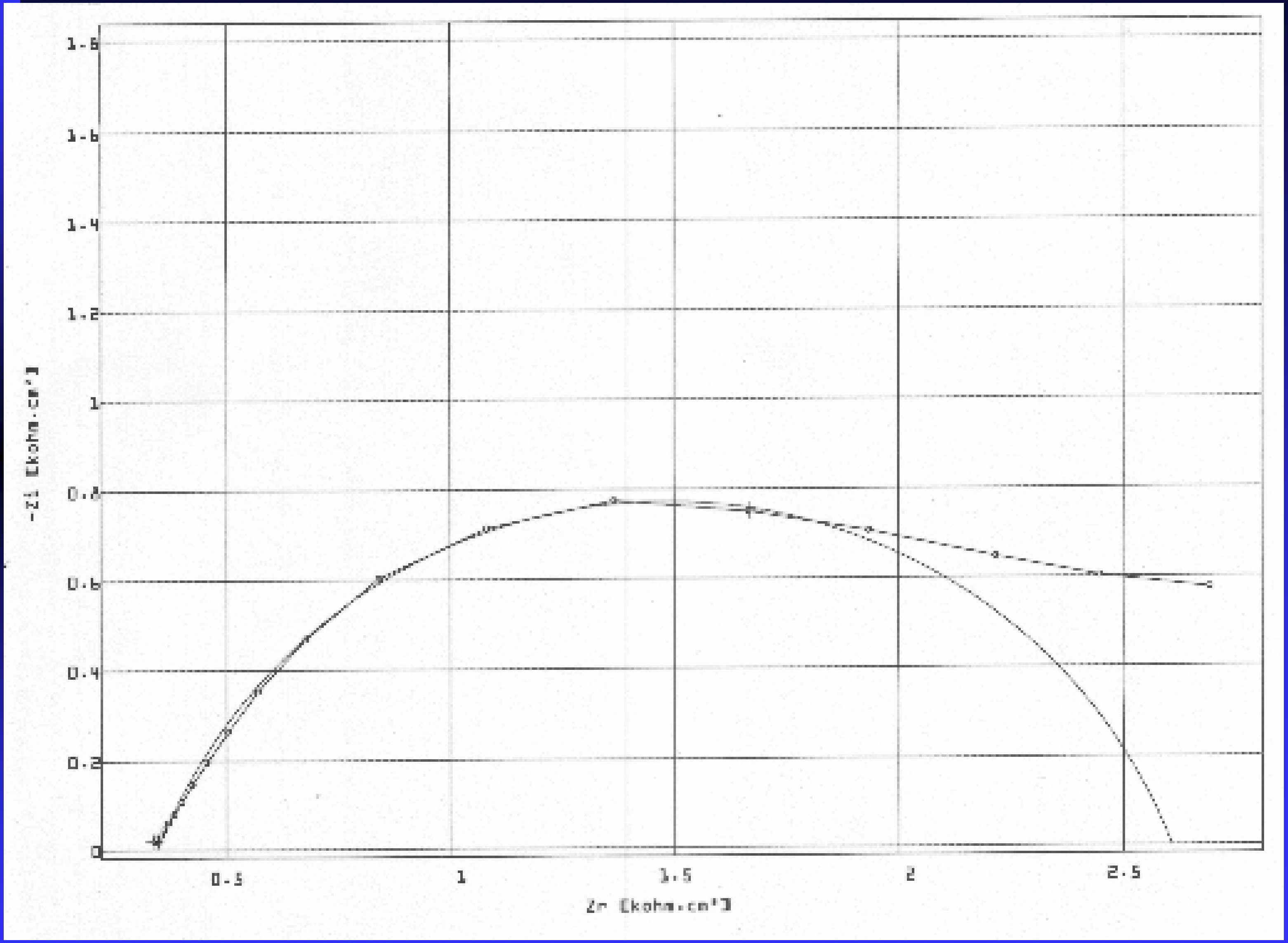


Set Up of the Electrodes

