Chapter – 1
A Brief Account On: Ionic Liquids with its Applications
1.01 Introduction

After releasing the book – ‘Silent Spring’ [1] in 1962 huge numbers of laws against chemical release and safety have been enacted. The environmental laws generated new ways of thinking about chemical safety and the environmental aspects of chemicals. It was recognized that chemistry is one of the key sciences in taking care of the environmental problems created by chemicals.

One of the important issues in green or sustainable chemistry is the use of the traditional volatile organic compounds (VOCs). VOCs have been used extensively to provide one or more liquid phases for chemical reactions, regulate temperatures, moderate exothermic reactions, cleans equipments and clothing, isolate and purify compounds by re-crystallization or extractions, generate azeotropes for separation, assist structural and/or analytical characterization of chemicals, etc [2]. While there are solvents that are available in nature and are environmentally benign, a large number of them are man-made and could result in serious environmental and health problems. For example, the destruction of ozone by chlorofluorocarbons in the upper atmosphere is well established and led to the replacement of refrigerants. The toxicity of some of the chlorinated solvents poses a threat to the workers and, if they enter the environment, to all of us. Solvents frequently cause fires and/or explosions resulting in destruction. Many chlorinated hydrocarbon solvents have already been banned or are likely to be banned in the near future.

The development of solvent-free alternative processes could be the best solution, especially when either one of the substrates or the product is a liquid and can be used as the solvent of the reaction. However, if a solvent is crucial to a process we should select solvents that will have no or limited impact on health and the environment. Nature provides only a
limited number of molecules that can be used as solvents either directly or after purification. *Although water is the most abundant solvent in Earth.*

VOCs has led to some major public concerns about their usage, some of which appear in the ‘problems’ box in **Fig 1.01**.

**Fig 1.01** Summary of the major uses and problems associated with solvents.

### 1.02 Role of green chemistry

Green Chemistry is defined as “the design, manufacture and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances”. Striving for a sustainable development is a necessary task for mankind. To improve the protection of human health and the environment from the risks that
can be posed by chemicals, and to strengthen the former legislative framework on chemicals of the European Union, on 1\textsuperscript{st} June 2007 the regulation REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) has been approved by the European Parliament. The REACH regulation and the twelve principles of green chemistry formulated by Anastas and Warner [3] can be seen as new important alternative tools for the assessment of hazards of substances and they can act as a guideline to help minimizing the hazard of a process, as well as increasing its overall sustainability. The twelve principles of Green Chemistry are given as bellow,

1. Prevention.
2. Atom Economy.
3. Less hazardous chemical syntheses.
4. Designing safer chemicals.
5. Safer solvents and auxiliaries.
6. Design for energy
7. Use of renewable feedstock.
8. Reduce derivatives.
10. Design for degradation.
12. Inherently safer chemistry for accident prevention.

This thesis focuses mainly on the recommendation of principle number 3\textsuperscript{rd}, 4\textsuperscript{th}, 6\textsuperscript{th}, 9\textsuperscript{th} and 12\textsuperscript{th} considered from the point of view of their usage.

In the context of green chemistry to take precautions to minimize the effects shown in Fig 1.01 of the solvents by improved recycling. But, it has limited success and cannot avoid some losses into the environment. Thus, the replacement of these hazardous compounds with innocuous
substitutes, as the 5th principle of Green Chemistry requires, seems to be the only valid alternative for a sustainable use of solvents.

Two main routes towards green solvents have been developed: i) the substitution of petro-chemically fabricated solvents with “bio-solvents” from renewable resources, and ii) the substitution of hazardous solvents with ones that show better EHS (Environmental, Health and Safety) properties. The first strategy relies on solvents produced from vegetation biomass such as ethanol by fermentation of sugar-containing feeds, starchy feed materials leading to the reduction of fossil fuel CO₂ emissions to the atmosphere. The second strategy is based both on the use of safe and innocuous organic solvents, as acetone and alcohols, and on new generation solvents, as ionic liquids and supercritical fluids.

Pfizer received a Presidential Green Chemistry Challenge Award in 2002 for redesigning the sertraline manufacturing process by improving of a three step sequence in to a single step using ethanol as the sole solvent. This eliminated the need to use, distill and recover four solvents (methylene chloride, tetrahydrofuran, toluene, and hexane) employed in the original process.

Ionic liquids are currently being investigated as replacements for VOCs in an increasing number of chemical processes [4].

1.03 Ionic liquids as room-temperature molten salts

One of the principal driving forces for the broad investigations in the area of new materials is the need to find replacements for environmentally hazardous volatile organic solvents in many different commercial chemical processes. Most of the familiar liquids are formed from neutral molecules and are non-ionic. There is a different class of room-temperature liquids that, unlike the molecular liquids, is constituted of ions. These liquids are
called ionic liquids (ILs). For a substance to be considered a room-
temperature ionic liquid (RTIL), its melting point should be below 100°C.

Molten salts are in general defined as liquid electrolytes which consist of simple anions and cations that pack efficiently and, therefore, have high lattice energy [5]. A typical characteristic of a salt is a high melting point and usually matter which contains only ions is considered to be a salt. The salt consists of small symmetric ions which have a high charge density and thus they can be effectively packed into a crystal lattice. When an ionic liquid is constructed, the size of the ion/ions is changed [6]. For example NaCl has a melting point of about 800°C, but when sodium is replaced by 1-butyl-3-methylimidazolium, [Bmim] the melting point decreases to about 60°C. When Na is replaced by [Bmim] the size of the cation is increased from 102 pm (6-coordinate ionic radius of sodium) to 350 pm (distance of imidazolium rings face to face in crystal lattice). Hence, Charge density gets decreased. Crystal lattice packing is affected, since sodium is a symmetrical ion (spherical) and imidazolium is a bulky asymmetrical ion. The crystal packing energy with [Bmim] is much higher and thus the melting point is lower.

ILs are different from the molten salts commonly studied in the mid-
to late-twentieth century. ILs May “Boost Clean Technology Development” and effectively launched a renaissance in scientific and engineering interest in both “salts” and “liquids”. Synonyms for materials that meet the working definition of ILs are ‘room temperature molten salts,’ ‘Fused salts,’ ‘NAILs’, ‘OILs,’ ‘ionic fluid’ and ‘liquid organic salt’.

1.04 A brief history

The early history of ILs began in 1914 when the first report of a room temperature molten salt was reported by Walden [7]. He reported the physical properties of ethylammonium nitrate, \([C_2H_5NH_3]NO_3\), which has a
melting point of $12^\circ C$, formed by the reaction of ethylamine with concentrated nitric acid. Hurley and Weir [8] stated that a room temperature IL could be prepared by mixing and warming 1-ethylpyridinium chloride with aluminum chloride. In 1970s and 1980s, Osteryoung et al [9, 10] and Hussey et al [11-13] carried out extensive research on organic chloride–aluminium chloride ambient temperature ILs and the first major review of room temperature ILs was written by Hussey [14]. The ILs based on AlCl$_3$ can be regarded as the first generation of ILs.

The hygroscopic nature of AlCl$_3$ based ILs has delayed the progress in their use in many applications since they must be prepared and handled under inert gas atmosphere. Thus, the synthesis of air and water stable ILs, which are considered as the second generation of ILs, attracted further interest in the use of ILs in various fields. In 1992, Wilkes and Zaworotko [15] reported the first air and moisture stable ILs based on 1-ethyl-3-methylimidazolium cation with either tetrafluoroborate or hexafluorophosphate as anions. Unlike the chloro-aluminate ILs, these ILs could be prepared and safely stored outside of an inert atmosphere. Generally, these ILs are water insensitive; however, the exposure to moisture for a long time can cause some changes in their physical and chemical properties. The ILs based on more hydrophobic anions such as tri-fluoromethanesulfonate (CF$_3$SO$_3^-$), bis-(trifluoro-methanesulfonyl) imide [(CF$_3$SO$_2$)$_2$N$^-$] and tris-(trifluoro-methanesulfonyl) methide [(CF$_3$SO$_2$)$_3$C$^-$] have been developed [16-18]. These ILs have received extensive attention not only because of their low reactivity with water but also because of their large electrochemical windows. Usually these ILs can be well dried the water contents below 1 ppm under vacuum at temperatures between 100$^\circ$C and 150$^\circ$C.

Beside Osteryoung, Wilkes, Hussey and Seddon who are pioneers in the field of ILs, there are several scientists, e.g. Rogers, Welton,
Wasserscheid, MacFarlane, Ohno, Endres, Davis, Jr Abbott, and others, whose work has a strong impact in introducing the ILs in many applications.

Rogers is one of the highly cited authors in the field of ILs. He focuses on the synthesis and characterization of environmentally friendly ILs as green solvents. Welton has published many papers dealing with the applications of ILs as solvents for synthesis and catalysis. He has given mechanism on how the ILs interacts with solute species to affect their reactivity and he has contributed on replacing environmentally damaging solvents with more benign alternatives [19]. Wasserscheid is an active member of the IL community and focuses on the preparation and characterization of ILs for use in the biphasic catalysis. Together with Welton, he edited a very important book entitled “Ionic Liquids in Synthesis”, which presents the synthesis and physicochemical properties of ILs as well as their use in catalysis, polymerization, and organic and inorganic synthesis [20]. MacFarlane has worked on the synthesis of new air and water stable ILs with the purpose of employing such ILs as indicators for sensing and displaying environmental parameters such as humidity. Ohno has concentrated his work on the synthesis of a series of polymerizable ILs and their polymerization to prepare a new class of ion conductive polymers. He has edited a book entitled, “Electrochemical aspects of ionic liquids”, which introduces some basic and advanced studies on ILs in the field of electrochemistry [21].

