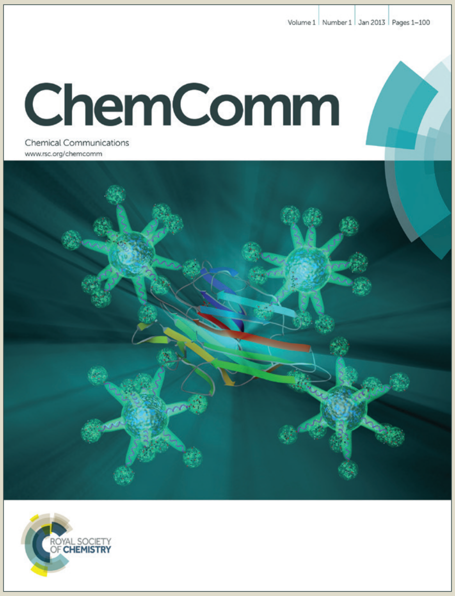
# ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

# Ionic Liquids as an electrolyte for the electro synthesis of organic compounds

Murugavel Kathiresan,* David Velayutham*

Electro Organic Division, CSIR-Central Electrochemical Research Institute, Karaikudi-630003, TamilNadu, INDIA.

E-mail: kathiresan@cecri.res.in, dvelayutham@rediffmail.com

## Abstract

The use of ionic liquids (ILs) as a solvent and an electrolyte for electro organic synthesis has been reviewed. Till date several ILs exists, however the ILs based on tetraalkylammonium, pyrrolidinium, piperidinium and imidazolium cations with $BF_4^-$, $PF_6^-$, and TFSI anions were widely used and explored to the most. Electro organic synthesis in ionic liquid media leading to the synthesis of wide range of organic compounds has been discussed. Anodic oxidation or cathodic reduction will generate a radical cation or anion intermediates respectively. These radicals can undergo self coupling or coupling with other molecules yielding organic compounds of our interest. The cation of the IL was known to stabilize the radical anion extensively. This stabilization effect has a specific impact on the electrochemical $CO_2$ reduction and coupling to various organics. Relative stability of the intermediates in IL leads to the formation of specific product in higher yields. Electrochemical reduction of imidazolium or thiazolium based ILs generates N-heterocyclic carbenes that was shown to catalyze wide range of base or nucleophile catalyzed organic reactions in IL media, an aspect that comes under organocatalysis. Electrochemical fluorination or selective electrochemical fluorination is another fascinating area that delivers selectively fluorinated organic products in $Et_3N.nHF$ or $Et_4NF.nHF$ adducts (IL) via anodic oxidation. Oxidative polymerization in ILs were explored to the most, although morphological changes were observed compared to the conventional methods, polymers were obtained in good yields and in some cases ILs were used as dopants to improve the desired properties.

Keywords: Electroorganic synthesis, ionic liquids, N-Heterocyclic carbenes, $CO_2$ reduction, organocatalysis, electro polymerization.

## 1. Introduction

Ionic liquids (ILs) are an eminent class of organic salts in liquid state presumably at lower temperatures (<100°C) containing mainly an organic cation and organic or inorganic anions. [1-2] Design of unsymmetrical organic cations (cations bearing different alkyl groups) preferably yields so called Room Temperature Ionic Liquids (RTILs, ionic liquids at room temperatures) .[3] Required functionalities can be introduced by alkylation and quarternization of amine or phosphines (in most cases) with alkylating agents of desire.[4] Usually the obtained salts were halide salts in a primary reaction step and these were ion exchanged by metathesis reactions to obtain the desired counter anion. Based on the substituents on the cation/anion their properties such as hydrophilicity, hydrophobicity, thermal stability, volatility, viscosity, acidity/basicity, electrochemical window, etc[5-8] can be tuned or in simple words, the physicochemical properties of the ionic liquid are determined by the substitutents on the cation/anions.[4, 8-9] These task specific ionic liquids are widely used in synthesis, analytical chemistry, pharmaceuticals, catalysis, sensors, extraction of metals, energy applications, etc. [10-25] In synthetic organic chemistry, they show great advantages over conventional organic solvents due to their unique properties such as non-flammability, low toxicity, favourable conductivity, negligible vapour pressure and high chemical/thermal stability.[26-27] Most of the cations and anions render inert nature at room temperature as well as at elevated temperatures. Due to their polar nature, they are known to dissolve wide range of organic compounds, gaseous molecules, organometallics and metal salts and these criterion makes them a best solvent suited for organic synthesis.[28]

Electro organic synthesis is a fascinating area which is more regarded to be green and eco-friendly compared to the conventional organic synthesis.[29-33] In electro organic synthesis, the electrons act as a reagent and the electrodes acts as a catalyst, whereas in conventional organic synthesis several reagents and solvents are needed to carry out such conversion.[30, 32] Both methods has their own advantages and limitations, however conventional organic synthesis leads the front in synthesizing wider range of organic substances, as electrochemical methods are limited by several factors. Ionic liquids play a dual role as an electrolyte and a solvent in electro organic synthesis, this gives us an additional advantage as it eliminates the use of an electrolyte and a solvent mixture.[23] Based on the nature of the cation and anion, they exhibit wide electrochemical potential window.[23, 34-35] Nevertheless, the stability of ILs, moisture uptake or chemical changes during prolonged electrolysis was not mechanistically investigated. Additionally, Inesi and co-workers showed that NHCs (N-heterocyclic carbenes) can be electro generated by the reduction of imidazolium and thiazolium based ionic liquids and they act as nucleophile / nucleophilic bases. Such electrogenerated bases were shown to catalyse variety of nucleophile or base catalysed reactions in IL media. Electrochemical $CO_2$ reduction in IL is an emerging area, as it is shown that $CO_2$ anion radical is extensively stabilized by cation of the RTIL which even shifts the reduction potential slightly positive.[36] $CO_2$ solubility in ILs is much higher than their solubility in conventional organic solvents.[37] Chemical reduction of $CO_2$ is very difficult as it needs higher temperature and pressures and the use of sophisticated catalysts, whereas the electrochemical methods offers a green pathway for the reduction of $CO_2$ at relatively lower temperature and pressures. Thus electrochemical method turns into an attractive route in this arena. Additional aspect in this area includes coupling of electro generated radicals to $CO_2$ and up conversion to carbamates or lactones or carboxylates,[38] etc., where $CO_2$ is utilized as a $C_1$ synthon.[39] Most of these aspects are aimed towards green synthesis. Even though the green aspects of ILs are strongly debated, we regard it as a green method by comparing the electrochemical routes to the available conventional synthetic methods.

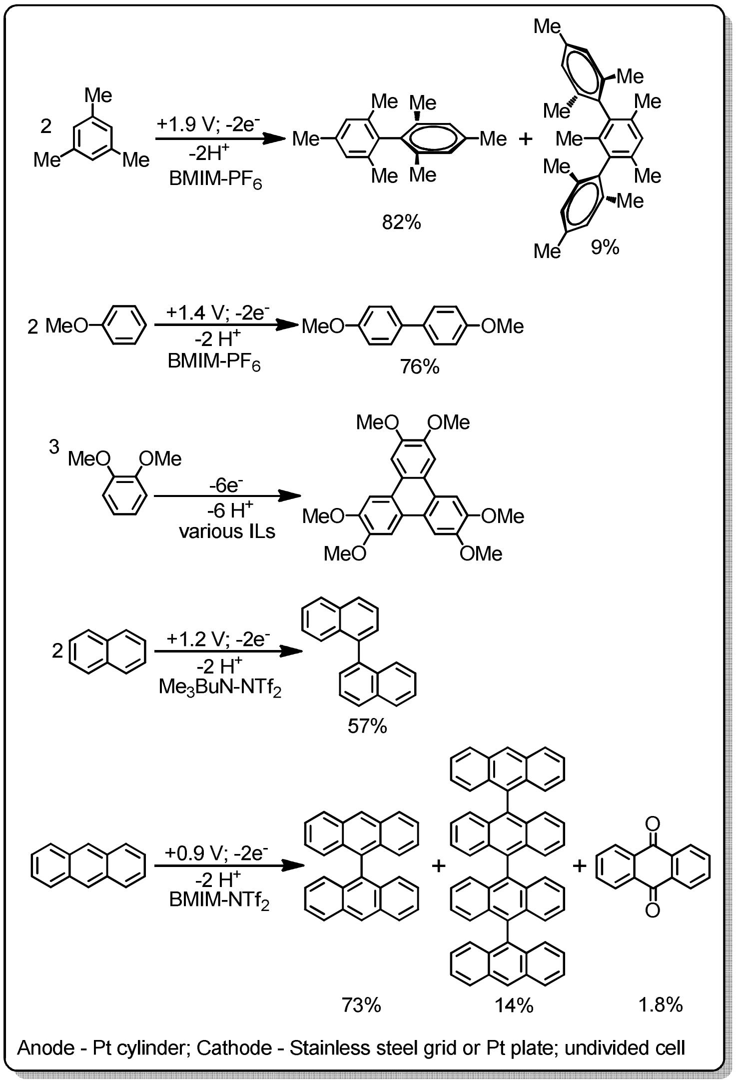
Several reviews have been published till date focusing on the synthesis, catalysis in ILs, and on the applications of ILs.[26-27, 29, 40-45] The focus of the current review is briefing the green aspects of electroorganic synthesis in RTILs. Accordingly the review is divided into several sections to address different types of reactions carried out in RTILs.

## 2. Electrochemical Oxidation reactions in Ionic Liquid media

Anodic oxidation and subsequent coupling (self-coupling or coupling to other substrates) or polymerizations in RTILs are well-known. Esmail et al studied the mechanism of electro-oxidation of mesalazine drug in ILs.[46] It was shown that the electro-oxidation of mesalazine drug in the presence of barbituric acid derivatives (acidic medium) leads to the formation of highly reactive quinone-imine which could be internally attacked by weak nucleophile $BF_4^-$ (from BMIM-$BF_4$ electrolyte). However addition of $H_3PO_4$ was shown to inhibit this reaction ($H_3PO_4$ deactivates the nucleophilic property of $BF_4^-$). Zhao et al reported the mechanistic investigation on the electro-oxidation of benzyl alcohol to benzaldehyde in a biphasic system consisting of supercritical $CO_2$ and ILs.[47] Primary amines were electrochemically oxidized in IL media to modify the electrode surface.[48] Recently, Herrero and co-workers reported that Pt (110) surface selectively activates CO oxidation in IL media.[49] Here, we restrict our focus to few renowned oxidation reactions in IL media. Although most of the polymerization reactions come under oxidation, they are discussed separately under the subsection, electrochemical polymerization.

### a) Oxidative self-coupling

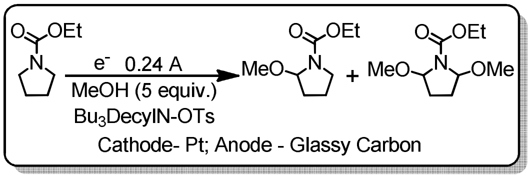
Jouikov and co-workers reported the electrochemical anodic oxidation of mononuclear (anisole, mesitylene) and fused polynuclear (naphthalene, anthracene) aromatic compounds to dimerized products in various ionic liquids (ILs).[50] Mesitylene upon anodic oxidation on Pt disc electrode yielded dimesityl (82%) and traces of *m*-terphenyl (9%) in BMIM-$PF_6$ (scheme 1). Under similar conditions, methoxy benzene yielded the dimerized product 4,4'-dimethoxybiphenyl (76%). Oxidation of 1,2-dimethoxybenzene (veratrole) in the presence of nucleophiles resulted in the formation of unsymmetrical dimeric and trimeric products containing one or two more veratrole units. Conversely, under non-nucleophilic conditions trimeric hexamethoxy-triphenylene was obtained, exemplifying the fact that a range of products can be obtained by changing the conditions and the solvent media. Further it was demonstrated that hexamethoxy-triphenylene can be easily oxidized to a radical cation and the radical cation forms polymeric tubular systems (stacks of hexamethoxytriphenylene fragment) of different morphology based on the IL used. Similarly the oxidation of fused ring systems such as naphthalene and anthracene yielded dimerized products as shown in Scheme 1.



**Scheme 1** Oxidative self-coupling of aromatic compounds in BMIM-$PF_6$.[50]

### b) Shono Oxidation

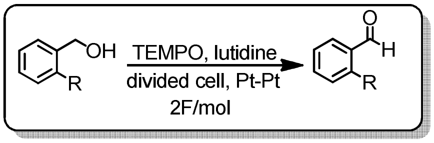
Handy and co-workers described the Shono oxidation of carbamates using ionic liquids as recyclable solvents, and the effects of viscosity of the medium were systematically investigated.[51] MeOH was used as the methoxylating agent in $Bu_3$DecylN-OTs ionic liquid (Scheme 2). Increase in yield was observed when the percentage of methanol was increased to 33%, attributed to the decrease in the viscosity of the solvent medium. Although the use of VOC (volatile organic compounds) was known to increase the conversion efficiency, their addition will reduce the wider electrochemical window of $Bu_3$DecylN-OTs IL. Nowadays, less viscous ionic liquids are available which will limit the use of VOCs and enhance the environmental friendly nature of ILs in electro organic synthesis.