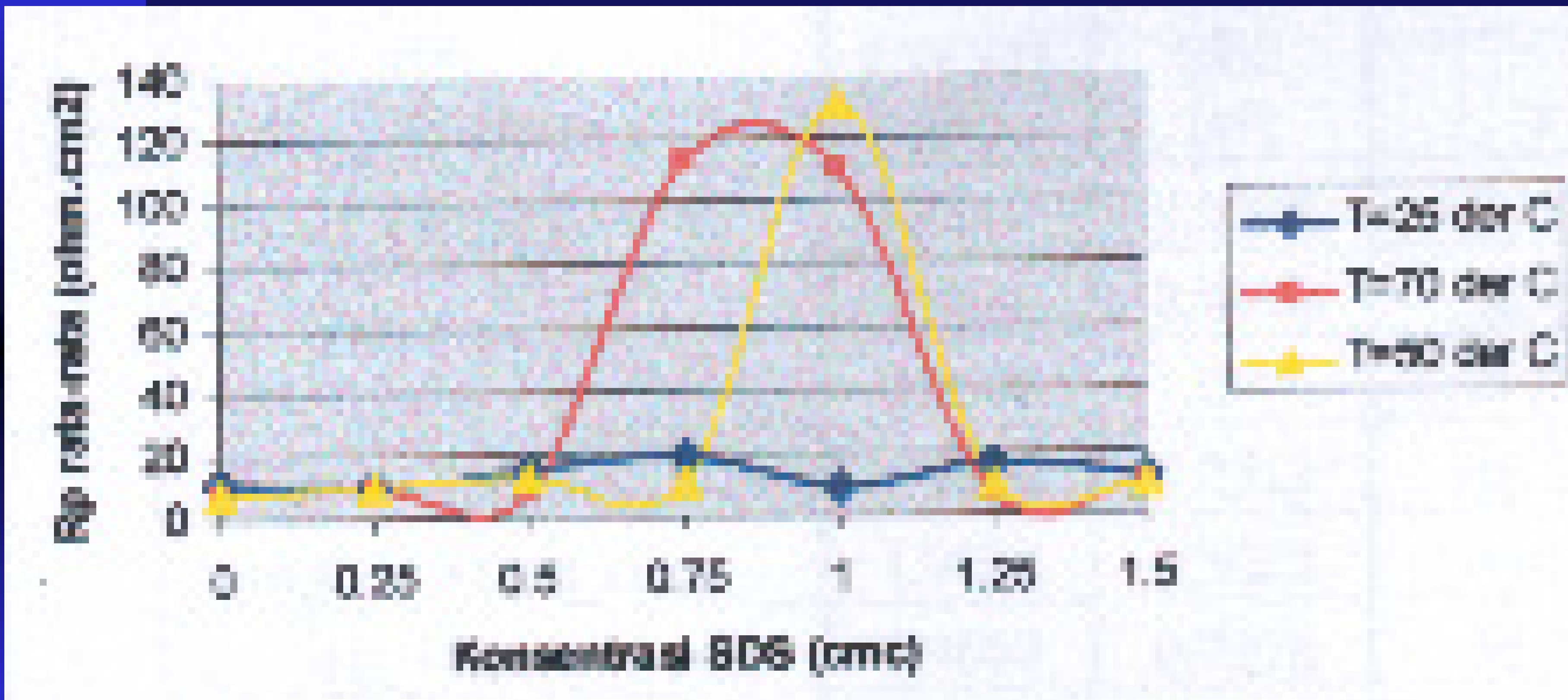