Davis, Jr, has introduced the concept of “task-specific ionic liquids” (TSILs) in the field of ILs. TSILs are ionic liquids in which a functional group is incorporated enabling the liquid to behave not only as a reaction medium but also as a reagent or catalyst in some reactions or processes. Abbott has recently developed a range of ionic compounds, which were fluid at room temperature. These ILs were based on simple precursors such as choline chloride (vitamin B₄) which is cheap and produced on a
multitonne scale and hence these ILs/deep eutectic solvents were applied to large scale processes for the first time. Using these liquids, a number of applications are now under development such as electrodeposition of metals, electropolishing and ore processing. Endres and Zein El Abedin, about 10 years ago started to study nanoscale processes at the interface electrode/IL using in situ (electrochemical) scanning tunneling microscopy (in situ-STM). They could show for the first time that Ge, Si, Se, Ta and Al can be electrodeposited in high quality in air and water stable ILs.

1.05 Generations of ILs

Recently due to implications of the ILs as solvents where the accessible physical property sets with many ILs (Fig 1.02: [Generation 1]) are often unique. There is now, growing interest in the materials applications of ILs which utilize novel tunable physical and chemical property sets (Fig 1.02: [Generation 2]) for such applications as energetic materials, lubricants, metal ion complexation, etc. ILs make a unique architectural platform on which, at least potentially, the properties of both cation and anion can be independently modified, enabling tunability in the design of new functional materials, while retaining the core desired features of an IL.

While a tremendous amount of recent research has focused on the physical properties of ILs, and more recently the chemical properties, the toxicity, a biological property, has been one of the most highly debated topics in this field. Indeed, toxicity is also a tunable property of ILs, and given the similarities between many common IL building blocks and active pharmaceutical ingredients (APIs) or API precursors, one wonders why the potential to utilize the biological properties of ILs has received passing interest at best (Fig 1.02: [Generation 3]). Biologically active ions have been used to make new ILs; however, the primary driver for these
materials has been the use of ions of known low toxicity to obtain the IL physical property set. ILs of antimicrobial quaternary ammonium cations have been known for quite some time and recently, these have been shown to retain their biological activity [22].

**Generation 1**: ILs with unique tunable properties.

- **Physical properties**: - melting point - density - viscosity - thermal stability - conductivity - hydrophobicity - refractive index

- **Chemical properties**: - chemical reactivity - high energy density - electrochemical window - flammability - co-ordination - solvation - chiral induction

**Generation 2**: ILs with targeted chemical properties combined with chosen physical properties.
**Generation 3**: ILs with biological properties.

### Biological property

1. **Antibacterial**
2. **Local anesthetic**
3. **Anticholinergic**
4. **Antifungal**

### Biological property

1. **Emollient**
2. **Anti-acne**
3. **Antibiotic**
4. **Anti-inflammatory**
5. **Drug (NSAID)**
6. **Vitamin**

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**Fig 1.02** The evolution of the scientific focus on ILs

### 1.06 Synthesis of ILs

As summarized in **Fig 1.03**, the typical preparation of an IL initially involves a quaternization reaction such as the alkylation of a 1-alkylimidazole by a halo-alkane. This step is generally followed by an acid-base neutralization or metathesis of the resulting halide salt with a Group 1A metal, ammonium, or silver salt of the desired anion to afford the IL, together with a stoichiometric amount of by-product (HX or MX, respectively) which must subsequently be removed. To date, the most commonly studied systems consist of a bulky, asymmetrically-substituted N-containing cation with varying heteroatom functionality paired with a charge-diffuse (poorly-coordinating) anion. So far, many classes of cation has been explored, particularly 1-alkyl-3-methylimidazolium, N-alkylpyridinium, N-methyl-N-alkylpyrroolidinium, and tetraalkylammonium type. This list is by no means exhaustive and other classes like phosphonium salts are finding greater utility daily. It should also be noted that ILs of various types are increasingly commercially available. On the
an anionic side, an assortment of inorganic or organic species have been used such as \([PF_6]^-\), \([BF_4]^-\), \([(CF_3SO_2)_2N]^-\), \([(C_2F_5SO_2)_2N]^-\), \([CF_3SO_3]^-\), \([(C_2F_5)_{3}PF_3]^-\), \([CF_3CO_2]^-\), \([NiCl_3]^-\), \([SCN]^-\), and \([(CN)_2N]^-\).

**Fig 1.03** Summary of general pathways for IL synthesis [23].

Typical structures combine organic cations with inorganic or organic anions:

**Fig 1.04** Representative cations and anions used as building blocks in IL formulation [23].
The rate of publication in the open literature has been rising at a greater than exponential rate for years (Fig 1.05), and this is tracked by the rate of appearance of patents (Fig 1.06) [23].

Fig 1.05 Steeper than exponential growth of ionic liquid publications, 1986-2006.

Fig 1.06 Annual growth of ionic liquid patents, 1996-2006.
1.07 General characteristics of ILs

As a solvent, IL possesses several advantages over conventional organic solvents, which make them environmentally compatible. ILs exhibit many properties which make them potentially attractive media for many organic transformations due to easy handling, recyclability and thus leading to cheap and environmentally benign reaction conditions

- They have essentially no vapor pressure, i.e. they do not evaporate and are easy to contain.
- They generally have reasonable thermal stability.
- They have high solvating capacity for both polar and non-polar compounds.
- They have good solubility of gases, e.g. H₂, CO and O₂, which makes them attractive solvents for catalytic hydrogenations, carbonylations, hydroformylations, and aerobic oxidations.
- They are immiscible with majority of organic solvents, e.g. alkanes, and, hence, can be used in two-phase systems. Similarly, lipophilic ionic liquids can be used in aqueous biphasic systems.
- Polarity and hydrophilicity/lipophilicity can be readily adjusted by a suitable choice of cation/anion and thus, ILs has been referred to as ‘designer solvents’.

1.08 Physical properties of ILs

Conductivity

ILs has reasonably good ionic conductivities compared with those of organic solvents/electrolyte systems (up to ~10 mS cm⁻¹) [20]. At elevated temperatures of e.g. 200°C a conductivity of 0.1 Ω⁻¹ cm⁻¹ can be achieved for some systems. However, at room temperature their conductivities are usually lower than those of concentrated aqueous electrolytes. Based on
the fact that ILs are composed solely of ions, it would be expected that ionic liquids have high conductivities.

**Viscosity**

Generally, ILs are more viscous than common molecular solvents and their viscosities are ranging from 10 mPa s to about 500 mPa s at room temperature. The viscosities of some popular air and water stable ILs at room temperature are: 312 mPa s for [Bmim] PF$_6$ [25]; 154 mPa s for [Bmim] BF$_4$ [26]; 52 mPa s for [Bmim] TF$_2$N [27]; 85 mPa s for [BMP] TF$_2$N [18]. The viscosity of ILs is determined by van der Waals forces and hydrogen bonding. Electrostatic forces may also play an important role. Alkyl chain lengthening in the cation leads to an increase in viscosity [27]. This is due to stronger van der Waals forces between cations leading to increase in the energy required for molecular motion. Also, the ability of anions to form hydrogen bonding has a pronounced affect on viscosity. The fluorinated anions such as BF$_4$ and PF$_6$ form viscous ILs due to the formation of hydrogen bonding [28]. In general, all ILs show a significant decrease in viscosity as the temperature increases.

**Density**

ILs in general are denser than water with values ranging from 1 to 1.6 g cm$^{-3}$ and their densities decrease with increase in the length of the alkyl chain in the cation [20]. For example, in ILs composed of substituted imidazolium cations and CF$_3$SO$_3$ anion the density decreases from 1.39 g cm$^{-3}$ for [Emim]$^+$ to 1.33 g cm$^{-3}$, for [EEim]$^+$, to 1.29 g cm$^{-3}$, for [Bmim]$^+$ and to 1.27 g cm$^{-3}$, for [BEim]$^+$ [20]. The densities of ILs are also affected by the identity of anions.
✓ **Melting point**

As a class, ILs has been defined to have melting points below 100°C and most of them are liquid at room temperature. Both cations and anions contribute to the low melting points of ILs. The increase in anion size leads to a decrease in melting point [29]. For example, the melting points of 1-ethyl-3-methylimidazolium type ILs with different anions, such as [BF₄]⁻ and [Tf₂N]⁻ are 15°C [30] and -3°C, [27] respectively.

✓ **Thermal stability**

ILs can be thermally stable up to temperatures of 450°C. The thermal stability of ILs is limited by the strength of their heteroatom–carbon and their heteroatom–hydrogen bonds, respectively [29]. Wilkes *et al* [20] reported that the ILs 1-ethyl-3-methyl-imidazolium tetrafluoroborate, 1-butyl-3-methyl-imidazolium tetrafluoroborate and 1, 2-dimethyl-3-propyl imidazolium bis(trifluorosulfonyl)imide are stable up to temperatures of 445°C, 423°C and 457°C, respectively.

✓ **Electrochemical window**

The electrochemical window is an important property and plays a key role in using ILs in electrodeposition of metals and semiconductors. By definition, the electrochemical window is the electrochemical potential range over which the electrolyte is neither reduced nor oxidized at an electrode. This value determines the electrochemical stability of solvents. As known, the electrodeposition of elements and compounds in water is limited by its low electrochemical window of only about 1.2 V. On the contrary, ILs have significantly larger electrochemical windows, e.g., 4.15 V for [Bmim] PF₆ at a platinum electrode [31], 4.10 V for [Bmim] BF₄ [31] and 5.5 V for [BMP] Tf₂N at a glassy carbon electrode [18]. In general, the wide electrochemical windows of ILs have opened the door to
electrodeposit metals and semiconductors at room temperature which were formerly obtained only from high temperature molten salts. For example, Al, Mg, Si, Ge, and rare earth elements can be obtained from RTILs. The thermal stability of ILs allows to electrodeposits Ta, Nb, V, Se and presumably many other ones at elevated temperature.