**Scheme 2** Shono Oxidation in Bu$_3$DecylN-OTs ionic liquid.[51]

### c) Oxidation of alcohols to carbonyl compounds

Troupel and co-workers exemplified the electrochemistry of TEMPO [(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl] mediated oxidation of alcohols to the corresponding carbonyl compounds in IL medium.[52] It was shown that TEMPO undergoes reversible redox in IL medium and generates a catalytically-active oxoammonium species that facilitates the oxidation of alcohols to the corresponding aldehyde or ketone products. TEMPO diffusion currents are suppressed in IL medium due to high viscosity in relation to the acetonitrile medium. Consequently, the reaction was performed in a mixture of solvents to reduce the viscosity of the IL. Primary alcohols were oxidized to their corresponding aldehydes in ≥90% yield when 2F/mol charge was applied. Reactions were carried out with benzyl alcohol; halosubstituted benzyl alcohols and conjugated systems. Irrespective of the substrate, aldehydes were obtained in good yield (Scheme 3). Even secondary alcohols were electro-oxidised to ketones in good yields (50-60%).

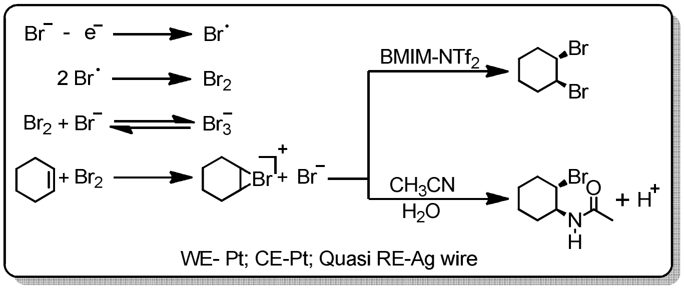


**Scheme 3** Tempo mediated electro-oxidation of alcohols[52]

Following the above procedure, Herath et al electrochemically oxidized benzylalcohol to benzaldehyde (90% yield) in BMIM-PF$_6$ ionic liquid.[53]

### d) Bromination reaction

The reactivity of electro generated bromine with cyclohexene in polar RTIL (Room Temperature Ionic Liquid) 1-butyl-3-methylimidazolium bis-[(trifluoromethyl)sulfonyl]imide (BMIM-NTf$_2$) and the traditional aprotic solvent acetonitrile was evaluated by Compton and co-workers.[54] Direct oxidation of bromide in BMIM-NTf$_2$ and acetonitrile resulted in similar voltammetric behaviour; however the reaction of electro generated bromine with cyclohexene yielded different products in these two solvents owing to the change in nucleophilicity. Bromination in ionic liquid yielded trans-1,2-dibromocyclohexane and bromination in acetonitrile yielded solvent incorporated *trans*-1-(*N*-acetylamino)-2-bromocyclohexane (Scheme 4).



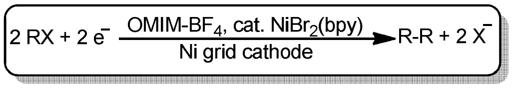
**Scheme 4** Reactivity of electro generated bromine in BMIM-NTf$_2$ and CH$_3$CN.[54]

## 3. Electrochemical Reduction reactions in Ionic Liquid media

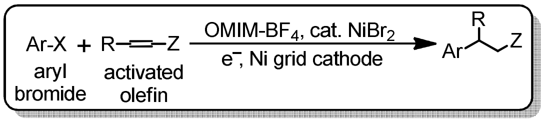
Electrochemical reduction and subsequent conversion to useful organics in RTILs were the far most investigated area compared to the electrochemical oxidation. Lu et al reported the electrochemical reduction of benzoylformic acid to 2-hydroxy-2-phenylacetic acid at 80°C in EMIM-Br ionic liquid.[55] Apart from direct electrochemical reduction (electrochemical reduction of carbonyl compounds to hydroxyl compounds, nitrocompounds to amines, etc.), certain species (carbonyl compounds, alkyl/aryl halides, α-haloketones, CO$_2$, etc.) undergo electrochemical reduction irreversibly to form a highly reactive radical intermediate, based on the conditions used, they either undergo self-coupling or reaction with other substrates to yield compounds of our interest (due to their high reactivity, their corresponding oxidation is not possible, i.e., they don't show redox behaviour under experimental conditions). Further it was shown by several groups that the anion radicals formed by electro-reduction in RTILs are extensively stabilized by the cations of the RTIL.[56] Reactions under this category can be divided into several subsections and they are discussed in detail.

### a) Electro-reductive coupling of organic halides (Ullmann reactions)

Direct or Ni-catalyzed electro-reductive homocoupling of organic halides and coupling of organic halides with activated olefins were first reported by Troupel and co-workers.[57] Direct electro-reductive homocoupling of aryl halides (identical to conventional copper catalyzed Ullmann reactions) on Ni grid cathode and Mg or Al sacrificial anode in OMIM-BF$_4$ IL gave excellent yields of the dimer, however alkyl halides showed only moderate conversion (Scheme 5). Authors further studied the Ni catalyzed electro-reductive coupling of aryl halides and activated olefins in OMIM-BF$_4$ IL, moderate yields were obtained for the reductive arylation (Scheme 6).



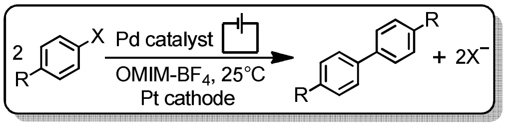
**Scheme 5** Ni(bpy) catalysed electro-reductive coupling of organic halides in OMIM-$BF_4$.[57]



**Scheme 6** Ni-catalysed electro-reductive arylation of activated olefins in OMIM-$BF_4$.[57]

An identical version of Ni catalyzed [$NiCl_2$(bpy)] electro-reductive dimerisation of bromobenzene and benzylbromide in BMIM-$NTf_2$ was reported by Jouikov and co-workers.[58] SS cathode and Al anode were used, lower yields were obtained for the dimerisation of bromobenzene (35%) and an excellent yield (75%) was reported for the dimerisation of benzylbromide. A few years later, Lu and co-workers reported the dimerisation of bromobenzene and benzylbromides using silver cathode in BMIM-$BF_4$ ionic liquid.[59] The reactions were performed at 60° C using Ag cathode and Mg anode. Poor yield was obtained for the dimerisation of bromobenzene (12% dimerized product), whereas moderate yields were reported for the dimerisation of benzylbromide (61%), 4-methyl (68%) and 4-chloro (40%) substituted benzylbromides.

As a further development in Ullmann coupling, classy Pd nanoparticles were generated in situ under electrochemical conditions and were used to catalyze homocoupling of arylhalides in ionic liquid media.[60] Wide range of arylhalides were homocoupled, moderate to excellent yields were obtained in most cases. In the case of substituted chlorobenzenes desired products were observed in traces (< 5%) [Scheme 7]. Ionic liquid was reported to stabilize the nanoparticle clusters. Pt cathode and Pd anode were used; upon applying constant potential, catalytic amount of Pd nanoparticles were generated on the anode surface. These electrogenerated Pd nanoparticles catalysed Ullmann coupling of aryl halides in ionic liquids and authors proposed a mechanism for such transformation.

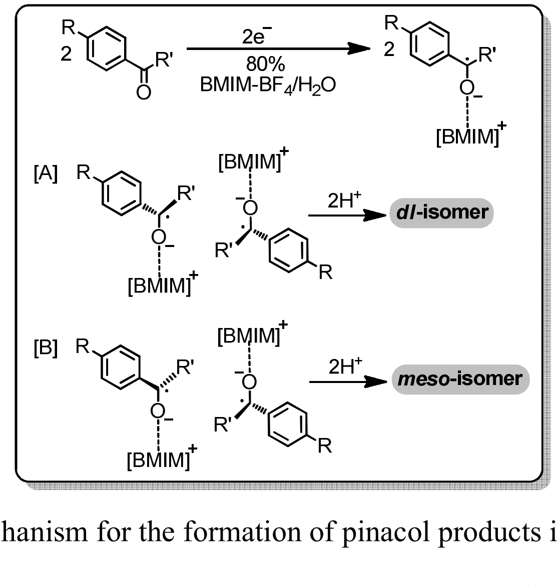


**Scheme 7** Electro generated Pd nanoparticle catalyzed Ullmann Coupling.[60]

## b) Pinacol Coupling

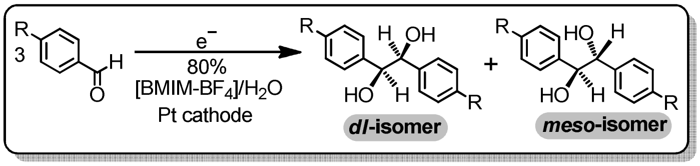
Systematic investigation of the influence of RTILs on stereo selectivity and kinetics of electrochemical pinacol coupling of acetophenone was accounted by Vaultier and co-workers.[61] The radical stability, dimerisation and facial orientation of the intermediates in ionic liquids leading to the D/L or meso isomer based on the ion-pair mechanism were investigated in this study in detail. In an another study, Andre et al evaluated the effects of viscosity, polarity and ionic solvation on the reactivity of radical anions in the irreversible dimerization of acetophenone radical anion in a series of 1,3-dialkylimidazolium based ionic liquids [EMIM-$NTf_2$ (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide), PMIM-$NTf_2$ (1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide), BMIM-$NTf_2$, HexMIM-$NTf_2$ (1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide), BMMIM-$NTf_2$ (1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide) and 1,2,3-trialkylimidazolium ($Et_3BuN$-$Tf_2$)].[62] Analogous to their previous report,[61] authors proposed that when the acetophenone radical anion gets ‘‘solvated’’ in imidazolium-based ionic liquids, a strong ionic interaction occurs between the radical anion and cation of the IL and this resulting charge stabilization allows a fast dimerization.

Electrochemical pinacol coupling of aromatic aldehydes and ketones in 80% BMIM-$BF_4$–$H_2O$ electrolytic medium was reported by Manchanayakage and co-workers.[63] Water was added to reduce the viscosity of IL. The products were obtained in high yields with moderate diastereoselectivity and authors illustrated the mechanism of product formation based on the ion-pairs formed between the imidazolium cation and anion radical formed by the reduction of carbonyls.

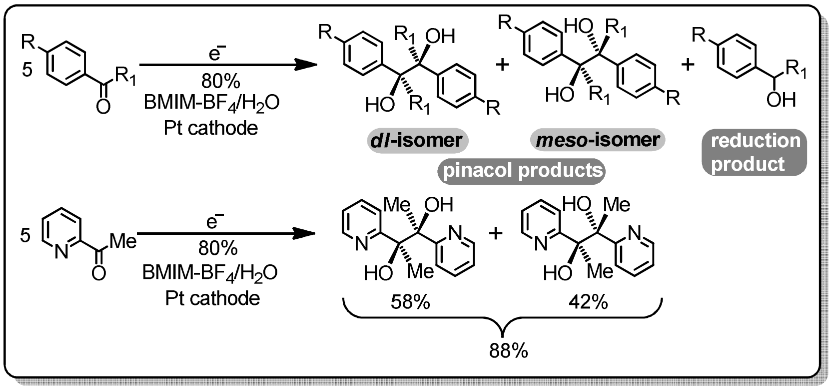


**Scheme 8** Mechanism for the formation of pinacol products in BMIM-$BF_4$.[63]

It was proposed that the imidazolium cation stabilizes the anion radical formed by the electro-reduction of aldehydes/ketones. The facial orientation of the intermediates defines the formation of d/l or meso isomer as described by Lagrost and co-workers report (Scheme 8).[61-62] Wide range of aromatic aldehydes were screened for their effectiveness and it was shown that electron rich benzaldehydes showed better conversion (>90%) whereas halobenzaldehydes resulted in moderate yields (~50%) [Scheme 9].



**Scheme 9** Electrochemical Pinacol coupling of aldehydes[63]



**Scheme 10** Electrochemical Pinacol coupling of ketones[63]

In the case of aromatic ketones, pinacol products were obtained in high yields with low to moderate diastereoselectivity. Electron rich aromatic ketones showed better conversion (>90%), halo aromatic ketones gave moderate yields (~50%) and bulky isobutyrophenone and benzophenone gave the reduced products (Scheme 10).