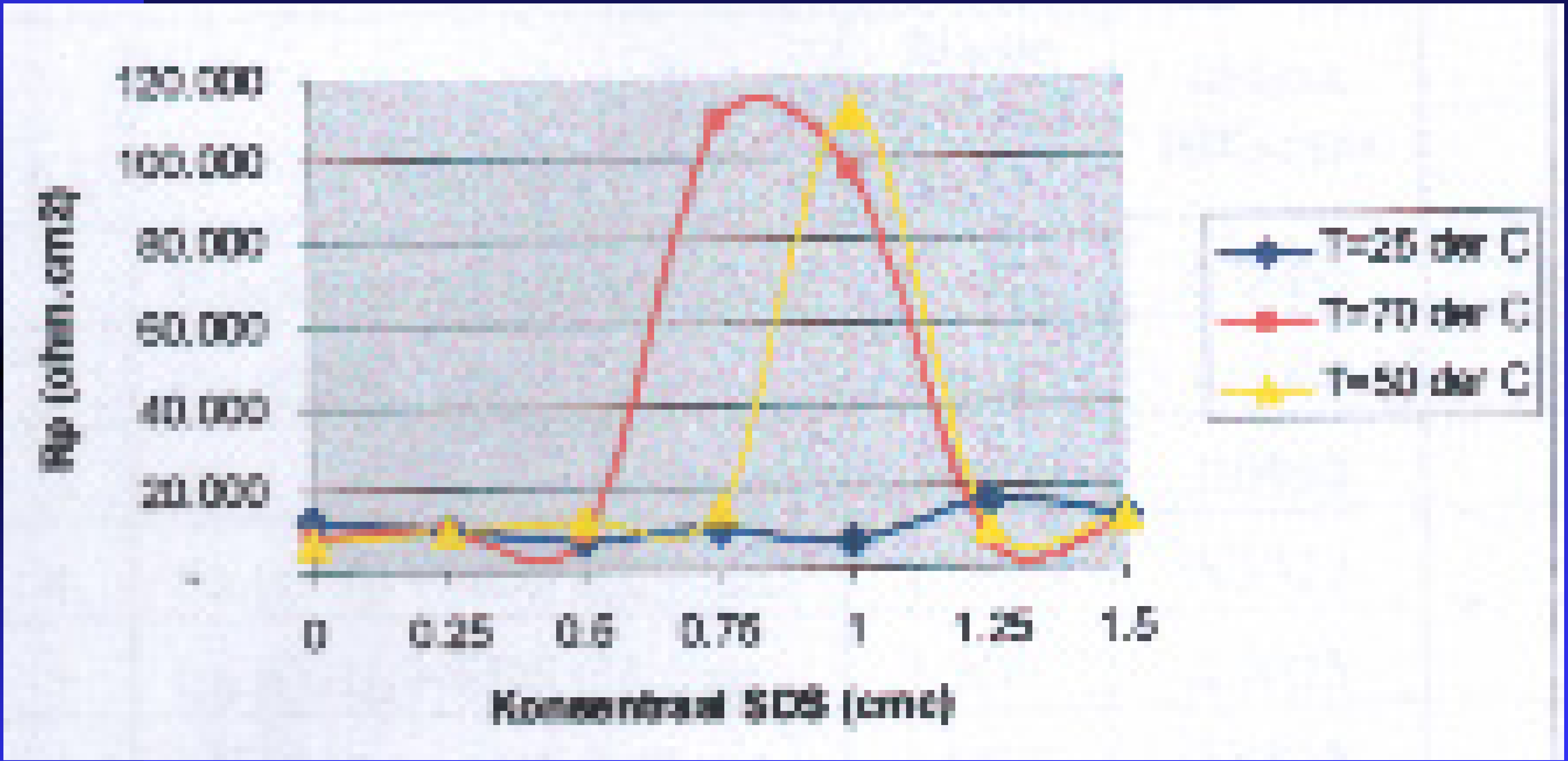
Typical Nyquist Plot from EIS



