Team of Ionic Liquids
Clean Process and Energy-Saving
**Brief Introduction**

The team of Ionic Liquids (ILs) clean process and energy-saving (ILC) was founded in 2001. The ILC team dedicates to comprehensive multi-scale research of ILs, i.e., molecule design, structure-property, large-scale preparation, industrial application, and system integration. Our vision is to create innovative green processes and technologies taking ILs as key solvents and catalysts. For the fundamentals of ILs, we mainly focus on the multi-scale theories, principles and methodologies of ILs, and establish a knowledge system of ILs including molecule, cluster, scale-up and integration. For the applications of ILs, we engage to developing three aspects of ILs-based green processes, i.e. separation, reaction and electrochemistry, in which the ILs act as solvents, catalysts and electrolytes, respectively.

**Research Activities**

1. **Structure-property relationship and molecular design of ILs**

Understanding the structure-property relationship of IL systems and developing novel property predictive methods for ILs are frontier hotspots in ILs research field. We established a comprehensive physicochemical property database of ILs, which is acknowledged as one of the most important databases worldwide. By scientifically classifying ILs, we proposed the periodic variation rule of physical properties of ILs versus the structure and molecular weight of cations and anions for the first time. By scientifically classifying and defining “ionic fragments”, we developed a novel “ionic fragment” contribution method for quantitatively predicting the properties of ILs. We also developed novel force fields and molecular dynamic simulation method for a series of ILs and systematically investigated the ion-ion and ion-molecule interactions in ILs systems. These achievements bring a major breakthrough in guiding the efficient and the quantities design of ILs from numerous number of cation-anion combination, which is recognized as a new approach for screening and designing ILs as catalysts and solvents.

2. **Reaction-transport coupling mechanism and system integration in ionic liquids systems**

The complex engineering phenomena in ILs are significantly different from those in the conventional systems, such as organic solvents, water, etc., which bring many challenges and even lead to some misunderstandings for the traditional chemical engineering laws and principles, and in this aspect there is nearly no reported work worldwide at present. Meanwhile, the current models and methods are not applicable to study the multi-scale properties and performance in ILs systems. As a result, scale-up of ILs-based processes becomes very difficult, high risk and time intensive. ILC invented a set of in-situ Reaction-Transport Tomography (iR2T) for measuring the transport-reaction coupling performance in ILs by taking into account the unique electric resistances and dynamic characteristics of ILs. By which the transport behaviours, such as formation, deformation, coalescence and the movement of CO₂ and air bubbles in ILs were directly observed, and the coupling mechanism of reaction and transport especially the single and synergistic action mechanism of cations and anions on reaction and separation performance in ILs were firstly revealed. At system level, we investigate process intensification and integrated innovation methodologies, developing new green technology by modeling, simulation and integration of ILs processes and accelerating the application of the ILs in reaction, separation and electrochemistry. The new technique and findings fill gaps in the scale up of ILs based reactors and processes, and contribute new knowledge to chemical engineering science.
3. Novel green ionic liquid-based technologies

As green solvents and catalysts, ILs are expected to replace traditional toxic and polluted ones, leading to the revolution in the traditional chemical industry. By taking into account the unique physicochemical and dynamic characteristic of ILs, ILC invented the electrostatic-hydrogen bond enhanced green technologies in gas separation, organic chemical production and electrolysis/battery electrolytes. For example, the first commercial plant for ILs production (capacity 200 tons/a); the first demonstration of NH$_3$ recovery (capacity 8,000,000 Nm$^3$/a) with ILs replacing the aqueous solvents; the first pilot plant of co-production of EG (ethylene glycol) and DMC (dimethyl carbonate) and the industrial process package with the capacity of 20,000 tons/a; the industrial demonstration plant of green process for production of MMA (methyl methacrylates) instead of toxic raw materials and solvents (capacity 10,000 tons/a); the new generation of lithium battery electrolytes with ILs as additives (capacity 500 tons/a). These innovative technologies have been well recognized and successfully applied by the international and Chinese accompanies, such as Ford Motor (USA), Bekaert (Belgium), Mitsubishi Materials Corp (Japan), Sinopec (China), PetroChina, CNOOC (China), HNEC (China), SCCWG (China), etc. The products of ILs and battery electrolytes have been used by more than 150 institutions and accompanies domestically and internationally.