### c) Electrochemical reduction of $CO_2$ in Ionic Liquid medium

$CO_2$ is one of the most abundant greenhouse gas that was widely linked to global warming.[64] As a consequence, the removal of $CO_2$ from the atmosphere and even more desirably converting it into useful chemicals is of great environmental importance. However, the limited known reactivity of $CO_2$ poses a difficult challenge from the chemical perspective. Researchers have used chemical,[65] photochemical and electrochemical methods for the reduction of $CO_2$ to obtain useful products such as hydrocarbons, alcohols or fuels. Among these, electrochemical reduction of $CO_2$ is an interesting and attractive technique due to its simple procedure and ambient operation conditions. It is noteworthy that the electrochemical $CO_2$ reduction is highly substrate (catalyst or electrode material) and solvent specific. Thus screening of various catalysts and solvents for the utilisation of $CO_2$ played a pivotal role. In this scenario, electrochemical reduction of $CO_2$ plays an important role as this technique proves out to be cheaper, eco-friendly and involves user friendly operation. Primarily there are two pathways for the electrochemical utilisation of $CO_2$,

i) direct electrochemical reduction of $CO_2$ to obtain hydrocarbons, carboxylic acids, alcohols or fuels,[66]

Ex. Formic acid was electrochemically synthesized by the reduction of $CO_2$ on a pre-anodised Pt microelectrode.[67] RTILs EMIM-$NTf_2$ and $C_4$mpyrr-$NTf_2$ were used in the presence of a proton source. If the Pt microelectrode was not pre-anodised, an irreversible wave was observed corresponding to the $H_2$ evolution.

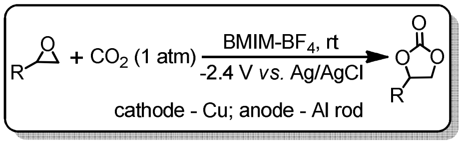
ii) coupling of $CO_2$ to electrochemically reduced organic molecules to synthesize chemicals that are interesting from the organic/pharmaceutical point of view.

Ex: In early 1970's, Weinberg et al reported the electrochemical reduction carboxylation of benzaniline in molten tetraethylammonium p-toluenesulfonate.[68] Benzaniline's imine derivative was carboxylated under electrochemical conditions to obtain α-amino acid in 60% yield.

Electrochemical $CO_2$ reduction in ionic liquids has several advantages such as low volatility and high solubility of $CO_2$ compared to other gases in RTILs.[69-71] Carbon-di-oxide can also be directly reduced in many RTILs to form the $CO_2^{\bullet-}$ radical anion via a single electron reduction, that is extensively stabilised by the cation of the RTIL. Additionally, many conventional $CO_2$ reduction techniques require high pressures of $CO_2$. The increased selectivity combined with the high $CO_2$ solubility in RTILs[72] has therefore provided attractive possibilities for $CO_2$ transformation by electrochemical reduction and co-reaction.[36] This includes the synthesis of organic products such as cyclic carbonates, carboxylates, carbamates and dimethyl carbonate, etc.[73-78] Apart from these, aromatic carboxylic acids were directly synthesized from their corresponding bromo precursors using Ag electrode.[38, 79]

**i) Synthesis of cyclic carbonates and dialkyl carbonates**

Organic carbonates are an important class of compounds that finds use as solvents in many industrial applications.[80-81] Though their biodegradability and low ecotoxicity are advantageous, the industrial synthesis of organic carbonates relies on the use of phosgene or propyleneoxide reagents which are toxic.[81] In this aspect, fixation of $CO_2$ to cyclic carbonates or alcohols by chemical or electrochemical methods becomes attractive.[77, 82-84] Shi and co-workers reported the electrochemical activation of $CO_2$ in RTILs and synthesis of cyclic carbonates by the electro catalytic cycloaddition of $CO_2$ to epoxides under mild conditions (Scheme 11).[85] Cu cathode and Mg or Al were used as sacrificial anodes, no change in selectivity or conversion was observed while using Mg or Al suggesting that the sacrificial anode does not play a role. On the other hand, the nature of RTIL was shown to play an important role in conversion. With BMIM-$BF_4$ as the solvent and electrolyte excellent conversion and selectivity was achieved. Good to excellent yields were obtained for the conversion of propylene oxide and styrene oxide, however moderate conversion was observed in the case of epichlorohydrin (Scheme 11).



**Scheme 11** Synthesis of cyclic carbonates[85]

Lu and co-workers reported the electrochemical synthesis of dialkyl carbonates from $CO_2$ and alcohols under mild conditions.[77] $CO_2$ saturated RTIL was prepared and subjected to cathodic reduction to generate $CO_2^{\cdot -}$ radical which was then reacted with alcohol in the presence of an alkylating agent to give the corresponding dialkyl carbonate (Scheme 12). Authors screened various cathodic materials such as Cu, Ti, Ag, Ni and SS for this conversion and found that Cu is very efficient. Various alcohols were screened and it was shown that primary alcohols showed better conversion than secondary alcohols, whereas tertiary alcohols and phenols were unreactive.

$$\mathrm{ROH} + \mathrm{CO_2} \xrightarrow[\text{2) R'I}]{\text{BMIM-BF}_4\ \text{1) e}^-} \mathrm{ROCO_2R'}$$

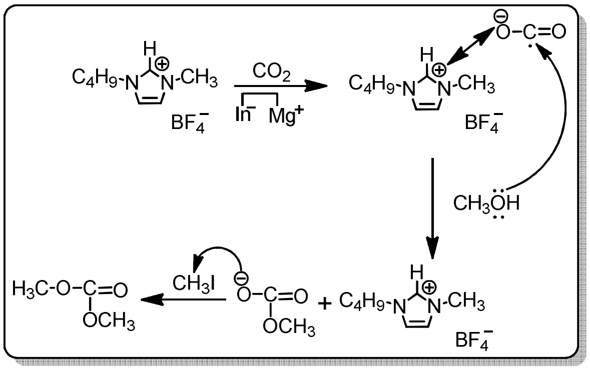
Cu cathode; Mg anode

**Scheme 12** Synthesis of dialkylcarbonates.[77]

Authors further tried the electrochemical activation of $CO_2$ and coupling with diols to form cyclic carbonates, however poor yields were obtained (12%) on Ni cathode and Mg anode at 50° C in BMIM-$BF_4$ ionic liquid.[75]

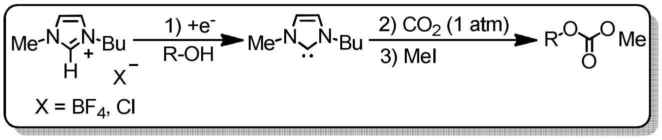
Dimethylcarbonate was electrochemically synthesized by electrochemical activation of $CO_2$ in a mixture of $CH_3OK$-$CH_3OH$-BMIM-Br ionic liquid.[86] Although various ionic liquid systems were screened, BMIM-Br in this case was shown to be effective. $CH_3OK$ played the role of co-catalyst, BMIM-Br ionic liquid as the supporting electrolyte. It was noteworthy that the co-catalyst $CH_3OK$ promotes the double electron reduction of $CO_2$, as seen from the increased current density. Effect of reaction temperature, time and influence of various anions of BMIM counterpart using platinum electrodes were evaluated. Although higher selectivity for the formation of DMC was achieved, reported yield was very very poor (~4%).

Bu and co-workers evaluated the reduction of $CO_2$ on Indium electrode in BMIM-$BF_4$ using MeOH and alkylating agent.[87] Authors suggested that $CO_2$ is activated on the In electrode surface by weak adsorption (Scheme 13). $CO_2^{\cdot-}$ thus formed on the electrode surface was stabilised by $BMIM^+$ through ion-pair formation. The anion radical then couples with MeOH to form $CH_3OCOO^{\cdot-}$ which then reacts with the alkylating agent to form the corresponding dialkyl carbonate in good yields. Recently, Cai and co-workers reported the electrochemical conversion of $CO_2$ to dimethyl carbonate on graphite electrode using amino functionalized ionic liquids as an electrolyte and co-catalyst.[88]



**Scheme 13** Mechanism of dimethyl carbonate formation[87]

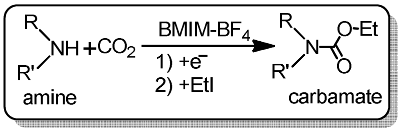
The dual role of RTIL as a green solvent and NHC precursor was explored by Lu and co-workers (Scheme 14).[89] 1 mmol alcohol was taken in 5 mL RTIL (BMIM-$BF_4$) and the solution was electrolyzed under galvanostatic conditions in $N_2$ atmosphere at 40°C. To this solution $CO_2$ was bubbled for 2 hr after which the alkylating agent (MeI) and the base ($K_2CO_3$) were added at 50°C and stirred for 5 h. Cathodic materials such as Ni, SS, Cu, Pt and Ti were scanned and Pt spiral wire was used as anode. Among all Ti as cathode showed better conversion and selectivity for the synthesis of dialkyl carbonates from $CO_2$ and alcohols. Primary alcohols showed better selectivity and conversion, secondary alcohols showed excellent selectivity but moderate conversion whereas tertiary alcohols and phenols remained unreactive.



**Scheme 14** Synthesis of dialkyl carbonates via electro generated NHCs[89]

### ii) Synthesis of Carbamates

Carbamates are organic compounds, derived from carbamic acid that finds applications as protecting groups for amino compounds, as preservatives, cosmetics and medicine.[90-91] Carbamates are generally synthesized by phosgenation technique, through rearrangement reactions, and from $CO_2$ electrochemical reduction and coupling with amines.[92-93] Among these electrochemical reduction of $CO_2$ and coupling with amines can be regarded as a green technique as the chemical methods involves toxic reagents. Electrochemical procedure for the synthesis of organic carbamates from amines and $CO_2$ by selective cathodic reduction of $CO_2$ in RTIL (BMIM-$BF_4$) under mild conditions was reported by Inesi and co-workers (Scheme 15).[74] The reactivity of aliphatic and aromatic amines were studied in electrolyzed $CO_2$-saturated RTIL solution. Synthesis was carried out in RTIL by cathodic activation of $CO_2$ at 55°C, 1 atm pressure of $CO_2$ in a divided glass cell set up. Carbamates were isolated in good to high yields on a Pt cathode, although Cu and Ni were evaluated under similar conditions, Pt showed better conversion giving the desired product in good yields. Substituted primary and secondary aliphatic amines resulted in good yields (~80%) whereas aniline gave only moderate yield (38%), however 4-chlorosubstituted aniline showed best conversion (76%). The electrochemical method illustrated here for the synthesis of carbamates is eco-friendly and greener compared to conventional chemical methods where toxic reagents or sophisticated catalysts were used.

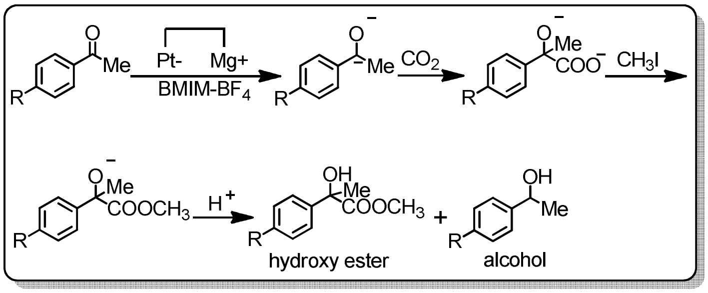


**Scheme 15** Electrochemical synthesis of Carbamates[74]

**d) Electrocarboxylation**

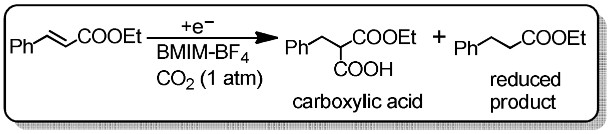
In the previous subsections, electrochemically reduced $CO_2$ was coupled to alcohols or amines to yield carbonates or carbamates. In electrocarboxylation, radical/anion generated by the electrochemical reduction of alkyl/aryl halides or carbonyls was coupled to $CO_2$ to yield the corresponding carboxylate derivative. Electrocarboxylation of benzyl chloride to phenylacetic acid at Ag cathode in $CO_2$ saturated BMIM-$BF_4$ was reported by Lu and co-workers.[79] Benzyl chloride was reduced to benzyl radical which was then coupled to $CO_2$ to yield the corresponding carboxylic acid, Ag-cathode/Mg-anode system at 50°C gave the best yield (45%). To some extent, homocoupled 1,2-biphenyl ethane was observed (12%). Mechanistic investigation on the electrocarboxylation of acetophenone in RTIL was recently reported by Zhao et al.[73] Although not much synthesis was reported in the work, a detailed mechanistic investigation of the influence of various parameters for the formation of α-hydroxy carboxylic acid was examined. Similarly Takahashi and co-workers reported the carboxylation of α-chloroethylbenzene in DEME-TFSI (N,N-Diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide ionic liquid compressed with $CO_2$.[94] Pt cathode and Mg anode were used, the experiments were conducted at different temperature and pressure, and however the carboxylic acids were obtained in poor yields (<20%). Very recently, an improved yield (~50%) for this reaction using supercritical $CO_2$ in DEME-TFSI ionic liquid was reported by Atobe and co-workers.[95] Similar conditions were applied to wide range of halo aromatics (bromo benzene, iodo benzene, chloro naphthalene, bromo naphthalene and iodo naphthalene) and moderate yields were reported.