1.09 Task-specific ionic liquids (TSILs)/Functionalized ionic liquids (FILs)

The prospect of designing ILs that exhibit specific properties to enhance catalytic activity opens up new dimensions and possibilities in catalysis and the design of so-called task specific ionic liquids (i.e., ionic liquids containing functional groups) is helping to push the boundaries of IL catalysis (Fig 1.07). A strategy of IL functionalization was first proposed by Kou [32]. The concept of TSILs, which incorporate functional groups designed to impart to them particular properties, stimulated applications extending far beyond those likely for more conventional ILs [33]. One important feature of these liquids is the possibility of tuning their physical and chemical properties by varying the nature of the anion and cation. It is evident that the number of possible combinations is extremely high, and it should be possible to tailor the best IL for any application [34].

Fig 1.07 Design of ionic liquid for specific applications [24].
The acidity of the C(2)-H in imidazolium cations is well known, and they can be deprotonated to form carbenes [35]. In order to improve the stability against basic ligands, the 2-methylimidazolium cation was introduced.

ILs containing thiol-functionalized imidazolium cations [36] for the modulation of gold surface properties were synthesized. ILs with nitrile-functionalized alkyltrifluoroborate anions [37-39], zwitterionic liquids [40, 41], and dual-functionalized ILs [37, 42] were reported.

The dicobalthexacarbonyl adduct of 1-allyl-3-propargylimidazolium tetrafluoroborate was the first IL bearing an organometallic moiety covalently attached to the cation [43]. 1, 3-dialkyne-functionalised imidazolium salts were described by Fei Z et al [44]. The chromium tricarbonyl fragment was introduced by Moret ME et al onto the imidazolium cation [45]. Imidazolium cations with ferrocenyl appendages were prepared [46]. Metal-containing imidazolium-based ILs were reviewed by Ding J et al [47].

ILs containing reducing (cyanoboranate, tri-chlorogermanate (II)) or oxidising anions (perchlorate, chlorate) open new areas in synthetic chemistry [48]. Different methods to prepare chiral ILs either from chiral starting materials or by asymmetric synthesis and their applications were reviewed [49]. In addition, 1-methyl-3-octylimidazolium tetra-fluoroborate was used for enbalming and tissue preservation and as a fixative for histological purposes [50, 51].

1.10 Dark side of ILs

The toxicity of ILs has recently aroused the awareness of chemists, especially those working in the area of green chemistry. The essential reason for believing ILs to be nontoxic, results from their nonvolatile
properties, which makes them potential green substitutes for conventional volatile organic solvents. Unfortunately, this green image is misplaced and has led to claims that ILs are nontoxic.

To synthesize TSILs, many different functional groups have been incorporated e.g., alkenes, alkynes, amines, amides, ethers, alcohols, acids, thiols, urea and thiourea, fluorous chains, glycidyl chains, phosphonyl, and ferrocenyl groups. Consequently, understanding the toxicity of these TSILs becomes more complicated because of the potential virulence of the incorporated functionalities. Although ILs may help reduce the risk of air pollution, their release to aquatic environments could cause severe water contamination because of their potential toxicity and inaccessible biodegradability. Despite a recent drop-off, the studies of IL toxicity including ecotoxicity have advanced at a significant rate and a great deal of information has been accumulated.

Wells and co-worker used measurements of Biochemical Oxygen Demand in five days (BOD5) to evaluate the biodegradation of ILs. They found that none of the selected ILs, which are based on imidazolium, pyridinium, phosphonium, and ammonium, showed any sign of biodegradation by the BOD5 method [52].

1.11 ILs degradation and bio-renewable ILs – a new concept

The above fact demonstrates that the commonly used ILs are not readily biodegradable. However, the properties of ILs can be tuned through structural adjustment. Therefore, various efforts to produce biodegradable and bio-renewable ILs have been undertaken. Scammells and co-workers used the concept of biodegradable surfactants to develop a series of biodegradable-improved imidazolium-based ILs incorporating ester or amide groups. The Closed Bottle Test showed that ILs with ester
functionality have enhanced biodegradation compared to the non-functionalized equivalents, [Bmim] [BF₄] and [Bmim] [PF₆]. The susceptibility of the ester group to enzyme hydrolysis was thought to be the explanation of the observed improvement.

Davis Jr. and co-workers used saccharin and acesulfame, of which alkali-metal salts are extensively used foodstuffs as non-nutritive sweeteners, to form ILs. Their work should be considered as the first that employs a nontoxic precursor to create new environmentally and toxicologically benign ILs.

Kou and co-workers employed a new generation of ILs, where the cations were derived directly from natural α-amino acids and α-amino acid ester salts. The synthesis of these ILs is simple and straightforward with many benefits including improved bio-renewable and biodegradable properties, maintanance of the chiral centre of the cation, and the possibility of additional functionalization being preserved. Consequently, the greenness level of this new generation of ILs has been enhanced to full-greenness using nontoxic inorganic or organic anions (Fig 1.08) [52].

![New generation ILs](image)

![Fully green ILs](image)

**Fig 1.08** Amino acid-based ionic liquids [52].
1.12 Applications of ILs in variety of fields

The reason for the increase in number of publications on ionic liquids can be attributed to the unique properties of these new materials. The Fig 1.09 summarizes potential and current applications of ionic liquids in various fields of science.

![Diagram of Applications of Ionic Liquids](image)

**Fig 1.09** Causeway to the future [53].

The current trend towards the commercialization of IL creates opportunities for new researchers to participate, while working with materials of known purities. Coincident with this development, there is a
growing realization that there exists a plethora of available low-melting salts never before exploited in a molten form, offering new opportunities for exploration and discovery. There is then no doubt that research into the use of ionic liquids as solvents, reagents, catalysts and materials will continue to grow. Indeed, for these remarkable salts, the future looks bright.

The scientific and technological importances of ILs today span a wide range of applications. We have focused this work on some of the most significant examples of recent key developments in ILs applications made possible by their unique solvent capabilities. Our main objective is to show the applications of ILs in crucial fields such as catalysis, nanomaterial and electrochemistry.

1.13 Catalysis in ILs

The key to waste minimization in chemicals manufacture is the widespread substitution of classical "stoichiometric" synthesis by atom-efficient, catalytic alternatives. In the context of homogeneous catalysis, efficient recycling of the catalyst is a *conditio sine qua non* for economically and environmentally attractive processes. Motivated by one or both of the above issues, much attention has been devoted to homogeneous catalysis in biphasic systems. Similarly, the use of ILs as novel reaction media may offer a convenient solution to both the solvent emission and catalyst recycling problem. Some unidentified mechanism is operating in olefin dimerisation. Nonaqueous biocatalysis and biochemical transformations in ILs were reviewed by Laus G et al [54].

It was known for many years that ILs could dissolve transition metal complexes and support organic chemistry. Chauvin and Osteryoung independently combined these ideas showing that nickel complexes dissolved in acidic chloroaluminate ILs catalyze the dimerization of alkenes
[55,56], while Osteryoung used Ziegler-Natta catalysts in a similar solvent to polymerize ethylene [57]. But it was Zaworotko’s water-stable ILs that contains tetrafluoroborate, hexafluorophosphate, nitrate, sulfate and acetate anions that really moved things forward. Using these ILs Chauvin and Dupont demonstrated their potential in hydrogenation catalysis [58] and showed that reaction rates and selectivities could be enhanced.

The catalyzed reactions that have been reported in ILs, are with varying degrees of success [59]. What has become apparent is that frequently used and well-established homogeneous catalysts need to be modified in order to work effectively in ILs. For example, it was shown that activation of a pre-catalyst can be thermodynamically hindered in an IL, affording no catalysis at all if reaction conditions are not adapted properly [60]. In addition to catalyst activation, sufficient retention of the catalyst in the IL is important in order to provide good recycling. The most versatile approach used to anchor homogeneous catalysts in IL phases is to attach charged groups to the ligands bound to the metal catalyst centre; some recent examples of ligands/catalysts modified in this manner are shown in Fig 1.10. Imidazolium groups have been widely used for this purpose, since the majority of catalyzed reactions reported to date have been carried out in imidazolium-based ILs.
Fig 1.10 Imidazolium tagged ligands/catalysts that enhance immobilization in ILs and improve catalyst recycling/reuse [55].

Other approaches have been used to facilitate catalyst reuse and in the context of continuous flow processes supported ionic liquid phase (SILP) catalysis has been quite extensively studied [61]. The general concept involves the immobilization of imidazolium and other ionic fragments onto solid supports using appropriate functional groups attached to the cation and a charged catalyst then resides within the ionic matrix. The concept is illustrated in Fig 1.11 for the racemic epoxidation of olefins using a peroxotungstenate catalyst, \([\{W(-O)(O_2)_{2}(H_2O)_{2}](\mu-O)\}^{2-}\), supported on ionic liquid modified silica [62]. The solid support was reacted with 1-octyl-3-(3-triethoxysilylpropyl)-4, 5-dihydroimidazolium, affording a \(\text{SiO}_2\) surface on which the IL is covalently bound. This heterogeneous catalyst was successfully used to epoxidise olefins using \(\text{H}_2\text{O}_2\) as oxidant.
and reaction rates were comparable to those observed under homogeneous conditions.