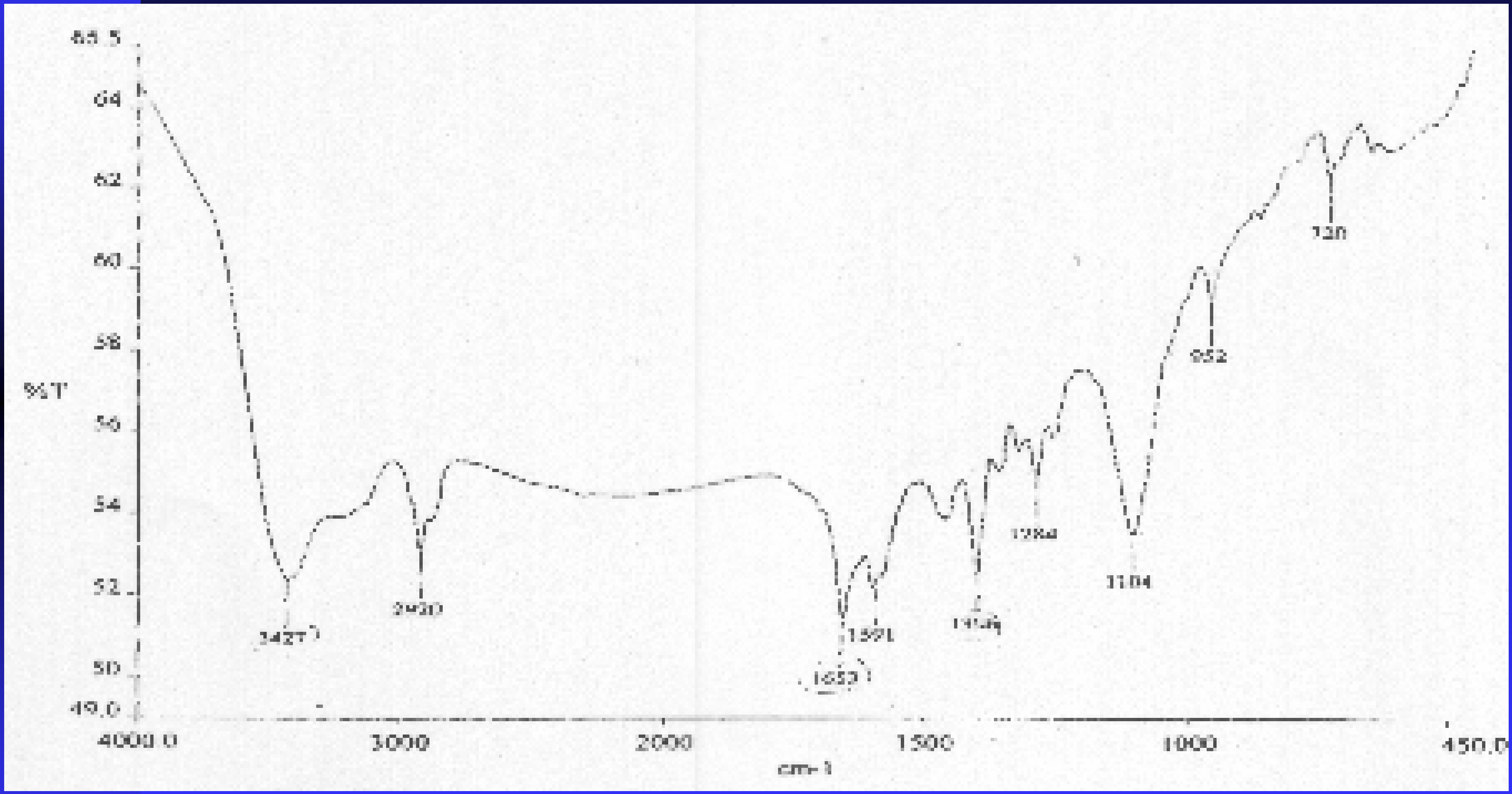
Results from EIS Measurements