Liu and co-workers performed electrochemical carboxylation of aromatic ketones in BMIM-$BF_4$ ionic liquid in an undivided cell under mild conditions (Scheme 16).[96] The influence of temperature, current density, charge passed, and electrode material and substrate concentration on the yields were systematically investigated. Pt as cathode and Mg as anode resulted in the best yield under optimized conditions, nevertheless the reported yields were only moderate (~50%).



**Scheme 16** Electrocarboxylation of aromatic ketones[96]

Electrocarboxylation of activated olefins using SS cathode, Mg anode in RTIL was reported by Lu and co-workers (Scheme 17).[97] As evident from Scheme 17, the obtained products were a mixture of monocarboxylic acid and hydrogenated product. Monocarboxylic acids were obtained in moderate yields (35-55%). However, the method turns out to be green and easier, as at the end of the reaction, both monocarboxylic acid and hydrogenated ester were purified by simple column chromatography. In conventional organic synthesis, BuLi or Grignard or cyanide reagents are needed to carry out such conversion and all these reactions needs dry solvents and inert conditions.



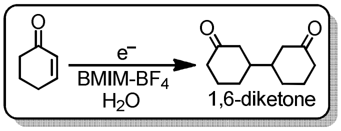
**Scheme 17** Electrocarboxylation of activated olefins[97]

### e) Synthesis of Aryl zinc compounds

Aryl zinc compound was successfully synthesized by Compton and co-workers by the electrochemical reduction of 1-bromo-4-nitrobenzene at zinc electrode in $C_4$mPyrr-$NTf_2$ ionic liquid.[98] Upon reduction, p-$BrC_6H_4NO_2$ forms a radical anion which then reacts with the Zn electrode to form aryl zinc product under vacuum. This mechanism was cross checked by introducing $CO_2$ gas into the system which led to the formation of 4-nitrobenzoic acid. $CO_2$ traps aryl zinc species to form deprotonated 4-nitrobenzoic acid and $Zn^{2+}$. This method sets an example for the synthesis of aryl zinc intermediates, a key compound for the synthesis of variety of substituted aromatics.

### f) Synthesis of 1,6-diketones from unsaturated ketone

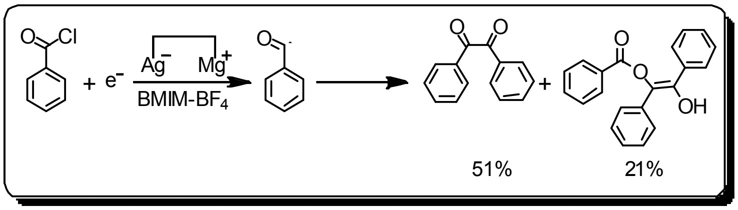
1,6-diketone (1,1'-bicyclohexyl)-3,3'-dione was synthesized by the electrochemical reductive coupling of 2-cyclohexen-1-one in BMIM-$BF_4$-$H_2O$ mixture (Scheme 18).[99] The electrochemical reduction selectively gave the regioselective product 1,6-diketone formed by the -C-C- coupling at the β-carbon in 90% yield. Effect of co-solvent on product conversion was studied systematically and it was found that 30% volume of $H_2O$ gave the best yields, suggesting that viscosity plays a critical role. Authors suggested that the cation of the ionic liquid and the formed anion radical results in an ion-pair and this interaction stabilises the intermediate (Scheme 18). The resonance stabilization of the radical favors coupling at the β-carbon.



**Scheme 18** Reaction mechanism for the reductive coupling of 2-cyclohexen-1-one in BMIM-$BF_4$/$H_2O$, $C_3$-$C_3$ coupling in 2-cyclohexen-1-one[99]

### g) Synthesis of benzil from benzoyl chloride

Benzil was synthesized electrochemically by the reduction of benzoyl chloride in BMIM-$BF_4$in an undivided cell set up using Ag cathode and Mg anode (Scheme 19).[100] The yield obtained under optimized condition was moderate (51%) and this was attributed to the formation of several intermediates from the electro generated anion radical. Electrochemically formed radical anion by the reduction of benzoyl chloride dimerizes to form benzil. In an additional step, it combines with another benzoyl chloride and this substantially reduces the dimer ratio (benzil). It is pretty much evident that the use of a divided cell set up for the formation of benzil in this case might not have a great influence on the yield.

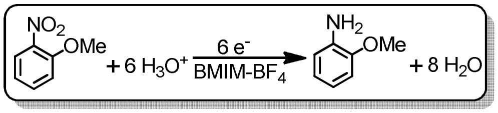


**Scheme 19** Mechanism of formation of Benzil from Benzoyl chloride.[100]

Compton and co-workers accounted the electrochemical reduction of $H^+$ and hydrogenation of –C=C– bonds in RTIL on a Pd microelectrode.[101] It was found that the electrode was in a passivated state in the beginning and pre-anodisation lead to a dramatic change. This triggered the change from hydrogen evolution to absorption. This study was only a mechanistic investigation for such an observation which was supported by a theoretical modelling.

Mechanistic investigation on the electrochemical reduction of nitrobenzene and 4-nitrophenol in BDMIM-$NTf_2$ IL showed the pathways for the formation of nitroso benzene, phenyl hydroxyl amine and azoxy benzene in aprotic media.[102]

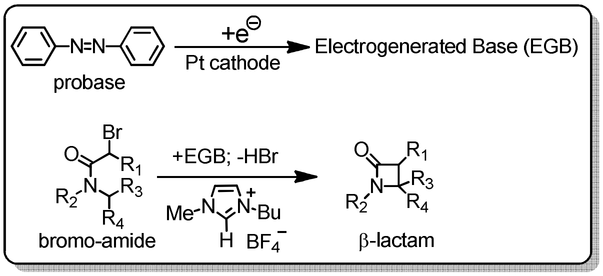
2-Anisidine was synthesised by the electrochemical reduction of 2-Nitroanisole in BMIM-$BF_4$ on a Cu-graphite couple electrodes under potentiostatic electrolysis at -1 V *vs.* SCE (Scheme 20).[103] Influence of various parameters such as applied potential, anode material, temperature, substrate concentration, amount of water, etc. were screened. Best yields obtained under optimized conditions were 41% (graphite anode) and 53% (plating Ru) at 50°C.



**Scheme 20** Reduction of 2-nitroanisole to 2-Anisidine.[103]

**h) Organocatalysis using electro generated bases**

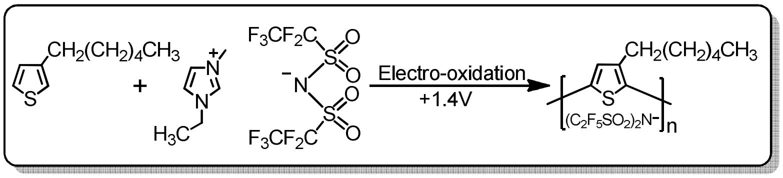
Cyclization of bromo amides to β-lactams can be facilitated by nucleophilic bases. Nucleophilic bases can be generated electrochemically by reducing probase such as 1,2-diphenyl-diazine and these electro generated base can facilitate the cyclization of bromoamides to β-lactams in RTIL as shown by Inesi and co-workers (Scheme 21).[104] Electro generated base deprotonates C4-proton generating a C4 carbanion, subsequent intramolecular nucleophilic substitution (C3-C4 bond formation) leads to the formation of β-lactams in good to excellent yields in RTILs. Diesters at C4 carbon gave better yields due to the enhanced acidity of the C4-proton.



**Scheme 21** Electro synthesis of β-lactams via electro generated base.[104]

## 4. Electrochemical Polymerization reactions in Ionic Liquid media

Electro polymerizations in ILs are highly explored by different research groups. Several reports are available on the electro synthesis and applications of poly(o-phenylenediamine)s,[105-106] poly(paraphenylene)s[107-108] polyaniline composites,[109-110] poly(3-alkyl) and poly(3-halo) substituted thiophenes in RTILs.[111-113] Butt and co-workers reported the direct electro polymerization of poly(3-hexylthiophene) on platinum coated flat silicon surfaces in hydrophobic ionic liquid media for Organic Field Effect Transistor applications (Scheme 22).[114] 3-hexylthiophene was taken in BMIM-TFSI or EMIM-PFSI [1-Ethyl-3-methylimidazolium bis(perfluoro-ethylsulfonyl)imide] hydrophobic ionic liquid and polymerized electrochemically (potentiostatic) at +1.4V using a three electrode set up (platinized substrate as working electrode, platinum rod as the counter electrode and Ag/AgCl as the reference electrode). Here, RTIL acts both as a dopant and an electrolyte.



**Scheme 22** Electro polymerization of 3-hexylthiophene in EMIM-PFSI IL[114]

Electrochemical homopolymerization of 3-chlorothiophene and copolymerization with 3-methylthiophene in BMIM-$PF_6$ using potentiostatic and galvanostatic methods was reported by Jin and co-workers.[115] Both homopolymer(PClT) and copolymer P(ClT-co-MeT) were characterized by cyclic voltammetry (CV), Fourier transform infrared spectroscopy (FTIR), spectroelectrochemical analysis and kinetic study in BMIM-$PF_6$ ionic liquid. Homopolymer revealed color changes between deep red and deep blue, whereas copolymer showed the most vivid change of color between bright red and greenish blue in fully reduced and oxidized states under spectroelectrochemical conditions. This work demonstrates that BMIM-$PF_6$ acts as an electrolyte, solvent and a medium for the characterisation of polymer films. Later, authors reported the electrochemical synthesis of poly(3-alkylthiophene) in BMIM-$PF_6$ and its application as electrochromic device.[116-117] 3-octylthiophene was electro polymerized on an ITO coated glass, ITO coated glass was used as the working electrode, Pt as the counter and Ag/AgCl or standard calomel electrode as the reference electrode. The so formed polymer film was characterized by spectroelectrochemistry and an ECD (ElectroChromic Device) setup was fabricated with the polymer film to screen for its efficiency as electrochromic device.

3-(4-fluorophenyl) thiophene (FPT) was electrochemically polymerized to PFPT on a platinum electrode in pure 1-ethyl- 2,3-dimethylimidazolium bis ((trifluoromethyl)sulfonyl) amide, EDMITFSI, and 1,3-diethyl-5-methylimidazolium bis ((trifluoromethyl)sulfonyl) amide, DEMITFSI ionic liquids by Belanger and co-workers.[118] PFPT loses its electroactivity upon cycling in pure ionic liquid and authors attributed such observation to the gradual deswelling of the polymer.

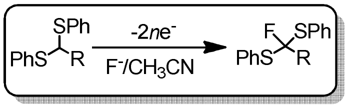
Ivaska and co-workers reported the electrochemical synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) in room-temperature ionic liquids with smaller inorganic anions, BMIM-$BF_4$, BMIM-$PF_6$ and bulky organic anions (BMIM) diethylene glycol monomethyl ether sulfate ($MDEGSO_4$) and BMIM octyl sulfate ($OctSO_4$) (solid at RT). Synthesized polymer films were characterized by CV and UV-Vis spectroelectrochemistry using RTIL as the solvent.[119-120] Zhu and co-workers electrochemically synthesized PEDOT in $BMIMBF_4$ ionic liquid for supercapacitor applications.[112] Snook and co-workers formed a superior porous layer with greater chargeability by co-depositing two different conducting polymers polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) in 1-butyl-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide $C_4$mpyrr-TFSI ionic liquid.[121] Electroco-deposited layers in RTIL showed enhanced morphology and higher ionic transport within the film. Very recently Nie and co-workers reported the use of BMIM-$BF_4$ as an initiator for the electro-induced cationic Polymerization of vinyl ethers.[122]

## 5. Electrochemical Partial Fluorination in Ionic Liquid media

Fluoro organics constitute an important class of organic compounds that finds use in the fields of agriculture, pharmaceuticals, materials science, etc. Syntheses of fluorinated compounds similar to other halogenated compounds are quite tedious. Fluorination of organic molecules needs special fluorinating reagents and conditions, most often these reagents are hazardous, toxic and highly corrosive. On the other hand, selective electrochemical fluorination or partial fluorination of organic compounds by electrochemical methods using $Et_3N.nHF$ or $Et_4NF.nHF$ were regarded to be green and eco-friendly as it employs mild and safe conditions. Initially $Et_3N.nHF$ and $Et_4NF.nHF$ were called as adducts, and since the mid of last decade, they were classified as ionic liquids. In electrochemical methods, often it was difficult to achieve product selectivity, as minor amounts of undesired products were also formed. Moreover, product selectivity depends on the applied potential/charge density and it varies based on the electrochemical method used (galvanostatic or potentiostatic) and other variables. Effect of substituents, operating conditions, solvents and additives on anodic fluorination were extensively studied in detail and reported.[123-126] Pioneering work on electrochemical fluorination was done by Fuchigami and co-workers. Reviews addressing on the electrochemical per fluorination or partial fluorination have already been published.[127-131] Herein, we discuss on the recent developments in this area.