![Diagram of olefin and epoxide conversion](image)

**Fig 1.11** A tungstenate catalyst immobilized on IL modified silica [55].

ILs have further proven to be excellent solvents to both immobilize and stabilize nanoparticle catalysts. Nanoparticles were first identified in ILs as species formed during Heck reactions using Pd(II) compounds as catalyst precursors [63] Dupont *et al* reported the controlled preparation of transition metal nanoparticles in ILs by reduction of the metal complex with molecular hydrogen in the absence of stabilizers, and demonstrated their applications in hydrogenation and C-C coupling reactions [64].

The variety of reactions in presence of ILs as catalyst as well as a media are mentioned below.


### Starting Materials

<table>
<thead>
<tr>
<th>Reagents and conditions</th>
<th>Products</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>R&lt;sup&gt;1&lt;/sup&gt;-CH&lt;sub&gt;3&lt;/sub&gt;-O&lt;sup&gt;-&lt;/sup&gt;OOH + R&lt;sup&gt;2&lt;/sup&gt;-Br</td>
<td>Bmim BF&lt;sub&gt;4&lt;/sub&gt; R.T. 30% NaOH</td>
<td>65</td>
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<tr>
<td>Ar&lt;sup&gt;1&lt;/sup&gt;-COCl + Ar&lt;sup&gt;2&lt;/sup&gt;-OH</td>
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<td>R-CHO + R&lt;sup&gt;1&lt;/sup&gt;NH&lt;sub&gt;2&lt;/sub&gt; + HO-P(OEt)&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>67</td>
</tr>
<tr>
<td>Ph-CH&lt;sup&gt;2&lt;/sup&gt;-CO&lt;sup&gt;-&lt;/sup&gt;Ph</td>
<td>CIL/CH&lt;sub&gt;3&lt;/sub&gt;CN, K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>68</td>
</tr>
<tr>
<td>Ph-CHO</td>
<td>EtO&lt;sub&gt;2&lt;/sub&gt;C-CO&lt;sub&gt;2&lt;/sub&gt;Et</td>
<td>69</td>
</tr>
</tbody>
</table>

### Additional Reaction

Ph<sub>2</sub>CH<sup>+</sup>N<sub>Ph</sub> + Bu<sub>2</sub>PdCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>

PdCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> at 100°C, 4h
Chapter I: A Brief Account On: Ionic Liquids with its Applications

Chemical reactions:

\[ \text{CH}_3\text{CO}_2\text{H} + \text{CH}_3(\text{CH}_2)_7\text{OH} \]

\[ \left[ (\text{C}_2\text{H}_5)_3\text{NH} \right][\text{HSO}_4] \]

\[ 90^\circ\text{C}, 4\text{h} \]

\[ \text{CH}_3\text{CO}_2(\text{CH}_2)_7\text{CH}_3 + \text{H}_2\text{O} \]

70

\[ \text{Cu(acac)}_2, \text{Bmim PF}_6 \]

\[ 60^\circ\text{C}, 6\text{h} \]

71

\[ \text{Bmim PF}_6, \]

\[ 5-25\text{ min.}, \text{R.T.} \]

71

\[ \text{Cu, R}_\text{f} \]

\[ 75^\circ\text{C}, 20\text{h} \]

72

\[ \text{Cmim HSO}_4 \]

\[ 80^\circ\text{C}, 15\text{ min} \]

73
Chapter-1: A Brief Account On: Ionic Liquids with its Applications

\[
\text{Hmim } \text{HSO}_4, \quad \text{NH}_4\text{NO}_3 \\
80^\circ\text{C}, \text{ Neat}
\]

\[
\text{Bmim BF}_4 \\
\text{K}_3\text{PO}_4 / \text{heat}
\]

\[
\text{Bmim PF}_6 \\
35 \text{ min}
\]

\[
[(\text{HSO}_3-\text{b})][\text{H}_2\text{SO}_4] \\
\text{H}_2\text{O}, 80^\circ\text{C}
\]

\[
\text{CIL } 20\%, 6\text{d}
\]

\[
\text{Emim BF}_4 \\
10 \text{ min}
\]
1.14 Ionic liquid in nanomaterials

Much more recently, “nano” has become the new hot topic in materials science. The common theme here is always “size matters” and over the last decades, researchers have developed exciting new materials with unique and tunable properties. The first use of the concepts found in 'nano-technology' was in "There's Plenty of Room at the Bottom," a talk given by physicist Richard Feynman at an American Physical Society meeting at Caltech on December 29, 1959. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, and so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and van der Waals attraction would become increasingly more significant, etc. This basic idea appeared plausible, and
exponential assembly enhances it with parallelism to produce a useful quantity of end products. The term "nanotechnology" was defined by Tokyo Science University Professor Norio Taniguchi in a 1974 paper as follows: "Nano-technology” mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or by one molecule."

Nanotechnology is one of the frontier areas of science due to its versatile application in various fields. Nanomaterials find applications in the fields such as miniaturization in electronics, catalysis, optics, biological and in the elegy sector. In addition, nanomaterials yield next-generation computer chips, better insulation materials, tougher and harder nanomaterials in cutting tools, for elimination of pollutants, high energy density batteries, efficient solar cells, high-power magnets, high-sensitivity sensors, automobiles with greater fuel efficiency, aerospace components with enhanced performance [82].

1.14.1 Role of surfactant

Surface active agents (usually referred to as surfactants) are amphipathic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8-18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic) (Fig 1.12). The hydrophilic portion can, therefore, be non-ionic, ionic or zwitterionic, and accompanied by counter ions in the last two cases. The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion-dipole interactions. It is this strong interaction with the water molecules that renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the
hydrocarbon chain out of the water and hence these chains are referred to as hydrophobic.

As noted, surface active agents also aggregate in solution forming micelles. The driving force for micelle formation (or micellization) is the reduction of contact between the hydrocarbon chain and water, thereby reducing the free energy of the system. In the micelle, the surfactant hydrophobic groups are directed towards the interior of the aggregate and the polar head groups are directed towards the solvent. These micelles are in dynamic equilibrium and the rate of exchange between a surfactant molecule and the micelle may vary by orders of magnitude, depending on the structure of the surfactant molecule.

Surfactants find application in almost every chemical industry, including detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibers, plastics. A fundamental understanding of the physical chemistry of surface active agents, their unusual properties and their phase behavior is essential for most industrial chemists. In addition, an understanding of the basic phenomena involved in the application of surfactants, such as in the preparation of emulsions and suspensions and their subsequent stabilization, in microemulsions, in wetting spreading and adhesion, etc., is of vital importance in arriving at the right composition and control of the system involved. This is particularly the case with many formulations in the chemical industry [83].
Surfactant structure:

![Surfactant Structure Diagram]

<table>
<thead>
<tr>
<th>Tail Group</th>
<th>Head Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Hydrophobic or Lipophilic)</td>
<td>(Hydrophilic or Lipophobic)</td>
</tr>
</tbody>
</table>

**Fig 1.12** Typical structure of surfactant.

### 1.14.2 General classification of surfactants

- **Anionic**
  - Carboxylic
  - Sulfuric esters
  - Alkane sulfonic acids
  - Alkyl aromatic sulfonic acids
  - Others: Phosphates, phosphoric acids, ...

- **Cationic**
  - Amine salts (primary, secondary, and tertiary)
  - Quaternary salts

- **Nonionic**
  - Ethers
  - Esters
  - Amides

- **Amphoteric**
1.14.3 ILs as surfactants

The physicochemical and solvation properties of ILs can be effectively “tuned” by simple tailoring of the substituent groups comprising the cation and/or anion. ILs possessing long aliphatic substituents has been reported to undergo micellization in aqueous solutions. However, current knowledge of IL micelle structure and behavior in aqueous solution is limited. Even less understood is the structure of ILs in solutions of organic solvent–water mixtures. Due to their structural tunability, ILs represents a unique class of “designer surfactants” in which the substituents on the headgroup can be widely varied [84]. ILs that carry long-chain alkyl groups are expected to be surface active (SAILs); this expectation has been verified, e.g., for 1, 3-dilalkylimidazolium chlorides, bromides, and tetrafluoro-borates [85]. SAILs can act as morphology templates for the synthesis of inorganic materials with novel or improved properties.

1.14.4 Introduction to Zinc Oxide
1.14.4.1 General introduction of ZnO

There are three most representing one-dimensional (1D) nanostructures that are being actively studied in nanotechnology: carbon nanotubes, silicon nanowires, and ZnO nanorods/nanowires. ZnO is one of the few dominant nanomaterials for nanotechnology. The absence of a centre of symmetry in its wurtzite structure, along with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties. ZnO is therefore widely used in mechanical actuators and piezoelectric sensors. In addition, ZnO is a wide band-gap (3.37 eV) compound semiconductor that is appropriate for short wavelength optoelectronic applications. The high exciton binding energy (60 meV) in
ZnO crystal allows efficient excitonic emission at room temperature. ZnO is transparent to visible light and its conductivity can be increased through doping. ZnO nanostructures have a wide range of high technology applications like surface acoustic wave filters, photonic crystals, photodetectors, light emitting diodes, photodiodes, gas sensors, optical modulator waveguides, solar cells and varistors. Up to now, different nanostructures of ZnO such as ZnO Cactus, ZnO Cake, Desert plant, Hexagonal rods, Bottle brush, Flower, Nano disc, Alligned nano rods and Thorn ball have been obtained in our research group (Fig 1.13).