Infrastructure

The ILC team has 96 members, including 8 professors, 20 associate professors, 15 assistant professors, 20 engineers, 8 administrators, and 25 graduate students. Over 20 self-designed equipment and instruments have been established, which supported high lever academic research and the innovation of technologies in ILC, and improved the whole ability of technical transformation. Some novel equipment and instruments are introduced as follows.

1. In-situ Reaction-Transport Tomography (iR2T) for measuring the transport-reaction coupling performance.

iR2T was self-designed and it can be used to measure the cross-sectional structure of multi-phase flow by means of the conductivity difference between different phases and obtain the two or three dimensional distribution information of real reaction process without interference of the fluid flow. It has become one of the important equipment to study experimentally the unique properties of unit scale up of ionic liquid systems.

2. Magnetic intensification research system

This system is composed of two sub-systems: the temperature control system and the superconducting magnet. The magnet has a room temperature bore with a diameter of 11 cm, and it can supply a strong magnetic field Tesla. Reactor loaded within the room temperature bore could be modulated from -30 to 200$^\circ$C by the temperature control system via a silicon oil media. Some chemical process, such as crystal growth, chemical reactions etc. could be tuned by employing the static magnetic field. It is well known that a magnetic field can interact with electron spins of radical pairs without contact. Therefore, the
spin conversions between singlet and triplet states of radical pairs appear in chemical reactions can be modulated by external magnetic field. In addition, energy of reaction systems will be improved with the presence of the magnetic field. This system is being used to study the magnetic field effects on some chemical processes involved with free radical in order to improve reaction rate and selectivity.

3. Multispectral coupling in situ instrument for ILs-involved electrochemical processes

In order to study the mechanism of ILs in electrochemical processes, we built an in-situ instrument for investigating the invalid mechanism of the ILs-based electrolytes by multispectral coupling. The interfacial reactions on the electrodes, the ongoing reactions or the ILs effects for the electrochemical reactions can be in situ monitoring with on-line gas chromatograph, in-situ IR, EQCM, etc., which will provide new insights into the properties of ILs and further explore their applications in electrochemistry.

## Research Progresses

### 1. The hydrogen bond and cluster in ionic liquids

The structure and interaction of ILs determines their unique properties. By employing the *ab initio* DFT and molecular dynamic simulation, the team investigated the molecular structure and ionic packing in liquid and crystal states of ionic liquids. It is found that the hydrogen bond is an important interaction between anion and cation and influences many properties of ionic liquids, which discovers the intrinsical difference between the high temperature molten salt and ionic liquid. When coupling with the strong electrostatic force, however, the hydrogen bond in ionic liquid is not consistent with the conventional hydrogen bond in organic solvent/water, and the feature of geometric, energetic, electronic, spectrum and dynamic have been proposed. The new interactive model provides a theoretical basis for innovation, diagnostic, control and optimization of property and application of ionic liquid.

### 2. Clean technology of methyl methacrylate (MMA)

MMA is an important monomer for plexiglass production. The traditional production process is the acetone cyanohydrine (ACH) method, which uses harmful hydrocyanic acid and sulphuric acid. A clean process called two-step selective
oxidation process was developed with isobutene as the raw material. Firstly, isobutene was selectively oxidized to MAL with a lattice oxygen catalyst. Secondly, MAL reacted with methanol and oxygen to produce MMA. A Pd-based noble metal catalyst and a flurry-bed reactor were designed. The CFD simulation and cold model test of the flurry bed reactor were studied. Also a green process for MAL separation with ILs was developed to improve the recovery rate of MAL. A demonstration plant of 20,000 t/a has been set up in China. We also developed a new coal-based clean process for MMA production with three steps and the pilot plant of 1,000 t/a is under construction.