### a) Selective ECF of dithioacetal derivatives

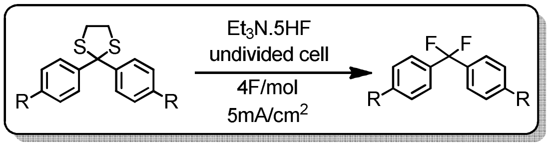
Very recently regioselective anodic fluorination of ethyl α,α- bis(phenylthio)acetate and its derivatives using $Et_3N{\cdot}nHF$ and $Et_4NF{\cdot}nHF$ (n = 3–5) to provide α-fluoro and/or fluorodesulfurization products was reported by Fuchigami and co-workers (Scheme 23).[132] It was noticed that the product selectivity depends on the substituents and supporting electrolyte used. Dithioacetal bearing strong electron withdrawing groups such as nitrile predominantly gave α-fluorinated product irrespective of the HF ionic liquid used, whereas the one with weak electron withdrawing group such as amide gave the fluorodesulfurization product.



**Scheme 23** Selective electrochemical fluorination of dithioacetal derivatives [132]

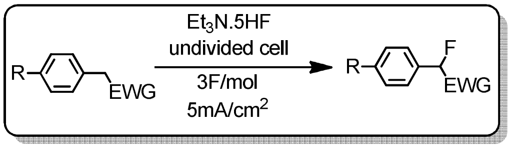
### b) Electrochemical fluorination using mediators

Anode passivation is a major problem in anodic fluorination as they form non-conducting polymer film on the anode surface which is then no longer electro active. This could be overcome by using mediators which enhances the reaction efficiency by fast electron transfer. Fuchigami et al demonstrated the use of different mediators that enhanced the formation of fluorinated products compared to direct selective electrochemical fluorination (Scheme 24). Mediators such as tetraalkylammonium halide salts,[133] polymer supported (difluoro)iodo benzene,[134] iodobenzene tagged ionic liquid,[135] and triphenylamine based ionic tags[136] were scanned for their effectiveness in anodic fluorination. Pathways for such catalysis were proposed by authors. Mediators were known to enhance the yield percentage compared to the yields obtained from the direct electrochemical selective fluorination without mediators. Fluorodesulfurized products were obtained in excellent yields and selectivity.



**Scheme 24** Mediator catalyzed anodic fluorodesulfurization

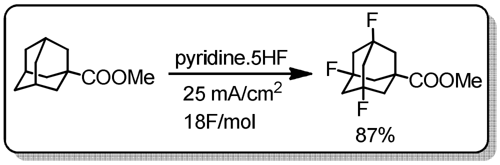
Similarly α-fluorination of substituted benzylic compounds bearing electron withdrawing groups was investigated (Scheme 25).[133,134,135] Use of mediators enhanced the yield of α-fluorinated product yield of substituted esters, nitriles and xanthate esters. At the end of the reaction, mediators were recycled and reused.



**Scheme 25** α-fluorination of substituted benzylic esters and nitriles[a]

### c) Synthesis of methyl-3,5,7-trifluoroadamantane-1-carboxylate

Monoi et al performed the anodic fluorination of methyl adamantane-1-carboxylate in pyridine–5HF under galvanostatic conditions, methyl-3,5,7-trifluoroadamantane-1-carboxylate was obtained in good yields (Scheme 26).[137]

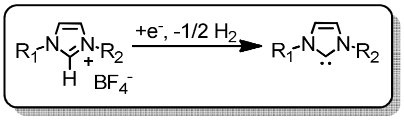


**Scheme 26** Synthesis of Fluoroadamantanes[137]

## 6. Miscellaneous Electrochemical reactions in Ionic Liquid media

### a) Organocatalysis by Electro generated NHCs

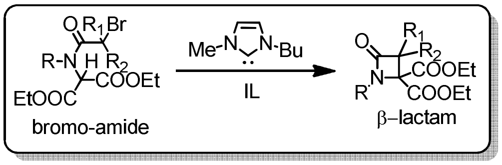
N-Heterocyclic carbenes are an intriguing class of carbon-containing compounds and one of the most investigated reactive species in the area of organic chemistry. They are neutral compounds that possess a divalent carbon atom with sextet of electrons. First investigation on the reactivity and stability of NHCs was made by Wanzlick in early 1960's and he reported on their application as ligands for metal complexes. However, NHCs remained unattracted for almost two decades until the discovery of the first stable, isolable and storable NHC by Arduengo et al in 1991. NHCs are synthesized by deprotonating the corresponding azolium salts such as imidazolinium, imidazolium, thiazolium, oxazolium, triazolium, pyrazolium and benzimidazolium. They can also be electrochemically synthesized by reducing the corresponding azolium salts (azolium ionic liquids) as shown by Gorodetsky et al (Scheme 27).[138] Imidazolium based ionic liquids are the largely investigated ionic liquid system in electrochemistry. Hence, the dual role of imidazolium ionic liquids as solvent and organocatalyst was extensively studied by several groups.[139-140] Pioneering work in this area was done by Inesi and co-workers.



**Scheme 27** Electrochemical reduction of Imidazolium IL to Carbene[138]

### i) Synthesis of β–lactams

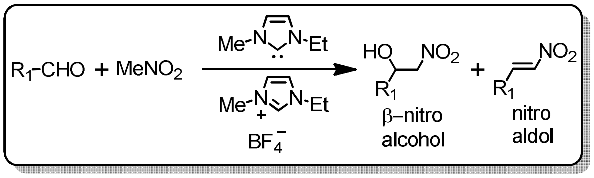
Similar to their work on the synthesis of β-lactams using electro generated base,[104] Feroci et al utilised electro generated NHCs as a base for the formation of β-lactams in BMIM-$BF_4$ IL (Scheme 28).[141] NHC was strong enough to deprotonate the proton at C4 carbon and the intramolecular cyclization lead to the formation of β-lactams in excellent yields. Cathodes such as Pt, Ti, Cu, Al and C and ionic liquids such as BMIM-$BF_4$, BMIM-$PF_6$, and BMIM-$MeSO_4$ were screened. The best yield was obtained with Pt cathode in BMIM-$BF_4$ medium.



**Scheme 28** Synthesis of β-lactams from bromamides catalyzed by electro generated NHC[141]

### ii) Henry Reaction

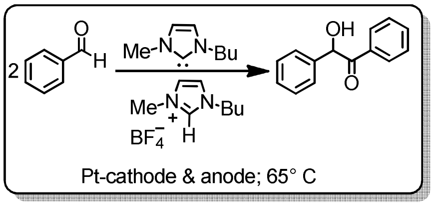
Henry reaction also called Nitro aldol reaction is a base catalyzed C-C bond forming reaction between nitroalkanes and aldehydes or ketones. Electro generated imidazolium based NHCs are stable nucleophiles/bases which can catalyze Henry reaction. Inesi and co-workers demonstrated the ability of electro generated NHCs towards the conversion of nitroalkanes to β-nitroalcohols under mild conditions in a very high yield (Scheme 29).[142] It was found that the yield and selectivity of β-nitroalcohols *vs.* nitroaldol condensation was highly affected by the concentration of NHCs, nature of RTIL and reaction time, however under optimized conditions, excellent yields were reported for β-nitroalcohols.



**Scheme 29** Electro generated NHC catalyzed Henry reaction in Ionic liquid.[142]

### iii) Benzoin Condensation

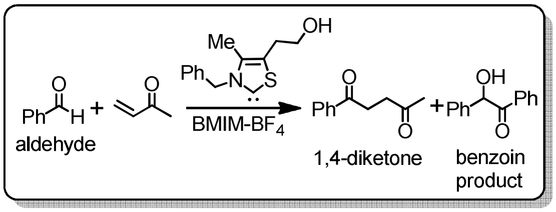
N-heterocyclic carbenes are very good nucleophiles that can catalyze variety of organic reactions. Inesi and co-workers used electro generated NHCs to catalyze benzoin condensation reaction in RTILs[143] and VOCs,[144] here we restrict our focus to the report in RTILs (Scheme 30).[143] A catalytic amount of carbene (20% with respect to benzaldehyde) was electrochemically generated to obtain benzoin in good yields (85%) in BMIM-$BF_4$ within 2 h.[143] Ionic liquids such as BMIM-$BF_4$, BMIM-$PF_6$, BMIM-$MeSO_4$ and BnMIM-$BF_4$ were screened, but best yields were obtained with BMIM-$BF_4$ and BnMIM-$BF_4$. Side product, i.e., the over reacted benzoin product was only observed at higher temperature (100° C) or when the reaction was let for longer time (20 h).



**Scheme 30** Electro generated NHC catalyzed benzoin condensation[143]

### iv) Stetter reaction

Stetter reaction is a 1,4-conjugate addition reaction of an aldehyde to an α,β-unsaturated compound which is generally catalyzed by a cyanide or a thiazolium salt. In the case of thiazolium salt catalyzed Stetter reactions, base such as $Et_3N$ or $K_2CO_3$ were used as a deprotonating agent. As a result, N-heterocyclic carbene is formed in situ and it mediates the C-C bond formation between the aldehyde and α,β-unsaturated compound by an umpolung mechanism. In a typical experimental setup, Inesi and co-workers electrochemically formed thiazolium-2-ylidenes (NHC) from the corresponding thiazolium salt [3-benzyl-5-(2-hydroxy ethyl)-4-methylthiazolium chloride or 3-ethyl-5-(2-hydroxyethyl)-4-methyl thiazolium chloride] (Scheme 31).[145] NHC was generated by bulk electrolysis under galvanostatic conditions at 65° C in VOCs (DMF, DMSO and $CH_3CN$) and BMIM-$BF_4$ ionic liquid. At the end of the electrolysis, aldehyde and excess of α,β-unsaturated compound were added, stirred for 2 h at 65° C and for 12 h at RT. The aldehyde first forms a carbene adduct which then undergoes 1,4 addition with α,β-unsaturated compound to yield 1,4-diketone or aldehyde to form the benzoin product. Surprisingly, benzoin products were formed in large amounts in comparison to 1,4-diketones in BMIM-$BF_4$ ionic liquid.



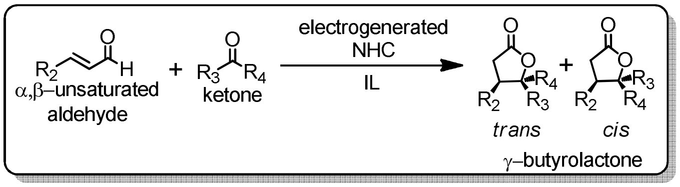
**Scheme 31** Electrochemical synthesis of 1,4-dicarbonyl compounds by electrolyses of thiazolium salt in BMIM-$BF_4$[145]

### v) Staudinger Reaction

Staudinger reaction is a [2 + 2] cycloaddition of imine to ketene that leads to the formation of β-lactam. Electro generated imidazolium based NHCs were used as an organocatalyst and a base in Staudinger synthesis for the formation of β-lactam from an acyl chloride and a deactivated imine in ionic liquids.[146] BMIM-$BF_4$ was electrolyzed galvanostatically using Pt cathode and anode at 60° C, to this solution, acyl chloride and deactivated imine were added and stirred for 2 h. Yields obtained under optimized conditions were around 60% and the selectivity of trans product formation was 90% as determined by $^1$H NMR. Later, the effect of temperature, substituents, presence of an external base was evaluated by Feroci and a tentative mechanism for the Staudinger synthesis in a very polar medium like ionic liquid was reported. The yields of isolated β-lactams were good and predominantly *trans* lactams were obtained with a good diastereomeric ratio.[147] The reactivity of electro generated imidazolium based NHCs towards alkylation and acylation reactions, in the synthesis of β-lactams, in Henry reaction, in the synthesis of thiones, and in benzoin condensation were carefully evaluated by Inesi and co-workers.[148] It was shown that NHCs are quite a strong base with a pKa of about 22 and a good nucleophile that could catalyze many organic reactions.