**Fig 1.13** Different ZnO nanostructures
ZnO films have been synthesized by several techniques such as molecular beam epitaxy, RF magnetron sputtering, chemical vapor deposition, physical vapor deposition, spray pyrolysis, chemical bath deposition, electrodeposition and aqueous chemical method (ACM). However, ACM technique presents several advantages as: inexpensive, easy procedure, possibility of large-scale deposition, low temperature growth and direct control over the film morphology [87, 88].

ACM greatly facilitate to grow 1D ZnO nanostructures by the thermal decomposition of hexamethylenetetramine (HMTA) and zinc acetate. To initiate the growth from the substrate, a thin layer of ZnO nanoparticles was grown on the substrate. HMTA is a highly water soluble, non-ionic tetradeutate cyclic tertiary amine. Thermal degradation of HMTA releases hydroxyl ions which react with $\text{Zn}^{2+}$ ions to form ZnO as follows [89, 90],

\[
(\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O} \xrightarrow{\Delta} 6\text{HCHO} + 4\text{NH}_3 \quad (1.1)
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad (1.2)
\]

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (1.3)
\]

\[
\text{Zn(OH)}_2 \rightarrow \text{ZnO}_{(s)} + \text{H}_2\text{O} \quad (1.4)
\]

The use of organic surfactants (structure directing agent) in ACM is extremely important due to their direct effect on morphological and structural properties. The surfactant molecules bind to the different ZnO surfaces and affect crystal growth [91].
1.14.4.2 Why nanostructured ZnO?

ZnO, as a wide band gap semiconductor (3.37 eV) with a large exciton binding energy of 60 meV, is widely used in optoelectronic devices, gas sensors [92], light-emitting diodes (LEDs), electron field emitters, and solar cells. ZnO is famous for its optical and gas sensing properties. Superior optical properties of ZnO with a large ratio of ultraviolet (UV) to visible photoluminescence (PL) emission intensities are in high demand of high crystallinity [93]. In contrast, the high gas sensing performance of ZnO needs a certain amount of structural defects with numerous oxygen vacancies, which play a key role in gas sensing reactions.

1.14.4.3 Structural properties of ZnO

Under conventional conditions, ZnO has the wurtzite structure, which has a hexagonal unit cell with space group C6mc and lattice parameters \( a = 0.32 \) and \( c = 0.52 \) nm. The oxygen anions and Zn cations form a tetrahedral unit as shown in Fig 1.14, the entire structure lacks of central symmetry. The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated \( \text{O}^{2-} \) and \( \text{Zn}^{2+} \) ions, stacked alternatively along the c-axis. Although the entire unit cell of ZnO is neutral, the distribution of the cations and anions could take specific configuration as determined by crystallography, so that some surfaces can be terminated entirely with cations or anions, resulting in positively or negatively charged surfaces, called polar surfaces. The polar charge dominated surfaces can give some unique growth phenomena, as will be illustrated later. The most common polar surface is the basal plane. The oppositely charged ions produce positively charged \( \text{Zn-(001)} \) and negatively charged \( \text{O-(001)} \) polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis as well as a
divergence in surface energy. To maintain a stable structure, the polar surfaces generally have facets or exhibit massive surface reconstructions, but Zn±(001) are exception, which are atomically flat, stable and without reconstruction.

**Fig 1.14** Hexagonal Wurtzite Crystal structure of ZnO

Understanding the superior stability of the ZnO (001) polar surfaces is a forefront research in today’s surface physics another polar surface is the (0111). By projecting the structure along (1210), beside the most typical ±(001) polar surfaces that are terminated with Zn and oxygen, respectively, ±(1011) and ±(1011) are also polar surfaces. The (1011) type surfaces are not common for ZnO, but they have been observed in a nanohelical structure. The charges on the polar surfaces are ionic charges, which are non-transferable and non-mobile. Because the interaction energy among the charges depends on the distribution of the charges, the structure is
arranged in such a configuration to minimize the electrostatic energy. This is the main driving force for growing the polar surface dominated nanostructures. Structurally, ZnO has three-types of fast growth directions: \( \{2\overline{1}10\} \) \( \{\pm[2\overline{1}10], \pm[1\overline{2}10], \pm[1\overline{1}20]\} \); \( \{0\overline{1}10\} \) \( \{\pm[0\overline{1}10], \pm[10\overline{1}0], \pm[\overline{1}100]\} \); and \( \{\pm[0001]\} \). Together with the polar surfaces due to atomic terminations, ZnO exhibits a wide range of novel structures that can be grown by tuning the growth rates along these directions. One of the most profound factors determining the morphology involves the relative surface activities of various growth facets under given conditions. Macroscopically, a crystal has different kinetic parameters for different crystal planes, which are emphasized under controlled growth conditions. Thus, after an initial period of nucleation and incubation, a crystallite will commonly develop into a three-dimensional object with well-defined, low-index crystallographic faces [94-96].

![Fig 1.15](image)

**Fig 1.15 (a-c)** Growth morphologies of 1D nanostructure and (d) Polar and non-polar surfaces of ZnO.

**Fig 1.15 (a–c)** shows a few typical growth morphologies of 1D nanostructure for ZnO. These structures tend to maximize the areas of the
(2110) and (1010) facets because of lower energy. The morphology shown in Fig 1.15 (d) is dominated by the polar surfaces, which can be grown by introducing planar defects parallel to the polar surfaces. Planar defects and twins are usually observed parallel to the (0001) plane, but dislocations are rarely seen.

1.14.5 Theoretical background of gas sensor

The word “sensor” is derived from the Latin word which means “to preserve”. A sensor therefore suggests some connection with human senses. It may provide us information about physical and chemical signals which could not be otherwise directly provided by our senses. A direct definition of sensor is, a device that responds to a physical (or chemical) stimulus (such as heat, light, sound, pressure, magnetism or a particular motion) and transmitting a resulting impulse (as for measurement or operating a control). Thus, a sensor can detect an input signal (or energy) and convert it in to an appropriate output signal (or energy).

1.14.5.1 Need for sensors

The technology necessary for the monitoring of gases has developed in parallel with the progressive industrialization of society through the course of the twentieth century. Even though the olfactory system of humans is excellent for the detection and identification of many odors, most hazardous gases or vapors can be recorded only at too high concentrations or cannot be detected at all [97]. Since, the organic fuels and other chemicals have become an essential part of domestic as well as industrial life and the awareness of the need to environment protection has grown, the specific needs for gas detection and monitoring have emerged. Gas detection instruments are increasingly needed for industrial health and
safety, environmental monitoring and process control. To meet this demand, considerable research into new sensors is underway, including efforts to enhance the performance of traditional devices, such as resistive metal oxide sensors, through nano-engineering. Generally, sensors provide an interface between the electronic equipments and the physical world typically by converting nonelectrical, physical or chemical quantities into electrical signals.

Currently, there are needs of gas monitoring which are divided in the following three broad categories [98].

(i) For oxygen, in connection with the monitoring of breathable atmospheres and for the control of combustion of processes i.e. in the boilers and internal combustion engines where, the oxygen concentration of 20 % and 0-5 %, respectively is required.

(ii) For the toxic gases (CO, H₂S, Cl₂, NO₂, etc.) in air, for the protection of human health, where the need is to monitor concentrations around the exposure limits which range from less than 1 parts per million (ppm) to several hundreds ppm.

(iii) For the flammable gases (C₂H₂, C₂H₄, C₃H₆, C₃H₈, LPG, etc.) in air to protect against the unwanted occurrence of fire or explosion. In this case, concentrations to be measured are in the range up to lower explosive level (LEL) which, for most gases, is up to a few percent.

In other words, for toxic gas applications, a sensor must be able to measure gases at low concentrations and the detection ranges are in ppm concentrations while, for combustible gas monitoring, a sensor must measure high gas concentrations, in the range of several percent. In order to detect measure and control these gases, one should know the amount and type of gases present in the ambient. Thus the need to monitor and
control these gases has led to the development of a variety of sensors using different materials and technologies.

In order to compare sensor and obtain a comprehensive overview of them, a flexible classification scheme has been proposed by White [99]. Sensors can be classified according to their principle of conversion (the physical or chemical effects on the basis of which they operate) as physical sensors and chemical sensors [100]. Physical sensors employ physical effects such as piezoelectric, magnetostriction, ionization, thermoelectric, photoelectric and magnetoelectric, etc.

![Classification of sensors according to principle of operation.](image)

**Fig 1.16** Classification of sensors according to principle of operation.

**1.14.5.2 Principle of operation of semiconducting oxide gas sensors**

The gas sensing mechanism of semiconducting oxide gas sensor can be easily understand by studying, the steps involved in the gas sensing mechanism as follows.
Stabilization of the sensor resistance

The stabilization of the sensor resistance in ambient air prior to exposure of gas is important, because it ensures stable zero level for gas sensing applications [101]. The semiconductor oxides are operating at higher temperature; the conduction electrons are thermally exited, which results into decrease in resistance of the sensor. When sensor is exposed to air, freshly prepared semiconductor oxide particles adsorb oxygen atom on the surface and the chemisorption process could be given by the following equation [102].

\[
\frac{1}{2}\text{O}_2^{\text{gas}} + 2\text{e}^- \rightarrow 2\text{O}^{\text{ads}}
\]  

(1.5)

The conduction electrons are trapped by the adsorbed oxygen and this results into the increased resistance of the sensor. The saturation in the resistance of the sensor was observed when thin monolayer of the oxygen gets chemisorbed on the surface of the sensor. Thus, the equilibration of the chemisorptions process results in stabilization of surface resistance \((R_a)\). Any process that disturbs this equilibrium gives rise to changes in the conductance of the semiconductors [103]. The oxygen adsorbate \(\text{O}^-\) is the most reactive with inflammable gasses within temperature range of 573 - 773 K [104].