3. New technique of synthesis of ethylene glycol catalyzed by ionic liquids

Ethylene glycol (EG), which is primarily used as a raw material for polyester production, has a strategic significance of the basic industries and new industries. A novel technology for the production of EG via hydrolysis or alcoholysis based on ionic liquid has been developed by ILC and the pilot plant has been built. Base on a 1000h successfully continuous test, the 20,000 t/a industrial demonstration plant is now under constructed. The novel technology is highly competitive due to its high single conversion and selectivity, low energy consumption, and simple process. This technology has passed detailed appraisal of science office of Chinese Academy of Sciences in 2011, and was evaluated as “top level in the world”.

4. Ionic liquid-based electrochemical techniques

Compared to the traditional organic solvents and molten salts, ionic liquids (ILs) are a class of low-temperature electrolytes with many attractive properties, such as low melting points, negligible vapor pressure and wide electrochemical windows. Thus, ILs are regarded as a promising class of electrolytes in the electrolysis, electroplating process, lithium ion battery and next-generation energy storage. Aiming at the high energy consumption of aluminum industry, heavy pollution of electroplating, and the poor performance of the traditional organic electrolytes in lithium ion batteries, we developed a new IL-based energy-saving electrolytic aluminum process, cyanide-free plating cleaning process and new type IL-based battery electrolytes, respectively. For example, we have built a production line for ILs-based battery electrolytes, and both the electrolytes and batteries were commercialized.
Selected Publications and Achievements

12. Award for National Natural Science of China (Second Class) in 2010 for the project titled "Structure-Property Relationship and Chemical Engineering Fundamentals of Ionic Liquids"
13. China Petroleum and Chemical Industry Association Scientific and Technological Progress Prize (First Class) in 2009 for the project titled "Structures, Properties and Applications of Ionic Liquids"
14. China Petroleum and Chemical Industry Association Technological Invents Prize (Second Class) in 2008 for the project titled "Clean Technology for Production of Methyl Methacrylate Instead of Toxic Raw Materials or Mediums"
15. Beijing Municipality Scientific and Technological Innovation Prize (Second Class) in 2007 for the project titled "Large Scale Preparation and Clean Process of Ionic liquids"

Research Professors

**Prof. Suojiang Zhang (Team Leader),** born in 1964, received his Ph.D. degree from the department of Chemistry of Zhejiang University in 1994. He won the scholarship of Japanese Ministry of Education and went to Japan to work with Professor Kazuo. In 1997, he joined in Mitsubishi Chemical Corporation and from 1998, he worked as a Senior Engineer and a Senior Consultant. From 2001, he started to work in IPE as the "Hundred Talents". He won the Second Class Prize of National Natural Science Award in 2010; First-class Award of China Petroleum & Chemical Industry Association Scientific and Technological Progress Prize in 2009; Second-class Award of China Petroleum & Chemical Industry Association Scientific and Technological Progress Prize in 2008; Young Knowledge Innovation Prize of Chinese Chemical Society-BASF in 2008, Second-class Award of Beijing Municipality Scientific and Technological Innovation Prize in 2007. Until now, a total of 180 SCI papers have been published in academic journals, four monographs have been written or edited, and more than 40 patents have been authorized.

**Affiliation**
Fellow, The Royal Society of Chemistry (RCS)
Chief Editor, Chinese Journal of Process Engineering
Prof. Xiangping Zhang was born in 1969 and received her Ph.D. degree in chemistry engineering from Dalian University of Technology in 2002. She was a postdoctoral fellow at the Institute of Process Engineering (IPE), CAS (2002-2004). She has been a professor of IPE since 2008. She was also as a visiting researcher in Norwegian University of Science and Technology in 2006. She was awarded the Second Prize of Natural Sciences, the Nomination Award of the 4th Top Ten Outstanding Women in Chinese Academy of Sciences in 2012. She has published about 132 papers in peer-reviewed journals, and obtained 15 issued Chinese invention patents and 1 issued PCT patent.

