Significant contribution:

Dr. Anbu Kulandainathan’s work during the last 5 years at CSIR-CECRI, Karaikudi, was significantly focused on (i) new strategy for the dyeing Industry to avoid pollution problems in the technology of DYEING OF COTTON FABRICS WITH VAT DYES, ii) the electro-organic synthesis of pharmaceutical intermediates, (ii) new types of electrodes and materials for electrochemical applications including electrosynthesis and power sources, (iii) Synthesis of nanostructured materials of a) ZnO as UV protecting materials b) SiO₂ for superhydrophobicity and c) TiO₂ for Self cleaning d) Hierarchical structured polymer grafted silver nanocomposite non-woven cellulose fabric for multifarious applications which were harvesting about 65 papers in internationally refereed journal, 12 patents and two technologies.

(i) Electrochemical Reduction of Vat dyes

Eliminating or minimizing the use of sodium dithionite and other sulphur-containing compounds during the vat-dyeing process is an important challenge in environmental chemistry. The main objective of my research is to find an alternative, environment friendly electrochemical vat dyeing process that completely eliminates the use of hydrosulphite, high temperature dyeing and also get rid of disposal of sulphur containing liquid waste. Ferrous/ Ferric complexes are being tried as an alternative in regenerated electrochemical vat dyeing process. Ferric triethanolamine complex in high alkaline medium is a very well-known redox mediator for reducing vat dyes in indirect electrochemical process. In this process, ferric triethanolamine can be reduced by electrochemical reduction method to ferrous triethanolamine (Fe³⁺→ Fe²⁺). This electrochemically reduced iron complex having the potential to reduce the vat dyeing molecules (the maximum potential for the reduction of vat dye is reported around -950 mV vs Hg/HgO/OH⁻, this reduced complex having the reduction potential above -1000 mV vs Hg/HgO/OH⁻). In our laboratory we have replaced triethanolamine with cheaper and greener chemicals. Ferric-oxalate-gluconate system was investigated for the electrochemical reduction of vat dyes. The present study shows that the Fe(III)-oxalate system can be stabilised in alkaline media in the presence of excess gluconate. Voltammetric investigations indicate that
the Fe(II)-TEA-gluconate system, as well as the Fe(II)-oxalate-gluconate system, catalyse the electrochemical vat dyeing system through the Fe(II)-gluconate intermediate. Both basic voltammetric investigations and laboratory scale vat dyeing experiments indicated that the Fe(III)-oxalate-gluconate system would be an alternative redox mediator for the process. The influence of the concentration of the complex-system on the build-up of color depth, shade and fastness are compared with samples of the standard dyeing procedure using sodium dithionite as reducing agent. The new process offers environmental benefits and also offers the prospects of improved process stability, because the reduction state in the dye bath can be readily monitored by measuring the equilibrium potential.

(ii) **Conducting Polymer Based Smart Textile**

Flexible conductive materials are the gateway to the new generation electronic devices that benefit from the ability to bend, fold, and rollup. Combining of flexibility and conductivity properties on a material is a difficult task. Textile materials have good mechanical stability and flexibility, but they are insulators as received. Integration of conducting polymers into these substrates can generate multifunctional properties with good mechanical properties and flexibility. Technological developments in these fibres and fabrics have created a whole range of smart and modern textiles which can be used in many applications. In this area we have developed polypyrrole or PEDOT/PSS coated textile substrates and studied their properties for utilisation in smart applications. Different methods were adopted for the making of polypyrrole coated textiles including *in-situ* polymerisation, electrochemical polymerisation and chemical vapour polymerisation techniques. Interaction of conducting polymer with textile substrates and their improved properties were examined. The conductivity value of $5 \times 10^{-1} \text{ S cm}^{-1}$ reported from these studies. We have investigated these materials for the application of electrochemical storage devices, thermal actuators and antimicrobial textiles. A prototype symmetrical supercapacitor using polypyrrole-textile composite electrode delivered the highest capacitance of $268 \text{ F g}^{-1}$. In another application, developed a circuit breaker for electronic and a robotic hand by utilising the unusual thermal responsive actuation of the PPy-viscose rayon composite. The simultaneous deposition of PPy and silver nanoparticle on textile materials showed an improvement in the conductivity as well as the antibacterial property for the textile material.
Hierarchical Structured Polymer Templated Silver Nanocomposite on Non-Woven Cellulose Fabric for Multifarious Applications