### vi) Synthesis of γ-butyrolactones

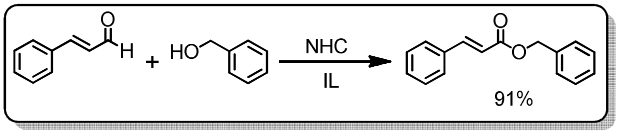
Electro generated NHCs were known to play a dual role as pre-catalysts and as solvent in the conjugate umpolung of α,β-unsaturated aldehydes to obtain cross-annulated γ-butyrolactones.[149] In a typical experiment, BMIM-$BF_4$ was electrolyzed and to this solution α,β-unsaturated aldehyde and ketone were added. Experiments were conducted in molecular solvents such as DMSO, $CH_3CN$ and DMF along with ionic liquids BMIM-$BF_4$, DMIM-$BF_4$, EMIM-$BF_4$ and BnMIM-$BF_4$. Best yields were obtained with BMIM$BF_4$ and BnMIM$BF_4$ ionic liquids at 80°C in 2 h (Scheme 32). It was found that the reaction in molecular solvents resulted in the formation of self-annulated γ-butyrolactones and lower yields were obtained for the desired cross-annulated γ-butyrolactones. In all these cases, both cis and trans products (predominant) are formed irrespective of the conditions used and they were purified by simple column chromatography. The advantage of these reactions in ILs were the reusability and short reaction time (2 h) whereas similar NHC catalysed reactions in molecular solvents took longer time for completion (16 h).[150-152]



**Scheme 32** Synthesis of γ-butyrolactones by electro generated NHCs in ILs[149]

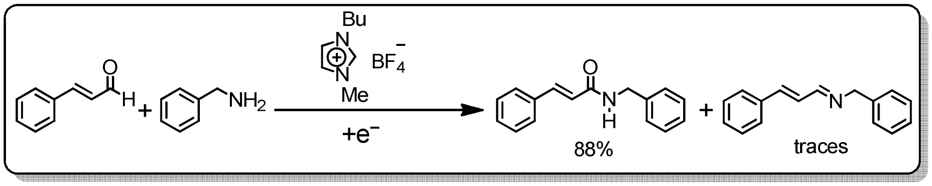
### vii) Esterification and internal redox amidation of α,β-unsaturated aldehydes

α,β-unsaturated aldehydes were esterified to saturated esters through umpolung reactions catalysed by electro generated NHCs in RTILs (Scheme 33).[153] Moderate to excellent yields were reported in RTILs. Formation of ester was affected by several factors such as mole ratio of aldehyde to alcohols, charge density, nature of IL used, etc. Wide range of α,β-unsaturated aldehydes and range of substituted cyclic, acyclic and benzylic alcohols were tested for their efficacies, esterified products were obtained in good to excellent yields (50-91%).



**Scheme 33** Esterification of α,β-unsaturated aldehydes[153]

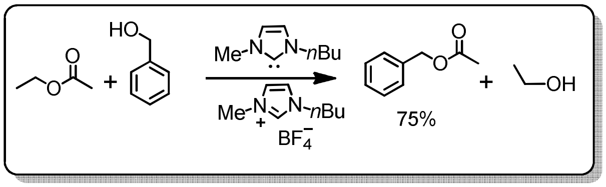
Similarly, α,β-unsaturated aldehydes and amines were converted to amides in very good yields in an amidation reaction catalyzed by electro generated NHCs (Scheme 34).[154] The selectivity of amidation to the imine formation was related to the molar ratio of electro generated NHC to aldehyde. Wide range of primary and secondary amines were tested for their efficacy with substituted α,β-unsaturated aldehydes, amides were obtained in moderate to good yields (50-88%).



**Scheme 34** Internal redox amidation[154]

### viii) Transesterification

Electro generated imidazolium based NHCs were used as a catalyst for transesterification reactions (Scheme 35).[155] NHCs were able to assist proton transfer from alcohol to ester efficiently. Wide range of substituted benzylic alcohols, alkanols and vinyl alcohols were transesterified by electro generated NHCs in ILs, moderate to very high yields were reported for the transesterified products. Mechanism for the electro generated NHC catalysed transesterification reaction was proposed by Inesi and co-workers.

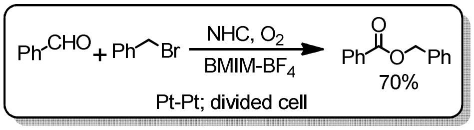


**Scheme 35** NHC-catalyzed transesterification reaction[a] of ester in BMIMBF$_4$[155]

[a] General conditions: divided cell; Pt electrodes, 60° C.

### ix) Oxidative esterification of aromatic aldehydes

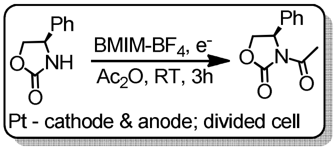
Aldehydes were successfully esterified with alkyl/benzyl halides by oxidative esterification catalyzed by electro generated imidazolium based NHCs (Scheme 36).[156] Two different pathways were proposed to explain the product formation. Wide range of aldehydes were oxidatively esterified by electro generated NHCs in RTILs and moderate to excellent yields were obtained under optimized conditions.



**Scheme 36** Mechanism of Oxidative esterification of aldehydes[156]

### x) *N*-acylation of chiral oxazolidin-2-ones

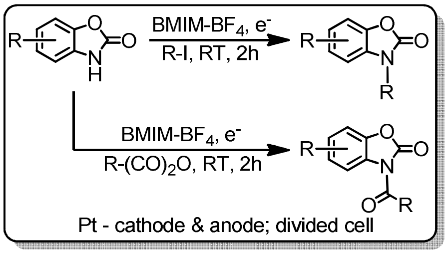
Chiral oxazolidin-2-ones were N-acylated in BMIM-BF$_4$ IL media using electrogenerated NHC as a base (Scheme 37).[157] BMIM-BF$_4$ solution containing oxazolidin-2-ones were electrolyzed under galvanostatic conditions using Pt-Pt electrode system. To this electrolyzed solution, saturated or unsaturated anhydride was added. Wide range of substituted chiral oxazolidin-2-ones and saturated or unsaturated anhydrides were tested for their efficacies. N-acylated products were isolated in good to elevated yields with total retention of the absolute configuration.



**Scheme 37** N-acylation of chiral oxazolidin-2-ones[157]

### xi) N-functionalization of benzoxazolones

Benzoxazol-*2(3H)*-ones were N-acylated and N-alkylated by electrogenerated NHC in BMIM-$BF_4$ ionic liquid (Scheme 38).[158] Wide range of substituted benzoxazolones were alkylated or acylated with alkyl halides or anhydrides (saturated or unsaturated) in good to excellent yields.



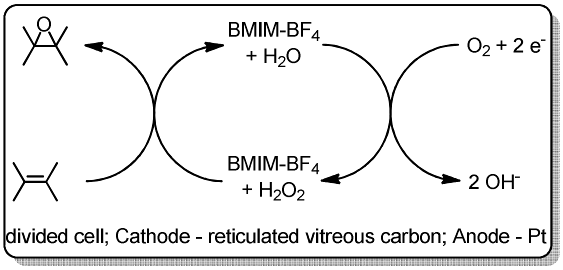
**Scheme 38** N-functionalization of Benzoxazolones[158]

**b) Functionalization of Nitroaromatic compounds**

Electrochemically promoted nucleophilic aromatic substitution reactions of hydrogen (NASH) or of a heteroatom (NASX) in RTILs was mechanistically investigated by Guirado and co-workers.[159] Nucleophiles such as classical hydride, methoxide, ketones, cyanides and amines were used, and the nitroarenes selected were 4-nitrotoluene, 1,3-dinitrobenzene, 2,4-dinitroaniline, 1,3,5-trinitrobenzene, 1,3-dinitronaphthalene, 1-chloro-2,4,6-trinitrobenzene and 2,4,6-trinitroanisole. BMIM-$PF_6$, BMIM-$BF_4$, BMIM-TFSI and BMIM-OAc ILs were chosen. Authors were able to isolate and investigate the nature and stability of σ-complexes. Oxidation peak is shifted based on the nature of the RTIL due to strong ion pairing between the σ-complex and cation of the RTIL. Use of RTILs as a solvent and an electrolyte showed an electro catalytic effect when compared to DMF+$TBABF_4$ mixture. The potential of $\sigma^H$ complex was shifted towards less positive potentials. Excellent yields were obtained for the H and X substituted nucleophilic substitution reactions, depicting higher yields, atom efficiency, and low cost of the reagents. The results were comparable with the control experiments done with 0.1 M TBA.$BF_4$ in DMF and in few cases higher yields was obtained in RTILs demonstrating an effective "green route" for synthesizing substituted nitroaromatic compounds.

**c) *in situ* epoxidation of alkenes**

Chan and co-workers performed *in situ* epoxidation of alkenes using electro generated hydrogen peroxide in BMIM-$BF_4$ NaOH/water mixture (Scheme 39).[160] It was shown that electrochemical reduction of $O_2$ in the presence of NaOH/water and BMIM-$BF_4$ IL will generate $H_2O_2$ *in situ* and this could be used for the epoxidation of alkenes. Wide range of substituted cyclohexene were epoxidized in good yields (~80%).



**Scheme 39** Mechanism of *in situ* epoxidation of alkenes using electro generated $H_2O_2$[160]

## 7. Conclusions

The use of ionic liquids (ILs) as a solvent and an electrolyte for electro organic synthesis has been reviewed. Although several ILs exists till date, ILs based on tetraalkylammonium, pyrrolidinium, piperidinium and imidazolium cations with $BF_4^-$, $PF_6^-$, TFSI anions were widely used and explored to the most. This is possibly due to the abundant availability and low-cost of the respective starting materials (except TFSI salts). Among the imidazolium based ILs, 1-butyl 3-methyl imidazolium cation was widely investigated in electro organic synthesis. Use of imidazolium salts as an electrolyte and solvent has an additional advantage that NHCs can be electrochemically generated *in situ*. Such electrogenerated nucleophilic base was shown to catalyze wide range of base or nucleophile catalyzed reactions in IL media. Here, we restricted our focus to the electro organic synthesis in IL media. Electrochemical oxidation or reduction will generate a radical cation or anion intermediates respectively and these radical intermediates, especially the radical anion were shown to be extensively stabilized by ILs. This stabilization effect has specific impact on the electrochemical $CO_2$ reduction and coupling and on the product formation. Relative stability of the intermediates leads to the formation of selective products in higher yields compared to the side products. Electrochemical reduction of $CO_2$ in ionic liquids is a promising area that needs further examination. Probably ILs can be called as “ruler of solvents” as far as $CO_2$ reduction is concerned, due to their electrochemical stability, wide electrochemical potential window, solubilising ability, stabilization of anion radical by the cation of the IL, etc. Here two aspects have to be considered, i) the direct electrochemical reduction of $CO_2$ and coupling with alcohols, amines to yield the corresponding carbonates and carbamates, and ii) the reduction of organic molecules such as haloarenes to radical species and subsequent coupling with $CO_2$ to yield the corresponding carboxylic acid. In bothways, electrochemical method utilizes $CO_2$ and efficiently converts them to their respective carboxyl derivatives. However, very little is explored as far as $CO_2$ reduction based electroorganic synthesis is concerned. Development and optimization of electrochemical methods will pave way towards the efficient functionalization of $CO_2$ to obtain a wide range of organic compounds/intermediates.

Electrochemical fluorination or selective electrochemical fluorination proves out to be a safe and an eco-friendly method for the generation of selectively fluorinated organic products in $Et_3N.nHF$ and $Et_4NF.nHF$adducts (IL) via anodic oxidation. Oxidative polymerization in ILs were explored to the most, although morphological changes were observed compared to the conventional methods, polymers were obtained in good yields and in some cases ILs were used as dopants to improve the desired properties. So far as electro organic synthesis is concerned, in most cases ILs were recycled and reused at the end of the synthesis by simple extraction with organic solvents and were reused over several cycles, this reusability was shown to have only minor impact on the lateral yields. Although majority of the researchers claim ILs are green solvents compared to volatile organic solvents, their main stress is on the recyclability and reusability, leaving the toxicity of ILs. Most of the ILs are expensive especially the commercially available ILs, hence scaling up the electrochemical synthesis at industrial scale becomes difficult in cost as well as volume viewpoint. In reactions where ILs were used as solvents, volatile organic solvents were used in the secondary step to extract the desired product. This secondary step is inevitable which restricts the green aspects of ILs or in simple words; ILs cannot be regarded as 100% green solvents. The question whether ionic liquids are green solvents is still uncertain and controversial. However, in comparison to VOCs, ILs can be regarded as green solvents, and in addition they replace the use of supporting electrolyte as far as electroorganic synthesis is concerned. Very little has been explored in this area in comparison to the conventional organic synthesis. More introspection in this area will definitely open up a way towards efficient green route for the synthesis of wide range of organics both in small-scale as well as at industrial scale.

## Acknowledgements

Dr. M. K thanks DST-INSPIRE for the INSPIRE faculty award and financial support, M.K and D.V extends their thanks to the Director, CSIR-CECRI.