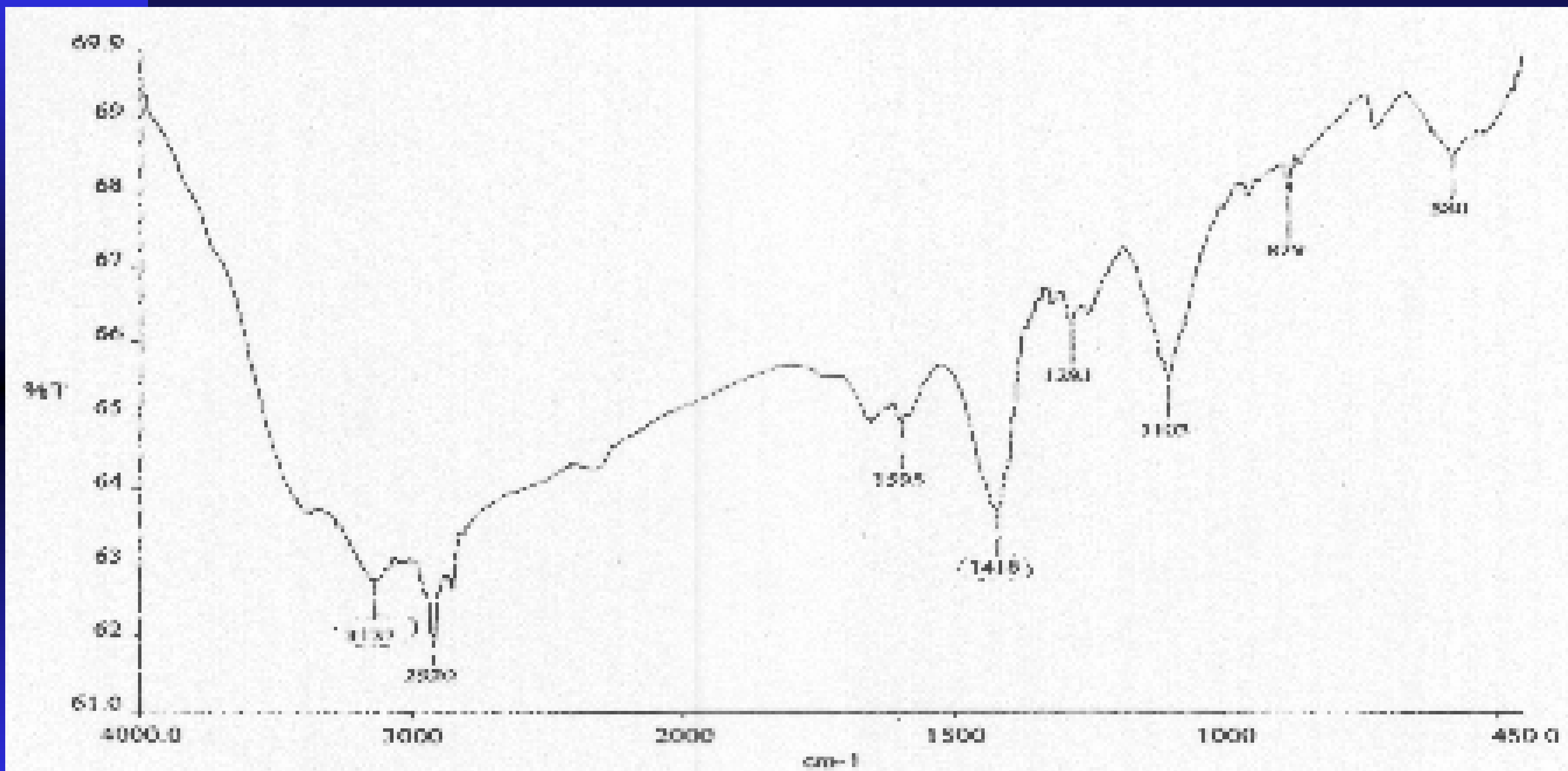
Results from EIS (cont'd)