Gas response of sensor material

When the sensor is exposed to the atmosphere containing the inflammable gases at the elevated temperature, the \(\text{O}^-\) adsorbate reacts with inflammable gas, removes oxygen from the surface in proportion to its concentration, thereby re-injecting electrons into the bulk of semiconductor shown by the following reaction (Fig 1.17)

\[
\text{C}_n\text{H}_{2n+2} + 2\text{O}^- \rightarrow \text{H}_2\text{O} + \text{C}_n\text{H}_{2n}^- + \text{e}^-
\]

(1.6)
Fig 1.17 Schematic model of gas sensing [105].

The reaction results into $C_nH_{2n-O}$ complex with water vapor and electrons re-inject into the bulk of semiconductor. The stabilized resistance ($R_a$) of the sensor decreased to the resistance ($R_g$), the change in the resistance of the sensor measured in terms of the gas response (S) of the sensor is defined as,

Gas response:

$$S \% = \frac{(R_a - R_g)}{R_a} \times 100$$  \hspace{1cm} (1.7)

With respect to time, maximum gas molecules react with chemisorbed oxygen and this result into saturation response of the sensor.

✓ Recovery of sensor material

Under exposure of fresh air, $C_nH_{2n-O}$ complex and water vapor removes out and again oxygen is chemisorbed on the metal-oxide surface,
and the sensor resistance recovers from $R_g$ to the saturation resistance $R_a$ and gas response $S \rightarrow 0$.

1.14.6 Literature survey on ZnO

<table>
<thead>
<tr>
<th>Year</th>
<th>Description</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>The electrical characteristics of ZnO thin films prepared by spray pyrolysis, were studied for ethanol sensors. The sensitivities of the films were measured at various temperatures and concentrations of ethanol. It is observed that the sensitivity increases with increasing working temperature. At higher ethanol concentrations, the sensitivity increases more rapidly with increasing temperature. Further, the films show fast response and recovery times at higher working temperatures. The sensing mechanism of the films towards ethanol vapor was explained by Sahay et al.</td>
<td>106</td>
</tr>
<tr>
<td>2007</td>
<td>Liao et al were studied a gas sensor using a single ZnO nanowire as a sensing unit. This ZnO nanowire-based sensor has quick and high sensitive response to $H_2S$ in air at room temperature. It was found that the gas sensitivity of the ZnO nanowires could be modulated and enhanced by $He^+$ implantation at an appropriate dose. A possible explanation was given based on the modulation model of the depletion layer.</td>
<td>107</td>
</tr>
<tr>
<td>2008</td>
<td>Using ZnO nanonails, a hydrazine electrochemical sensor were fabricated by Zhang et al, which showed a high and reproducible sensitivity of $8.56 \ \mu A cm^{-2} \ \mu M^{-1}$</td>
<td>108</td>
</tr>
</tbody>
</table>
with a response time less than 5 s, a linear range from 0.1 to 1.2 µM and a correlation coefficient of $R=0.999$. The limit of detection (LOD), based on the S/N ratio, was estimated to be 0.2 µM.

<table>
<thead>
<tr>
<th>Year</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>2008</td>
<td>Brush-like hierarchical ZnO nanostructures assembled from initial 1D ZnO nanostructures were prepared from sequential nucleation and growth following a hydrothermal process by Umar et al. The morphology, structure, and optical property of hierarchical ZnO nanostructures were characterized by XRD, FE-SEM, and PL studies. The FE-SEM images showed that the brush-like hierarchical ZnO nanostructures are composed of 6-fold nanorod-arrays grown on the side surface of core nanowires. Compared with ZnO nanowires, brush-like hierarchical ZnO nanostructures easily fabricated satisfactory ethanol sensors. The main advantages of these sensors were featured in excellent selectivity, fast response, high response (sensitivity), and low detection limit (with detectable ethanol concentration in ppm).</td>
</tr>
<tr>
<td>2009</td>
<td>Hierarchically three-dimensional (3D) porous ZnO architectures were synthesized by Zhang et al via template-free, economical hydrothermal method combined with subsequent calcinations. First, a precursor of hierarchical basic zinc carbonate (BZC) nanostructures self-assembled by sheet-like blocks was prepared. Then calcinations of the precursor produced hierarchically 3D porous ZnO architectures composed of</td>
</tr>
</tbody>
</table>
interconnected ZnO nanosheets with high porosity resulting from the thermal decomposition of the precursor. The products were characterized by XRD, FTIR, TG-DTA, SEM, TEM, and Brunauer-Emmett-Teller N$_2$ adsorption-desorption analyses. Control experiments with variations in solvent and reaction time respectively revealed that ethanol was responsible for the formation of the BZC precursor, and the self-assembly of BZC nanosheets into hierarchically 3D architectures was highly dependent on the reaction time. Gas sensing tests showed that these hierarchically porous ZnO architectures were highly promising for gas sensor applications, as the gas diffusion and mass transportation in sensing materials were significantly enhanced by their unique structures.

| 2009 | Vertical ZnO nanowires with a very high aspect ratio of more than 250 were synthesized by Kang et al via CVD on vertical nanowires grown by hydrothermal growth (HG) without using the metal catalyst. The underlying vertical nanowires were grown by the HG process (HG-nanowire) enhanced nucleation of ZnO during the followed ZnO synthesis by CVD. Hydrogen-gas sensitivity was measured from the synthesized ZnO nanowires. High sensitivity of 72% and response time as fast as 30 s was observed at 200 °C from the vertical ZnO nanowires grown by CVD on the HG-nanowire, which was much higher than the sensitivity value of 50% from the vertical HG-nanowire and the value of 35% |
from the vertical CVD nanowires without the HG-nanowire. The results indicate that the method synthesizing the vertical ZnO nanowires by combining the HG process and thermal CVD was promising way to fabricate both the vertical nanowires and the highly sensitive gas sensors.

2010 An environmentally friendly antisolvent approach, which involves only biocompatible chemicals and mild processing conditions, was developed by Dong et al to prepare various ZnO nanostructures including twin-cones and nanorods with controllable dimensions. The method was based on the dissolution of ZnO powders in a deep eutectic solvent (DES), followed by precipitation of ZnO nanostructures from the DES upon introduction of an antisolvent. Through suitably modulating the processing conditions, such as the ethanol content of the antisolvent and the injection time of the ZnO-containing DES, the morphology of the resulting ZnO nanostructures can be readily controlled. Anisotropic crystal growth was achieved without severe reaction conditions, such as high temperatures and high vacuums, or use of environmentally harmful chemicals, such as long carbon chain surfactants and capping reagents.

2010 Different ZnO nanostructures such as nanowires, nanobelts and tetrapods were grown and used for preparation of thick film (with random grain boundaries)
as well as isolated nanowire/nanobelt gas sensors by SK Gupta et al. Sensitivity of different type of sensors was studied for H$_2$S and NO gases. The results shown that the response of ZnO sensors to H$_2$S arises from grain boundary only whereas both grain boundaries and intragrain resistances contribute towards response to NO. In addition, oxygen vacancies in the lattice were also seen to help in improvement of sensor response. Room temperature operating H$_2$S and NO sensors based on ZnO nanowires were demonstrated. Further, sensors based on isolated nanobelts were found to be highly selective in their response to NO.

<table>
<thead>
<tr>
<th>Year</th>
<th>Authors</th>
<th>Methodology</th>
<th>Sensor Type</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>Park et al.</td>
<td>Fabricated a novel method</td>
<td>ZnO nanorod array</td>
<td>Highly sensitive chemical sensors</td>
</tr>
<tr>
<td>2010</td>
<td></td>
<td>on a Pt-coated Si substrate, with a top-top electrode configuration</td>
<td></td>
<td>Room temperature operating H$_2$S and NO sensors</td>
</tr>
<tr>
<td>2010</td>
<td>Large-scale uniform ZnO dumbbells and ZnO/ ZnS hollow nanocages were successfully synthesized via a facile hydrothermal route combined with subsequent etching treatment. The nanocages were formed through preferential dissolution of the twinned (0001) plane of ZnO dumbbells. Due to their special morphology, the hollow nanocages show better sensing properties to</td>
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</table>
ethanol than ZnO dumbbells. The gain in sensitivity is attributed to both the interface between ZnO and ZnS heterostructure and their hollow architecture that promotes analyte diffusion and increases the available active surface area.

1.15 Ionic liquids in electrochemistry

1.15.1 Energy storage devices (Supercapacitance)

Energy storage and power management are becoming increasingly important as many countries are placing greater emphasis on electrical production from renewable sources. As the contribution of electricity generated from renewable sources (wind, wave and solar) grows, the inherent intermittency of supply from such generating technologies can only be addressed by a step-change in energy storage. Quite simply, energy-storage technologies will be vital to a future clean-energy landscape, ensuring secure and continuous supply to the consumer from a more distributed and intermittent supply base. This will be true for both on- and off-grid applications [116]. With a fast-growing market for portable electronic devices and the development of hybrid electric vehicles, there has been an ever increasing and urgent demand for environmentally friendly high-power energy resources.

Supercapacitors, also known as ultracapacitors, electric double layer capacitors (EDLCs) or electrochemical supercapacitors are the electrochemical energy storage devices in which the electric charge is stored in the electrical double layer formed at the interface between electrode and an electrolyte solution. These devices can provide high power capability, excellent reversibility and long cycle life. Typically they
exhibit 20-200 times larger capacitance per unit volume or mass than conventional capacitors.