## Abbreviations

$BF_4$ – tetrafluoroborate

BMIM – 1-butyl-3-methyl imidazolium

BMMIM – 1-butyl-2,3-dimethyl imidazolium

BMPyrd or C$_4$mpyr – N-butyl-N-methyl pyrrolidinium

Bu$_3$DecylN– Tributyldecyl ammonium

BnMIM – 1-benzyl-3-methyl imidazolium

CE – Counter Electrode

DEME – (N,N-Diethyl-N-methyl-N-(2-methoxyethyl) ammonium

DMF – Dimethyl formamide

DMIM – 1-decyl-methyl imidazolium

EMIM – 1-ethyl-3-methyl imidazolium

HexMIM – 1-hexyl-3-methyl imidazolium

ILs – Ionic liquids

MDEGSO$_4$ – diethylene glycol monomethyl ether sulfate

MeSO$_4$ – methyl sulfate

NHCs – N-heterocyclic Carbenes

OAc – acetate

OctSO$_4$ – octyl sulfate

OMIM – 1-octyl-3-methyl imidazolium

OTs – Tosyl

PF$_6$ – hexafluorophosphate

PMIM – 1-propyl-3-methyl imidazolium

RE – Reference Electrode

RT – Room Temperature

RTIL – Room Temperature Ionic Liquid

TEMPO – [(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl]

Tf – triflate

TFSI or $NTf_2$ – Bis(trifluoromethanesulfonyl)imide

VOCs – Volatile Organic Compounds

WE – Working Electrode

**References**

1. J. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*,1992, 965-967.
2. Y. Chauvin, L. Mussmann and H. Olivier, *Angew. Chem. Int. Ed.*, 1996, **34**, 2698-2700.
3. R. Ratti, *Adv. Chem.*, 2014, **2014**, 16.
4. Y. Jin, S. Fang, J. Zhang, Z. Zhang, K. Yu, J. Song, L. Yang and S.-i. Hirano, *Ind. Eng. Chem. Res.*, 2014, **53**, 2860-2871.
5. D. R. MacFarlane, J. M. Pringle, K. M. Johansson, S. A. Forsyth and M. Forsyth, *Chem. Commun.*, 2006, 1905-1917.
6. Z.-B. Zhou, H. Matsumoto and K. Tatsumi, *Chem. Eur. J.*, 2005, **11**, 752-766.
7. M. Kozelj, A. Guerfi and K. Zaghib, *J. Mater. Chem. A*, 2014, **2**, 15964-15971.
8. N. Terasawa, S. Tsuzuki, T. Umecky, Y. Saito and H. Matsumoto, *Chem. Commun.*, 2010, **46**, 1730-1732.
9. P. S. Kulkarni, L. C. Branco, J. G. Crespo, M. C. Nunes, A. Raymundo and C. A. M. Afonso, *Chem. Eur. J.*, 2007, **13**, 8478-8488.
10. G. Cevasco and C. Chiappe, *Green Chem.*, 2014, **16**, 2375-2385.
11. S. Sathyamoorthi, V. Suryanarayanan and D. Velayutham, *J. Power Sources*, 2015, **274**, 1135-1139.
12. S. A. Forsyth, D. R. MacFarlane, R. J. Thomson and M. von Itzstein, *Chem. Commun.*, 2002, 714-715.
13. J. Stoimenovski, D. MacFarlane, K. Bica and R. Rogers, *Pharm. Res.*, 2010, **27**, 521-526.
14. V. Armel, J. M. Pringle, M. Forsyth, D. R. MacFarlane, D. L. Officer and P. Wagner, *Chem. Commun.*, 2010, **46**, 3146-3148.
15. Z. Fei, T. J. Geldbach, D. Zhao and P. J. Dyson, *Chem. Eur. J.*, 2006, **12**, 2122-2130.

16. D. Wei and A. Ivaska, *Anal. Chim. Acta*, 2008, **607**, 126-135.

17. S. Pandey, *Anal. Chim. Acta*, 2006, **556**, 38-45.

18. K. Bica, H. Rodriguez, G. Gurau, O. Andreea Cojocaru, A. Riisager, R. Fehrmann and R. D. Rogers, *Chem. Commun.*, 2012, **48**, 5422-5424.

19. P. C. A. G. Pinto, D. M. G. P. Ribeiro, A. M. O. Azevedo, V. Dela Justina, E. Cunha, K. Bica, M. Vasiloiu, S. Reis and M. L. M. F. S. Saraiva, *New J. Chem.*, 2013, **37**, 4095-4102.

20. C. Jouannin, C. Tourne-Peteilh, V. Darcos, T. Sharkawi, J.-M. Devoisselle, P. Gaveau, P. Dieudonne, A. Vioux and L. Viau, *J. Mater. Chem. B*, 2014, **2**, 3133-3141.

21. D. R. MacFarlane, N. Tachikawa, M. Forsyth, J. M. Pringle, P. C. Howlett, G. D. Elliott, J. H. Davis, M. Watanabe, P. Simon and C. A. Angell, *Energy Environ. Sci.*, 2014, **7**, 232-250.

22. R. Giernoth, *Angew. Chem. Int. Ed.*, 2010, **49**, 2834-2839.

23. M. Galiński, A. Lewandowski and I. Stępniak, *Electrochim. Acta*, 2006, **51**, 5567-5580.

24. K. Larsson and K. Binnemans, *Green Chem.*, 2014, **16**, 4595-4603.

25. T. V. Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, **4**, 1659-1663.

26. J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508-3576.

27. T. Welton, *Chem. Rev.*, 1999, **99**, 2071-2084.

28. C. C. Weber, A. F. Masters and T. Maschmeyer, *Green Chem.*, 2013, **15**, 2655-2679.

29. J.-i. Yoshida, K. Kataoka, R. Horcajada and A. Nagaki, *Chem. Rev.*, 2008, **108**, 2265-2299.

30. R. Francke and R. D. Little, *Chem. Soc. Rev.*, 2014, **43**, 2492-2521.

31. J. B. Sperry and D. L. Wright, *Chem. Soc. Rev.*, 2006, **35**, 605-621.

32. B. A. Frontana-Uribe, R. D. Little, J. G. Ibanez, A. Palma and R. Vasquez-Medrano, *Green Chem.*, 2010, **12**, 2099-2119.

33. K. A. Ogawa and A. J. Boydston, *Chem. Lett.*, 2015, **44**, 10-16.

34. L. E. Barrosse-Antle, A. M. Bond, R. G. Compton, A. M. O'Mahony, E. I. Rogers and D. S. Silvester, *Chem. Asian J.*, 2010, **5**, 202-230.

35. M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621-629.

36. D. C. Grills, Y. Matsubara, Y. Kuwahara, S. R. Golisz, D. A. Kurtz and B. A. Mello, *J. Phys. Chem. Lett.*, 2014, **5**, 2033-2038.
37. N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P. Fennell, *Energy Environ. Sci.*, 2010, **3**, 1645-1669.
38. R. Matthessen, J. Fransaer, K. Binnemans and D. E. De Vos, *Beilstein J. Org. Chem.*, 2014, **10**, 2484-2500.
39. B.-L. Chen, Z.-Y. Tu, H.-W. Zhu, W.-W. Sun, H. Wang and J.-X. Lu, *Electrochim. Acta*, 2014, **116**, 475-483.
40. V. I. Pârvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615-2665.
41. T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2008, **108**, 206-237.
42. N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123-150.
43. Q. Zhang, S. Zhang and Y. Deng, *Green Chem.*, 2011, **13**, 2619-2637.
44. S. Zhang, J. Sun, X. Zhang, J. Xin, Q. Miao and J. Wang, *Chem. Soc. Rev.*, 2014, **43**, 7838-7869.
45. M. A. P. Martins, C. P. Frizzo, A. Z. Tier, D. N. Moreira, N. Zanatta and H. G. Bonacorso, *Chem. Rev.*, 2014, **114**, PR1-PR70.
46. T. Esmail and A. Amani, *J. Envir. Res. Dev.*, 2012, **7 (2A)**, 1026.
47. G. Zhao, T. Jiang, W. Wu, B. Han, Z. Liu and H. Gao, *J. Phys. Chem. B*, 2004, **108**, 13052-13057.
48. J. Ghilane, P. Martin, H. Randriamahazaka and J.-C. Lacroix, *Electrochem. Commun.*, 2010, **12**, 246-249.
49. F. A. Hanc-Scherer, C. M. Sánchez-Sánchez, P. Ilea and E. Herrero, *ACS Catal.*, 2013, **3**, 2935-2938.
50. M. Mellah, J. Zeitouny, S. Gmouh, M. Vaultier and V. Jouikov, *Electrochem. Commun.*, 2005, **7**, 869-874.
51. S. Bornemann and S. T. Handy, *Molecules*, 2011, **16**, 5963-5974.
52. R. Barhdadi, C. Comminges, A. P. Doherty, J. Y. Nédélec, S. O'Toole and M. Troupel, *J. Appl. Electrochem.*, 2007, **37**, 723-728.
53. A. C. Herath and J. Y. Becker, *Electrochim. Acta*, 2008, **53**, 4324-4330.
54. G. D. Allen, M. C. Buzzeo, I. G. Davies, C. Villagrán, C. Hardacre and R. G. Compton, *J. Phys. Chem. B*, 2004, **108**, 16322-16327.
55. J.-X. Lu, Q. Sun and M.-Y. He, *Chinese J. Chem.*, 2003, **21**, 1229-1230.
56. I. Reche, I. Gallardo and G. Guirado, *New J. Chem.*, 2014, **38**, 5030-5036.

57. R. Barhdadi, C. Courtinard, J. Y. Nedelec and M. Troupel, *Chem. Commun.*, 2003, 1434-1435.
58. M. Mellah, S. Gmouh, M. Vaultier and V. Jouikov, *Electrochem. Commun.*, 2003, **5**, 591-593.
59. D. Niu, A. Zhang, T. Xue, J. Zhang, S. Zhao and J. Lu, *Electrochem. Commun.*, 2008, **10**, 1498-1501.
60. L. D. Pachón, C. J. Elsevier and G. Rothenberg, *Adv. Synth. Catal.*, 2006, **348**, 1705-1710.
61. C. Lagrost, P. Hapiot and M. Vaultier, *Green Chem.*, 2005, **7**, 468-474.
62. F. Andre, P. Hapiot and C. Lagrost, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7506-7512.
63. H. Kronenwetter, J. Husek, B. Etz, A. Jones and R. Manchanayakage, *Green Chem.*, 2014, **16**, 1489-1495.
64. M. Ramdin, T. W. de Loos and T. J. H. Vlugt, *Ind. Eng. Chem. Res.*, 2012, **51**, 8149-8177.
65. G. Fiorani, W. Guo and A. W. Kleij, *Green Chem.*, 2015, **17**, 1375-1389.
66. J. Albo, M. Alvarez-Guerra, P. Castano and A. Irabien, *Green Chem.*, 2015, **17**, 2304-2324.
67. B. C. M. Martindale and R. G. Compton, *Chem. Commun.*, 2012, **48**, 6487-6489.
68. N. L. Weinberg, A. Kentaro Hoffmann and T. B. Reddy, *Tetrahedron Lett.*, 1971, **12**, 2271-2274.
69. Y. Oh and X. Hu, *Chem. Soc. Rev.*, 2013, **42**, 2253-2261.
70. L. A. Blanchard, D. Hancu, E. J. Beckman and J. F. Brennecke, *Nature*, 1999, **399**, 28-29.
71. J. F. Brennecke and B. E. Gurkan, *J. Phys. Chem. Lett.*, 2010, **1**, 3459-3464.
72. Z.-Z. Yang, Y.-N. Zhao and L.-N. He, *RSC Adv.*, 2011, **1**, 545-567.
73. S.-F. Zhao, M. Horne, A. M. Bond and J. Zhang, *Green Chem.*, 2014, **16**, 2242-2251.
74. M. Feroci, M. Orsini, L. Rossi, G. Sotgiu and A. Inesi, *J. Org. Chem.*, 2007, **72**, 200-203.
75. H. Wang, L.-X. Wu, Y.-c. Lan, J.-Q. Zhao and J.-X. Lu, *Int. J. Electrochem. Sci.*, 2011, **6**, 4218-4227.
76. H. Wang, X.-M. Xu, Y.-C. Lan, H.-M. Wang and J.-X. Lu, *Tetrahedron*, 2014, **70**, 1140-1143.
77. L. Zhang, D. Niu, K. Zhang, G. Zhang, Y. Luo and J. Lu, *Green Chem.*, 2008, **10**, 202-206.