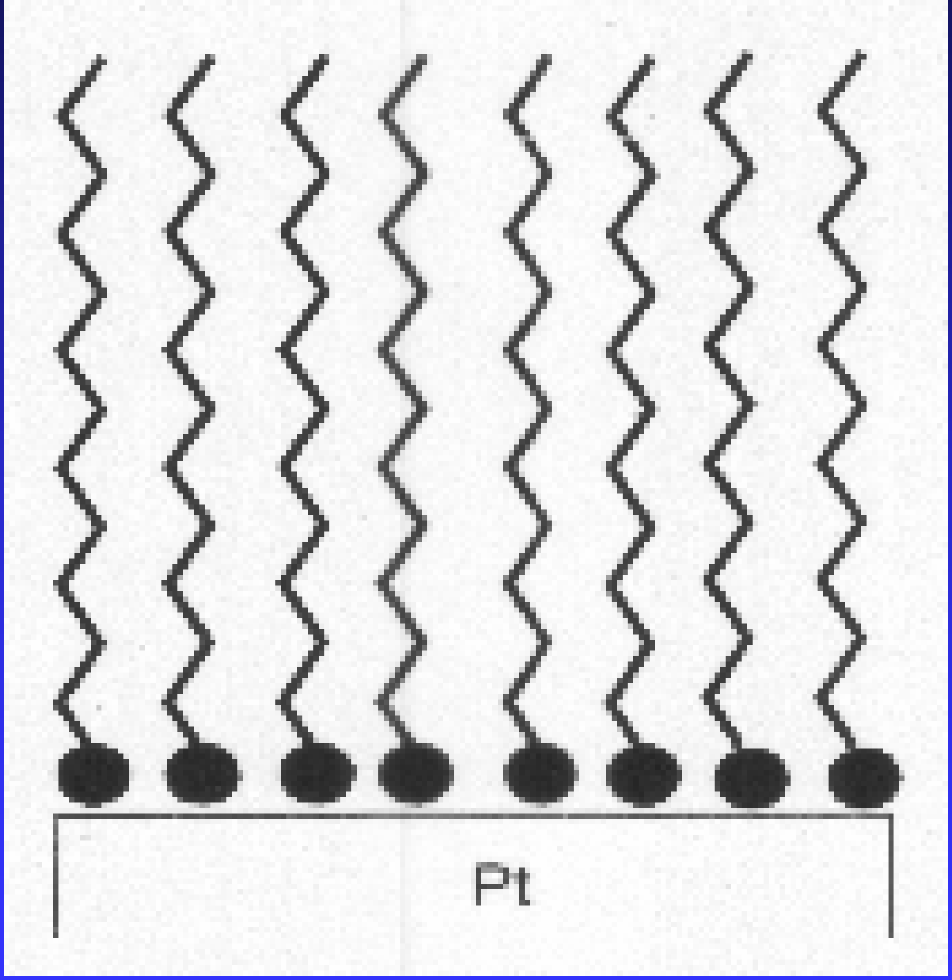
Results from FTIR Spectroscopy



Result from FTIR (cont'd)