A more recent application is the use of supercapacitors in emergency doors on the Airbus A380, highlighting their safe and reliable performance. One of the most promising applications is their use in low-emission hybrid electric vehicles, and fuel cell vehicles. In such cases, supercapacitors are coupled with primary high-energy batteries or fuel cells to serve as a temporary energy storage device with a high-power capability to store energies when braking. Supercapacitors are likely to show an equal importance to batteries for future energy storage systems [117-121]. As illustrated in Fig 1.18, where various energy conversion and storage devices are compared and presented in the simplified ‘Ragone plot’, supercapacitors occupy an important position in terms of the specific energy as well as the specific power.

![Fig 1.18 Energy-storage Ragone plot](image-url)
1.15.2 Supercapacitor

Since supercapacitors are characterized by fast discharge rates and low maintenance, the demand for them is predicted to be most extensive in frequency regulation applications. The other area for significant growth is in regenerative braking for grid-connected light rail systems. Conventionally, supercapacitors have been categorized into two types: electrochemical double layer capacitors (EDLCs) and pseudocapacitors based on the Faradic electrochemical redox mechanism of charge storage. The electrochemical interface between an electrode and electrolyte has long been known to behave like a capacitor and thus the name “double-layer” is often commonly used while referring to the capacitor phenomenon. The rapid response of the interface to changes in electrode potential and high reversibility has been exploited in EDLCs. Pseudocapacitors on the other hand are devices based on electrode charge storage accompanied by highly reversible Faradaic electrochemical redox surface processes [122]. The Fig 1.19 shows the taxonomy of the supercapacitor.

![Supercapacitor Taxonomy](image)

**Fig 1.19** Taxonomy of the supercapacitor
1.15.3 The energy storage mechanism of EDLCs

Conventional capacitors store little by way of energy, due to the limited charge storage areas and geometric constrains of the separation distance between the two charged plates. However, supercapacitors based on the EDL mechanism can store much more energy because of the large interfacial area and the atomic range of charge separation distances. As schematically illustrated in Fig 1.20, the concept of the EDL was first described and modeled by von Helmholtz in the 19th century, when he investigated the distribution of opposite charges at the interface of colloidal particles [123].

![Fig 1.20 Schematic diagrams of an electrochemical double layer type capacitor showing the charged (left) and discharged (right) states [122].](image)

1.15.4 Capacitor construction

A wide variety of EDLC materials and processes for cell construction currently exist. This part covers the properties of various available materials and describes the aspects of each alternative that have a significant impact on device performance.
1.15.4.1 Electrolytes

The capacitance of an EDLC is greatly influenced by the choice of electrolyte. The ability to store charge is dependent on the accessibility of the ions to the porous surface-area, so ion size and pore size must be optimal. The best pore size distribution in the electrode depends upon the size of the ions in the electrolyte, so both electrode and electrolyte must be chosen together.

1.15.4.2 Problems regarding conventional electrolyte

The attainable cell voltage of a supercapacitor will depend on the breakdown voltage of the electrolyte, and hence the possible energy density (which is dependent on voltage) will be limited by the electrolyte. Power density is dependent on the cell’s ESR (equivalent series resistance), which is strongly dependent on electrolyte conductivity. There are currently two types of electrolyte in use in EDLCs: organic and aqueous. Organic electrolytes are the most commonly used in commercial devices, due to their higher dissociation voltage. The aqueous electrolytes feature a small working window, usually 0.7-0.8 V vs 2.7 V for organic electrolytes [124]. Although organic electrolytes have relatively large electrochemical windows of stability, they pose serious health and safety problems because they are volatile, flammable, and sometimes toxic. Now the most commonly used organic electrolyte in supercapacitors tetra-ethyl-ammonium tetra-fluoro-borate dissolved in acetonitrile is highly toxic, flammable and explosive substance and as a result the use of supercapacitors with such electrolyte is forbidden in public transport in a number of countries [125].
1.15.4.3 Need of suitable electrolyte

To find a more suitable electrolyte to optimize the performance of supercapacitors is of great importance. Room temperature ionic liquids (RTILs) are molten salts with a melting point close to or below room temperature. They are composed of ions of opposite charges that only loosely fit together (usually bulky organic cations and smaller anions). The properties of high conductivity ($10^{-1} - 10^{-2}$ Sm$^{-1}$), non-volatility, low toxicity, large electrochemical window (i.e. the electrochemical potential range over which the electrolyte is neither reduced nor oxidized on electrodes, commonly larger than 3.0 V) and good electrochemical stability, high ionic mobility, so that they can be used as solvent-free “green” electrolytes for high voltage supercapacitors and sensors [126].

But they are typically high viscosity liquids and have low ionic conductivity at room temperature, which inevitably affect their performance. Therefore, designing an IL with high conductivity and a large voltage window for practical applications is still challenging. Given that high purity ILs are of great importance for long cycle lives of a supercapacitor, hydrophobic ILs are preferable due to a more readily attainable high level of purity. It is worth noting that two principle factors are involved in the conductivity of the electrolyte system: (1) the ability of the salt dissociation to give out free charge carriers like cations and anions; and (2) the mobility of the dissociated ions in the electrolyte system. Hence, further research could be carried out to design ILs with a combination of ions having high dissociation constants, low molecular weight and with a wide electrochemical stability window.

1.15.4.4 Electrode materials

Selection of electrode materials plays a crucial role in determining the electrical properties of a supercapacitor. Double-layer charge storage
is a surface process, and the surface characteristics of the electrode greatly influence the capacitance of the cell. Carbon is the most widely used electrode material, but considerable research is being conducted into metal-oxides and conducting polymers.

1.15.4.5 Metal oxides

Metal-oxides present an attractive alternative as an electrode material because of high specific capacitance and low resistance, possibly making it easier to construct high-energy, high-power EDLCs. Extensive research into ruthenium oxides has been conducted for military applications, where cost is presumably less of an issue than it is for commercial ventures. The US Army Research Lab has assembled prototype cells with an energy density of 8.5 Wh/kg and a power density of 6 kW/kg [127]. Academic institutions have focused on searching for other, cheaper, materials to use instead of ruthenium-oxides, but the selection has traditionally been limited by the use of concentrated sulfuric acid as an electrolyte. It was believed high capacitance and fast charging was largely a result of H sorption, so a strong acid was therefore necessary to provide good proton conductivity. This resulted in a narrow range of possible electrode materials, however, since most metal-oxides break down quickly in acidic solutions. Milder aqueous solutions such as potassium chloride have therefore been considered for use with metal-oxides such as manganese-oxides. Although manganese oxide electrodes currently appear to possess lower specific capacitances than ruthenium-oxides, the lower cost and milder electrolyte may be enough of an advantage to make them variable alternative. Metal-oxide electrodes can only be used with aqueous electrolytes, thereby limiting the achievable cell voltage. Gains in power density from lower resistance are therefore often offset by losses due to the lower operating voltage.
Fig 1.22 Schematic diagrams showing the presence of a thin oxide layer over nanoparticle VN generated by a two-step ammonolysis approach, shown to exhibit very high capacitances of up to 1340 F g\(^{-1}\) [122].

1.15.4.6 Why copper oxide?

Copper oxides exist in two stable forms, the cuprous oxides Cu\(_2\)O and the cupric oxides CuO. These two oxides have very different colors, crystal structures, and physical properties. Simple chemistry tells that these differences are mainly due to the fact that Cu in Cu\(_2\)O is in the Cu\(^{+}\) state. Cu\(_2\)O is a red-colored cubic semiconductor that displays a wealth of interesting excitonic levels. CuO on the other hand has a dark, iron gray color and crystallizes in a more complicated monoclinic tenorite structure exhibiting interesting antiferromagnetic ordering. CuO has also known as p-type semiconductor that exhibits a narrow band gap (1.2 eV) [128]. Due to the appearance of high Tc superconductors of CuO materials, it has received much attention since 1986. Their superconductivities are controlled by the structure, composition and the type and density of
carriers. It also exhibits other interesting properties. For example, monoclinic CuO solid belongs to a particular class of materials known as Mott insulators, whose electronic structures cannot be simply described using conventional band theory. Recent studies by several groups indicate that it could exist in as many as three different magnetic phases. It was a 3D collinear antiferromagnet at temperatures below 214 K. When the temperature was raised, it first became an intermediate noncollinear incommensurate magnetic phase up to 230 K and then acted like a 1 D quantum antiferromagnetic material. The temperature dependent dielectric constant of polycrystalline CuO exhibits a striking feature of very high dielectric constant (~2 x 10^4) comparable to those of the recently reported high dielectric materials CaCu_3Ti_4O_12 (CCTO) and Li and Ti doped NiO (LTNO) ceramics. With regard to its commercial value, it has been widely exploited for use as a powerful heterogeneous catalyst to convert hydrocarbons completely into carbon dioxide and water. It is also potentially useful in the fabrication of lithium-copper oxide electrochemical cells [129]. Recently it is to be found useful for supercapacitor application [130].