78. Y.-C. Lan, H. Wang, L.-X. Wu, S.-F. Zhao, Y.-Q. Gu and J.-X. Lu, *J. Electroanal. Chem.*, 2012, **664**, 33-38.
79. D. Niu, J. Zhang, K. Zhang, T. Xue and J. Lu, *Chinese J. Chem.*, 2009, **27**, 1041-1044.
80. B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, *Chem. Rev.*, 2010, **110**, 4554-4581.
81. S. Huang, B. Yan, S. Wang and X. Ma, *Chem. Soc. Rev.*, 2015, **44**, 3079-3116.
82. M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514-1539.
83. J. Wang, J. Leong and Y. Zhang, *Green Chem.*, 2014, **16**, 4515-4519.
84. B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang and S.-J. Zhang, *Green Chem.*, 2015, **17**, 108-122.
85. H. Yang, Y. Gu, Y. Deng and F. Shi, *Chem. Commun.*, 2002, 274-275.
86. D. Yuan, C. Yan, B. Lu, H. Wang, C. Zhong and Q. Cai, *Electrochim. Acta*, 2009, **54**, 2912-2915.
87. F. Liu, S. Liu, Q. Feng, S. Zhuang, J. Zhang and P. Bu, *Int. J. Electrochem. Sci.*, 2012, **7**, 4381-4387.
88. B. Lu, X. Wang, Y. Li, J. Sun, J. Zhao and Q. Cai, *J. $CO_2$ Utilization*, 2013, **3–4**, 98-101.
89. L.-X. Wu, H. Wang, Y. Xiao, Z.-Y. Tu, B.-B. Ding and J.-X. Lu, *Electrochem. Commun.*, 2012, **25**, 116-118.
90. M. Honda, S. Sonehara, H. Yasuda, Y. Nakagawa and K. Tomishige, *Green Chem.*, 2011, **13**, 3406-3413.
91. A. K. Ghosh and M. Brindisi, *J. Med. Chem.*, 2015, **58**, 2895-2940.
92. O. Kreye, H. Mutlu and M. A. R. Meier, *Green Chem.*, 2013, **15**, 1431-1455.
93. D. Chaturvedi, *Tetrahedron*, 2012, **68**, 15-45.
94. Y. Hiejima, M. Hayashi, A. Uda, S. Oya, H. Kondo, H. Senboku and K. Takahashi, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1953-1957.
95. H. Tateno, K. Nakabayashi, T. Kashiwagi, H. Senboku and M. Atobe, *Electrochim. Acta*, 2015, **161**, 212-218.
96. Q. Feng, K. Huang, S. Liu, J. Yu and F. Liu, *Electrochim. Acta*, 2011, **56**, 5137-5141.
97. H. Wang, G. Zhang, Y. Liu, Y. Luo and J. Lu, *Electrochem. Commun.*, 2007, **9**, 2235-2239.
98. S. Ernst, S. E. Norman, C. Hardacre and R. G. Compton, *Phys. Chem. Chem. Phys.*, 2014, **16**, 4478-4482.

99. A. Jones, H. Kronenwetter and R. Manchanayakage, *Electrochem. Commun.*, 2012, **25**, 8-10.

100. Q. Feng, K. Huang, S. Liu, H. Wang and W. Yan, *J. Phys. Org. Chem.*, 2012, **25**, 506-510.

101. B. C. M. Martindale, D. Menshykau, S. Ernst and R. G. Compton, *Phys. Chem. Chem. Phys.*, 2013, **15**, 1188-1197.

102. D. S. Silvester, A. J. Wain, L. Aldous, C. Hardacre and R. G. Compton, *J. Electroanal. Chem.*, 2006, **596**, 131-140.

103. Y.-Z. Liu, M.-Y. Lin, L.-P. Xiao, K. Zhang and J.-X. Lu, *Chinese J. Chem.*, 2008, **26**, 1168-1172.

104. G. Sotgiu, I. Chiarotto, M. Feroci, M. Orsini, L. Rossi and A. Inesi, *Electrochim. Acta*, 2008, **53**, 7852-7858.

105. D. Zane, A. Raffaele, A. Curulli, G. B. Appetecchi and S. Passerini, *Electrochem. Commun.*, 2007, **9**, 2037-2040.

106. Y. Du, H. Wang, A. Zhang and J. Lu, *Chin. Sci. Bull.*, 2007, **52**, 2174-2178.

107. T. Carstens, S. Zein El Abedin and F. Endres, *ChemPhysChem*, 2008, **9**, 439-444.

108. M. Al Zoubi and F. Endres, *Electrochim. Acta*, 2011, **56**, 5872-5876.

109. D. Wei, C. Kvarnström, T. Lindfors and A. Ivaska, *Electrochem. Commun.*, 2006, **8**, 1563-1566.

110. D. Wei, C. Kvarnström, T. Lindfors and A. Ivaska, *Electrochem. Commun.*, 2007, **9**, 206-210.

111. M. Biso, M. Mastragostino, M. Montanino, S. Passerini and F. Soavi, *Electrochim. Acta*, 2008, **53**, 7967-7971.

112. K. Liu, Z. Hu, R. Xue, J. Zhang and J. Zhu, *J. Power Sources*, 2008, **179**, 858-862.

113. Y. Pang, X. Li, G. Shi, F. Wang and L. Jin, *Thin Solid Films*, 2008, **516**, 6512-6516.

114. S. Ahmad, R. Berger, H. U. Khan and H.-J. Butt, *J. Mater. Chem.* , 2010, **20**, 5325-5334.

115. Y. Pang, H. Xu, X. Li, H. Ding, Y. Cheng, G. Shi and L. Jin, *Electrochem. Commun.*, 2006, **8**, 1757-1763.

116. Y. Pang, X. Li, H. Ding, G. Shi and L. Jin, *Electrochim. Acta*, 2007, **52**, 6172-6177.

117. Y. Pang, X. Li, G. Shi and L. Jin, *Int. J. Electrochem. Sci.*, 2007, **2**, 681-688.

118. E. Naudin, H. A. Ho, S. Branchaud, L. Breau and D. Bélanger, *J. Phys. Chem. B*, 2002, **106**, 10585-10593.

119. P. Damlin, C. Kvarnström and A. Ivaska, *J. Electroanal. Chem.*, 2004, **570**, 113-122.

120. P. Danielsson, J. Bobacka and A. Ivaska, *J. Solid State Electrochem.*, 2004, **8**, 809-817.
121. G. A. Snook and A. S. Best, *J. Mater. Chem.* , 2009, **19**, 4248-4254.
122. F. Yang, J. Yang, K. Zheng, J. W. Stansbury and J. Nie, *Macromol. Chem. Phys.*, 2015, **216**, 380-385.
123. N. Ilayaraja, D. Velayutham and M. Noel, *J. Fluorine Chem.*, 2009, **130**, 656-661.
124. N. Ilayaraja, A. Manivel, D. Velayutham and M. Noel, *J. Fluorine Chem.*, 2008, **129**, 185-192.
125. T. Fuchigami, *J. Fluorine Chem.*, 2007, **128**, 311-316.
126. S. Inagi, T. Sawamura and T. Fuchigami, *Electrochem. Commun.*, 2008, **10**, 1158-1160.
127. M. Noel, V. Suryanarayanan and S. Chellammal, *J. Fluorine Chem.*, 1997, **83**, 31-40.
128. L. Conte and G. Gambaretto, *J. Fluorine Chem.*, 2004, **125**, 139-144.
129. K. M. Dawood, *Tetrahedron*, 2004, **60**, 1435-1451.
130. T. Fuchigami and T. Tajima, *J. Fluorine Chem.*, 2005, **126**, 181-187.
131. T. Fuchigami and S. Inagi, *Chem. Commun.*, 2011, **47**, 10211-10223.
132. B. Yin, S. Inagi and T. Fuchigami, *Beilstein J. Org. Chem.*, 2015, **11**, 85-91.
133. K. Takahashi, S. Inagi and T. Fuchigami, *J. Electrochem. Soc.*, 2013, **160**, G3046-G3052.
134. T. Sawamura, S. Kuribayashi, S. Inagi and T. Fuchigami, *Adv. Synth. Catal.*, 2010, **352**, 2757-2760.
135. T. Sawamura, S. Kuribayashi, S. Inagi and T. Fuchigami, *Org. Lett.*, 2010, **12**, 644-646.
136. K. Takahashi, T. Furusawa, T. Sawamura, S. Kuribayashi, S. Inagi and T. Fuchigami, *Electrochim. Acta*, 2012, **77**, 47-53.
137. M. Monoi and S. Hara, *J. Fluorine Chem.*, 2012, **140**, 28-30.
138. B. Gorodetsky, T. Ramnial, N. R. Branda and J. A. C. Clyburne, *Chem. Commun.*, 2004, 1972-1973.
139. M. Feroci, M. Orsini, L. Rossi and A. Inesi, *Curr. Org. Synth.*, 2012, **9**, 40-52.
140. M. Feroci, I. Chiarotto and A. Inesi, *Curr. Org. Chem.*, 2013, **17**, 204-219.
141. M. Feroci, I. Chiarotto, M. Orsini, G. Sotgiu and A. Inesi, *Adv. Synth. Catal.*, 2008, **350**, 1355-1359.
142. M. Feroci, M. N. Elinson, L. Rossi and A. Inesi, *Electrochem. Commun.*, 2009, **11**, 1523-1526.

143. M. Orsini, I. Chiarotto, M. N. Elinson, G. Sotgiu and A. Inesi, *Electrochem. Commun.*, 2009, **11**, 1013-1017.

144. I. Chiarotto, M. Feroci, M. Orsini, M. M. M. Feeney and A. Inesi, *Adv. Synth. Catal.*, 2010, **352**, 3287-3292.

145. M. Orsini, I. Chiarotto, G. Sotgiu and A. Inesi, *Electrochim. Acta*, 2010, **55**, 3511-3517.

146. M. Feroci, I. Chiarotto, M. Orsini and A. Inesi, *Chem. Commun.*, 2010, **46**, 4121-4123.

147. M. Feroci, *Int. J. Org. Chem.*, 2011, **1**, 191-201.

148. M. Feroci, I. Chiarotto, M. Orsini, G. Sotgiu and A. Inesi, *ECS Trans.*, 2010, **25**, 1-11.

149. M. Orsini, I. Chiarotto, M. M. M. Feeney, M. Feroci, G. Sotgiu and A. Inesi, *Electrochem. Commun.*, 2011, **13**, 738-741.

150. K. Hirano, I. Piel and F. Glorius, *Adv. Synth. Catal.*, 2008, **350**, 984-988.

151. Y. Li, Z.-A. Zhao, H. He and S.-L. You, *Adv. Synth. Catal.*, 2008, **350**, 1885-1890.

152. V. Nair, S. Vellalath and B. P. Babu, *Chem. Soc. Rev.*, 2008, **37**, 2691-2698.

153. M. Feroci, I. Chiarotto, M. Orsini, R. Pelagalli and A. Inesi, *Chem. Commun.*, 2012, **48**, 5361-5363.

154. M. Feroci, I. Chiarotto and A. Inesi, *Electrochim. Acta*, 2013, **89**, 692-699.

155. I. Chiarotto, M. Feroci, G. Sotgiu and A. Inesi, *Eur. J. Org. Chem.*, 2013, **2013**, 326-331.

156. G. Forte, I. Chiarotto, A. Inesi, M. A. Loreto and M. Feroci, *Adv. Synth. Catal.*, 2014, **356**, 1773-1781.

157. I. Chiarotto, M. M. M. Feeney, M. Feroci and A. Inesi, *Electrochim. Acta*, 2009, **54**, 1638-1644.

158. I. Chiarotto, M. Feroci, M. Orsini, G. Sotgiu and A. Inesi, *Tetrahedron*, 2009, **65**, 3704-3710.

159. H. Cruz, I. Gallardo and G. Guirado, *Green Chem.*, 2011, **13**, 2531-2542.

160. M. C.-Y. Tang, K.-Y. Wong and T. H. Chan, *Chem. Commun.*, 2005, 1345-1347.

**Author Profiles:**

Dr Kathiresan Murugavel graduated from the University of Madras with both Bachelor's (2004) and Master's degrees (2006), and received his PhD from the University of Osnabrueck, Germany in 2010 under the guidance of Prof. Lorenz Walder. He then moved to the University of Basel, Switzerland to conduct his postdoctoral research with Prof. Marcel Mayor. He was awarded the DST-INSPIRE Faculty award in Dec 2013. Since March 2014, he has been working as a DST-INSPIRE faculty member at the Electro Organic Division, CSIR-Central Electro Chemical Research Institute, Karaikudi, India. His current research interests include electroorganic synthesis, electrochemical $CO_2$ reduction and conversion to useful organics, synthesis of dendrimers, oligophenylene ethynylene molecules, and macrocycles, along with investigating their supramolecular aspects and applications towards photophysical and biological applications.

Dr David Velayutham graduated from Madurai Kamaraj University with both Bachelor's (1982) and Master's degrees (1984). He has joined CSIR-Central ElectroChemical Research Institute as a Junior Scientist in 1987 and received his PhD from the Alagappa University in 1993. He then moved to the University of Duisburg, Germany as a Post Doctoral Fellow (1994) for a period of 18 months after which he resumed his duty in CSIR-CECRI. He is currently working as a Chief Scientist in ElectroOrganic Division, CSIR-CECRI, Karaikudi, TamilNadu, INDIA. His current research interests include electro organic synthesis, electrochemical fuorination and synthesis of ionic liquids for electrochemical application including super capacitor and lithium ion batteries.