Discussion



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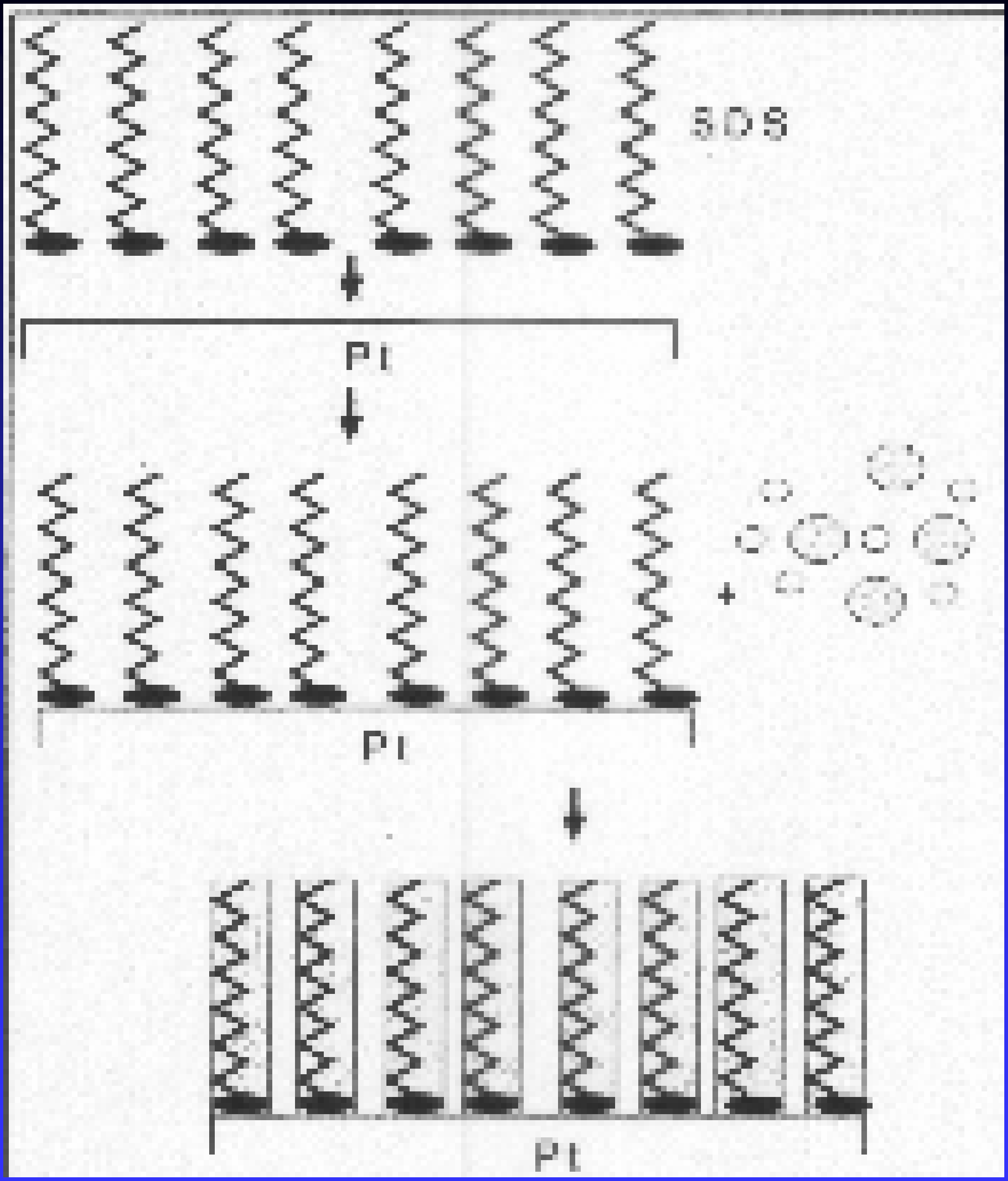
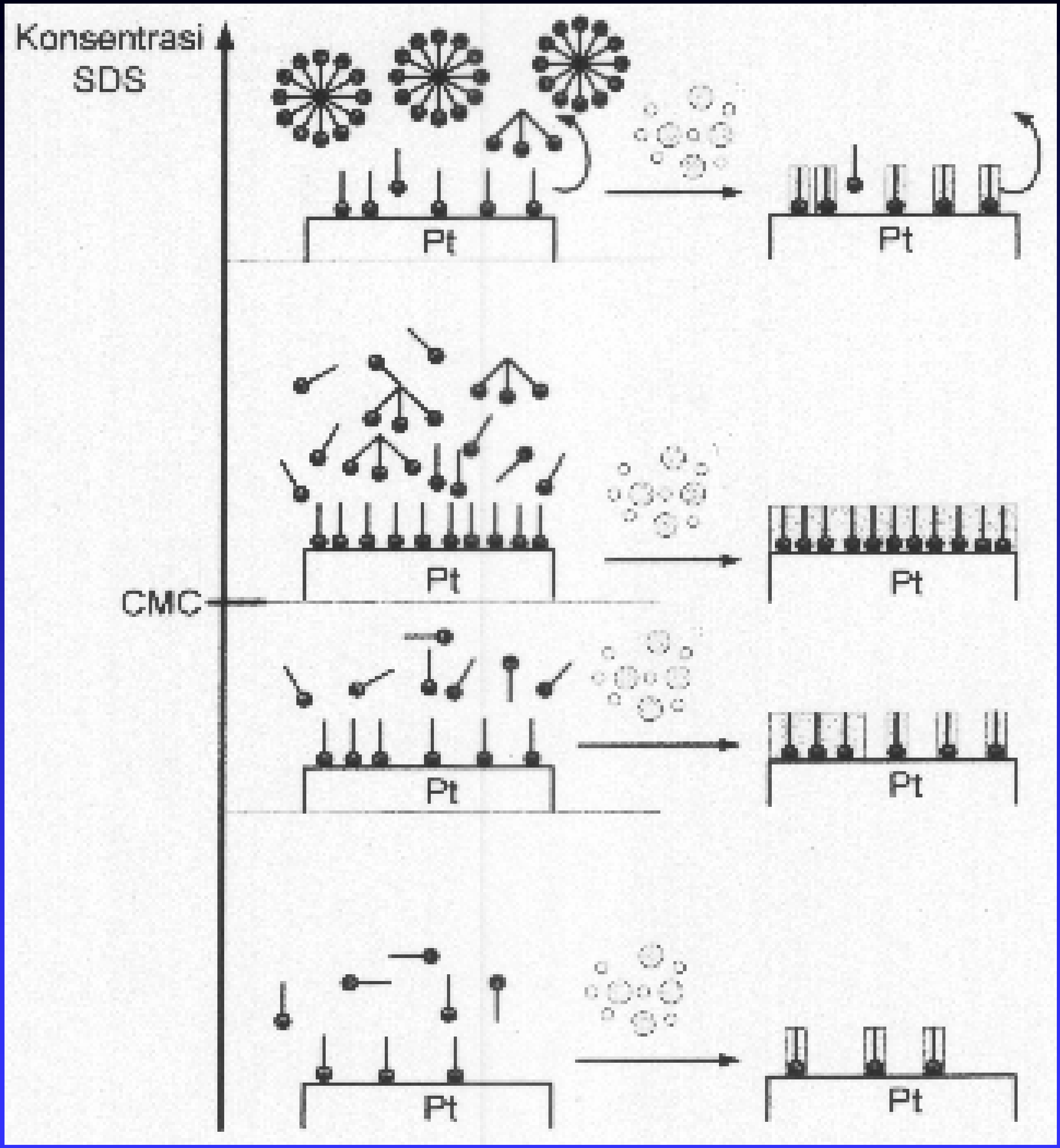


Discussion



Concluding Remarks

- Coherent calcium carbonate nanofilm can be grown within abiotic aqueous environment on SDS surfactant as template
- EIS could be succesully employed to follow the development of inorganic nanofilm on top of conductive substrate

Prospective Collaboration

Further Works – Determination of :

- Crystal Phases
- Crystal Growth Habit
- Orientation/Direction of Crystal Face
- Morphology and Texture of Nanofilm
- Modes of Film Spreading
- Growth Kinetics of Nanofilm
- Mechanical Properties of Nanofilm

Further Works on Experimental Set Up :

- Integration with Hydrothermal Crystallizer (under construction) for experiment with other biomineral systems
- Detachable Metal Electrode Substrates for further characterization

Expected Access to Regional Facilities for Further Works and/or Collaboration

- Langmuir-Blodgett Trough/Balance Facilities
- Grazing Incidence XRD (GIXRD)
- Atomic Force Microscopes (AFM)
- Transmission Electron Microscopes (TEM)
- Scanning Imaging Mass Spectrometer (SIMS)

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