Lotus mimicking surface is established via a simple and easily reproducible strategy to introduce multifunctional properties on hydrophilic cellulose surface with polymer grafted silver nanowires as a core-shell nanostructure. Superhydrophobic surface with polymer template on cellulose was formed by the amide bond between the anhydride units of polymer and initially aminosiloxane functionalized cellulose. Furthermore, hierarchical short linear silver nanowire were uniformly produced throughout the above functionalized surface, with an average diameter of 60 nm and length of 288 nm, using a mild reducing agent at 60 °C. This biodegradable nanocomposite based cellulose fabric surface was demonstrated as a) Superhydrophobic b) Membrane for Oil-Water separation c) Excellent killing efficiency towards antimicrobial activity against *E. coli* and *S. aureus* and d) pH responsive sustained release of colloidal silver.
Scheme for the synthesis of Cellulose based multifunctional fabrics
Electrosynthesis and Catalysis of Metal Organic Frameworks for Carbon dioxide sequestration and Electrochemical Energy Devices

Metal organic frameworks (MOFs) is emerging as a new class of porous crystalline materials, consists of both inorganic and organic moieties, exclusively assembled by two main components of inorganic metal ions or clusters and organic linkers, by strong coordination bonds. Further it gives a new development on the interface between materials science and molecular coordination chemistry. MOFs can exhibit tunable chemical functionality, exceptionally high surface areas (500–6500 m²g⁻¹) with large pore sizes (3–35 Å) and tailorable nanoporous host materials as robust solids. These materials are having rigid pores, which are not collapsed upon addition or removal of solvent or other guest molecules occupying the pores. They are often highly crystalline, porous with high structural and thermal stability. The variation of ligand structure, spacer length, metal atom, and synthetic procedure has given rise to the formation of a large number of porous compounds with correspondingly large variety of properties and applications. In general, chemical and hydrothermal methods are extensively used for the synthesis of MOFs. However, these methods often suffer either usage of various oxidising/reducing agents or high temperature with long duration. Whereas, electrochemical synthesis is an effective and simple method which averts the usage of oxidising/reducing agents and also it can be carried out in room temperature with comparatively very short duration. MOFs are synthesised economically with high yield and investigated their applications in various fields.

Cu-BTC MOF is explored as a good electrochemical catalyst for carbon dioxide reduction and as a chemical catalyst for the conversion of nitrophenol to aminophenol. Recently organic electrode materials have gained more attention towards energy storage applications. However, small organic molecules have several drawbacks such as solubility in organic electrolyte and low thermal stability as compared to inorganic molecules. We are addressed water free Cu-BDC has been evaluated as a new anode material for lithium ion battery application and achieved 84% capacity with good capacity retention. In another application the electrochemically synthesised Al-BTC is mixed with poly ethylene oxide (PEO) polymer and demonstrated as a potential polymer electrolyte for lithium ion battery. In general transition meal oxides are well known material for supercapacitor
application; and achieved a specific capacitance of 28.11 F g\(^{-1}\) with an electrochemically synthesised Ni-BTC MOF as an electrode material.

(v) **Electro Organic synthesis of pharmaceutical intermediates:**

Electrosynthesis of triphenylphosphine and chloromethyl azetidinone ester are very important chemicals in Pharma Industries. They are synthesised electrochemically in good yield using novel routes of ionic liquids and two phase electrolysis respectively. Site directed bromination of aromatic compounds by an electrochemical method has also been carried out. *Synthesis of chloromethyl azetidinone ester technology was transferred to M/s SPIC Pharma, Chennai under DSIR Project Scheme.*
(vi) **Mediated redox system for Electro Organic synthesis:**
Synthesis of naphthoquinone, benzaldehyde, anthraquinone employing electrochemically generated/regenerated ceric salt. The technology developed now involves the generation/regeneration of ceric methanesulphonate in methanesulphonic acid employing a DSA/O₂ electrode in an undivided cell.

(vii) **Paired and non-paired electrochemical synthesis of L-Cysteine and L-cysteic acid from L-Cystine:**
L-Cysteine, L-Cysteic acid their derivatives having largest applications in food, pharmaceutical, and personal care industries. Developed a flow cell set up for the electrochemical synthesis of L-Cysteine hydrochloride monohydrate. The electrode materials, electrolyte composition, concentration of the reactant, current density, efficiency, time and flow rate are optimized for the production of L-Cysteine hydrochloride monohydrate. Paired electrochemical synthesis of L-Cysteic acid and L-Cysteine from L-Cystine are also developed, which improves notably the economic parameters of the synthesis. **THIS PROJECT WAS MAINLY CARRIED OUT FOR M/s VIJAYAM BIOCYTES Pvt. Ltd., CHENNAI.**

(viii) **Nano structural materials of ZnO, TiO₂, Al₂O₃ and Fluoro functional groups as UV protecting and superhydrophobic fibers:**
Developed methods to prepare stable solutions of different nano-metaloxides both by chemical and electrochemical methods for incorporating into cellulose matrix for smart applications such as fire retardant, superhydrophobicity and UV Protection textiles.