1.15.4.7 Crystal structure of CuO

The CuO has a considerably more complicated tenorite structure, similar to AgO. The monoclinic unit cell (space group C\textit{\text{6}}\textit{\text{2h}}) contains four molecules. The crystal parameters were measured to be \(a=4.6837\ \text{\AA}\), \(b=3.4226\ \text{\AA}\), \(c=5.1288\ \text{\AA}\), and \(\beta=99.54^\circ\). The coordination of atoms in CuO is such that each ion has four nearest neighbors of the other kind. In the (110) plane, each Cu atom is linked to four nearly coplanar O atoms at the corner of an almost rectangular parallelogram. The Cu-O bond lengths in this plane are 1.88 and 1.96 \text{\AA}, respectively, which are larger than those in the cuprous oxide. The next to Cu-O bond lengths perpendicular to the
plane are much greater, so an octahedral type of coordination can be ruled out. The O atom is coordinated to four Cu atoms in the form of a distorted tetrahedron. It is generally believed that the bonding in CuO is a mixture of ionic and covalent bonding, although the oxidation state of Cu in CuO is unquestionably +2. The transition-metal monoxides such as CoO and NiO, on the other hand, crystallize in the rock salt structure with much higher symmetry. Thus, this may indicate a fundamental difference in electronic states between the CuO crystal NiO or CoO crystal [131].

![Crystal structure of monoclinic CuO](image)

**Fig 1.23** Crystal structure of monoclinic CuO
1.15.5 Literature survey on ionic liquid based supercapacitor

<table>
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<th>Year</th>
<th>Description</th>
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<tr>
<td>1999</td>
<td>Amorphous MnO$_2$.nH$_2$O in a mild 2 M KCl aqueous electrolyte proves to be an excellent electrode for a faradic electrochemical capacitor cycled between -0.2 and +1.0 V versus SCE studied by Yuan et al. In this potential range, it had ideal behavior with a specific capacitance of ca. 200 F/g, excellent cyclability at 2 mA/cm$^2$ over 100 cycles, and a short-circuit initial current density of 0.23 A/cm$^2$ with a total released charge of 3.8 C/cm$^2$ as compared to 0.32 A/cm$^2$ and 11.1 C/cm$^2$ for RuO$_2$.nH$_2$O in 5.3 M H$_2$SO$_4$.</td>
<td>132</td>
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<td>2001</td>
<td>A totally solid state electric double layer capacitor was fabricated using an alkaline polymer electrolyte and an activated carbon powder as electrode material. The polymer electrolyte serves both as separator as well as electrode binder. The capacitor has a three-layer structure: electrode–electrolyte–electrode with a final thickness of ca. 1.5–2 mm, diameter of 1.8 cm (surface of 2.5 cm$^2$) and a mass of ca. 300–500 mg. Cyclic voltammetry, galvanostatic cycling and impedance spectroscopy was used for the determination of the electrochemical performance of prototype capacitors and a capacity of ca. 1.7–3.0 F for a 1 V voltage range was measured by Lewandowski et al.</td>
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<td>2005</td>
<td>Portet et al was studied the performances of 4 cm$^2$ supercapacitor cells assembled with 200 µm thick active material films composed with activated carbon and</td>
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carbon nanotubes mixture in organic electrolyte. Galvanostatic and electrochemical spectroscopy impedance measurements were carried out. Galvanostatic measurements showed that both internal resistance and specific capacitance decrease when the carbon nanotubes content increases in the active material. With 15% of carbon nanotubes, the internal resistance is $0.65 \ \Omega \ \text{cm}^2$ and the specific capacitance is $90 \ \text{Fg}^{-1}$ measured at $20 \ \text{mAc}^{-2}$. The performance was stable during 10,000 cycles. The characterization of the frequency behavior was made by Electrochemical Impedance Spectroscopy. For 15% of CNTs content in the active material, the relaxation time ($\phi = -45^\circ$) is divided by 3 as compared to a supercapacitor using pure activated carbon electrodes.

2006 A novel hybrid nano-structured manganese dioxide/activated carbon supercapacitor with lithium hydroxide electrolyte, in which the MnO$_2$ positive material was prepared using a solid-state reaction route. The electrochemical behaviors of MnO$_2$ electrodes in 1 M LiOH and 1M KOH electrolytes, respectively, were characterized by cyclic voltammetry and electrochemical impedance spectroscopy methods. The results indicated that the reaction mechanism of MnO$_2$ electrode in LiOH electrolyte appears to be Li$^+$ ion insertion/extraction in MnO$_2$ solid, which was different with that electrode in KOH electrolyte. Charge/discharge experiments showed that the rate dischargeability of the MnO$_2$/AC capacitor...
with 1M LiOH electrolyte was excellent, and the cyclic stability of the MnO_{2}/AC capacitor with 1 M LiOH electrolyte was better than that with 1M KOH electrolyte.

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<td>2006</td>
<td>A nano-structured CoAl double hydroxide with an average particle size of 60–70 nm was prepared by Wang et al via chemical co-precipitation. It was used as a positive electrode for the asymmetric hybrid supercapacitor in combination with an active carbon negative electrode in KOH electrolyte solution. The electrochemical capacitance performance of this kind of hybrid supercapacitor was investigated by means of cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge–discharge tests. A specific capacitance of 77 Fg^{-1} with a specific energy density of 15.5wh kg^{-1} was obtained for the hybrid supercapacitor within the voltage range of 0.9–1.5V. The supercapacitor exhibited a good cycling performance and keep 90% of initial capacity over 1000 cycles.</td>
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| 2006 | Highly oriented pyrolytic graphite (HOPG) in a solution of \((\text{C}_2\text{H}_5)_4\text{NBF}_4\) in propylene carbonate (PC) was investigated by Campana et al, as a model system for the electrochemical double-layer capacitor (EDLC) negative electrode. For the intercalation of \((\text{C}_2\text{H}_5)_4\text{N}^+\) into HOPG could be monitored by means of in situ atomic force microscopy (AFM). In analogy to the behavior in Li^{+} containing solution, the formation of a surface film on the negative electrode could be detected. The question was addressed if this film might serve as a |

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solid electrolyte interphase preventing sustained solvent decomposition.

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<td>2008</td>
<td>The nano-sized columned β-FeOOH was prepared by Jin et al for the hydrolysis process and its electrochemical capacitance performance was evaluated in Li$_2$SO$_4$ solution. A hybrid supercapacitor based on MnO$_2$ positive electrode and FeOOH negative electrode in Li$_2$SO$_4$ electrolyte solution was designed. The electrochemical tests demonstrated that the hybrid supercapacitor has an energy density of 12Wh kg$^{-1}$ and a power density of 3700 Wkg$^{-1}$ based on the total weight of the electrode active materials with a voltage range 0–1.85V. This hybrid supercapacitor also exhibits a good cycling performance and keeps 85% of initial capacity over 2000 cycles.</td>
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<td>2008</td>
<td>In this work, carbon-coated lithium-ion intercalated compound LiTi$_2$(PO$_4$)$_3$ and MnO$_2$ have been synthesized and they deliver a capacity of 90 and 60 mAh/g in 1M Li$_2$SO$_4$ neutral aqueous electrolyte in with safe potentials without O$_2$ and H$_2$ evolution, by Luo et al. The novel hybrid supercapacitor in which MnO$_2$ was used as a positive electrode and carbon-coated LiTi$_2$(PO$_4$)$_3$ as a negative electrode was assembled and the LiTi$_2$(PO$_4$)$_3$/MnO$_2$ hybrid supercapacitor showed a sloping voltage profile from 0.7 to 1.9V, at an average voltage near 1.3V, and delivers a capacity of 36 mAh/g and an energy density of 47 Wh/kg based on the total weight of the active electrode materials. It exhibits a</td>
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<td>2009</td>
<td>A new polymer blend electrolyte based on poly vinyl alcohol and poly styrene sulphonic acid has been studied by Kumar et al., as an electrolyte for supercapacitors. A carbon–carbon supercapacitor was fabricated using this electrolyte and its electrochemical characteristics and performance was studied. The conductivity was calculated using the bulk impedance obtained through impedance spectroscopy. The real and imaginary parts of the electrical modulus of samples showed a long tail feature, which attributed to high capacitance of the material. The super capacitor showed a fairly good specific capacitance of 40 F g$^{-1}$ and a time constant of 5 s.</td>
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<td>2010</td>
<td>In this work Pena et al was explored the electrochemical properties of two lithiated iron oxide powders for supercapacitor purposes. These samples mainly consisted of α-LiFeO$_2$ in nanosized or micrometric form. Electrolyte was an aqueous 0.5 M Li$_2$SO$_4$ solution and voltage range study was between 0 and −0.7V vs. a Ag/AgCl reference electrode. As expected, electrochemical performance was dependent on the particle size. When electrolyte was de-aerated a stable</td>
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capacitance of \( \approx 50 \text{F}_{\text{g}}^{-1} \) is provided by the nanosized sample for several hundred cycles. Other sulfate based salts (\( \text{Na}_2\text{SO}_4 \), \( \text{K}_2\text{SO}_4 \), \( \text{Cs}_2\text{SO}_4 \)) were investigated as electrolytes but only \( \text{Li}_2\text{SO}_4 \) leads to a stable capacitance upon cycling, probably due to lithium intercalation. An hybrid cell consisting of this sample and \( \text{MnO}_2 \) as negative and positive electrodes, respectively, delivered 0.3 F cm\(^{-2} \) (10 F g\(^{-1} \)). Although these values are lower than reported for other aqueous hybrid cell, \( \alpha \)-\( \text{LiFeO}_2/\text{MnO}_2 \) asymmetric capacitor was interesting from both, an economic and an environmental point of view.
1.16 References

49) Ding J, Armstrong DW, Chirality, **2005**, 17, 281.
Chapter 1: A Brief Account On: Ionic Liquids with its Applications


Chapter 1: A Brief Account On Ionic Liquids with its Applications


Chapter-I: A Brief Account On: Ionic Liquids with its Applications