Affiliations
Editor board member, Chemical Progress (in Chinese)

Research Interests
Process system integration; Molecular level-based process simulation; Environmental impact assessment; Techno-economic assessment of processes; Properties and thermodynamic models of ionic liquid solvent; Ionic liquid-based new solvents/absorbents for cleaner and energy saving processes.

Prof. Xingmei Lv, born in 1968, got her B. Sc in 1989 and M.Sc in 1992, both from Liaoning University, then received her Ph.D. in 2005 from Qinghai Institute of Salt Lake, CAS. She has been full professor of chemical engineering at Institute of Process Engineering, CAS since 2012. She is mainly engaged in fundamental and applications of ionic liquids (ILs). She proposed a new theory for ionic liquids—the Interstice Model with Prof. Jiazhen Yang which enables to calculate the average volume and the volume fraction of the interstices of ILs and also to predict the thermal expansion coefficient and physicochemical properties of ILs. She further developed the new technology of degradation of Polyethylene terephthalate (PET) catalyzed by ILs which enables increase efficiency of PET degradation. She also studies the pretreatment methods of biomass with ILs, finding the useful additives in ILs and a two-step IL pretreatment method for high-efficiency delignification of biomass.

Affiliations
Vice Director of the Beijing key lab of Ionic Liquids and Clean Process.
The Committee Member of Ionic Liquids Specialized Committee of China.

Research Interests
Reconstruction of ILs database, separation, transformation and material preparation of biomass in IL; Degradation of PET catalyzed by IL; Electro-deposition of Metals and their alloy in IL.
**Prof. Yanqiang Zhang**, born in 1975, received his B.S. from Dalian University of Technology (China) in 1997. After graduation, he worked in the polymer industry for five years. From 2002, he studied in Institute of Process Engineering (IPE) of CAS, and obtained his Ph.D. degree in applied chemistry in 2008. He then went to University of Idaho (USA) as a postdoctoral fellow with Prof. Jean’ne M. Shreeve. In 2013, he finished his postdoc program, and came to work in IPE as a professor. From 2002 to now, his research interests are design and synthesis of functional ionic liquids, including NH₂⁻ and BH-based, nitrogen-rich ionic liquids, and so on. Especially, he prepared series of energetic ionic liquids (or salts), for example the dicyanoborate ionic liquids, which are hypergolic with oxidizers (HNO₃, N₂O₄, etc.) to be the potential replacement of dimethylhydrazine as the green fuels of bipropellants. He has published more than 20 papers in top academic journals, such as Angew. Chem. Int. Ed., Chem. Eur. J., J. Mater. Chem., Inorg. Chem., and so on. Also, his work was positively cited. He was selected in the fourth batch of the “Thousand Talents Program for Young Scholars” of China in 2012. He was appointed as the Outstanding Staff Award of the Team of Ionic Liquids Clean Process and Energy-saving in 2013 and 2014.

**Research Interests**

Design and synthesis of energetic ionic liquids (or salts) as the ingredients of propellants; Synthesis and stabilization of high-nitrogen (or all-nitrogen) compounds in low temperature; Electronic structure calculations of high-density energetic materials.

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**Prof. Haitao Zhang**, born in 1978, received his B.E. degree in Chemical Engineering from Central South University in 2000, and PhD degree in Condensed Matter Physics from University of Science & Technology of China in 2006. After obtaining his PhD degree, he worked as a postdoctoral fellow at Department of Materials & Engineering in National University of Singapore, and National Institute for Materials Science (Japan, 2006-2011). He joined in the Institute of Process Engineering (CAS) in 2011 as a professor. He has rich expertise in soft chemical synthesis, microstructural characterization, ultrathin-film fabrication and nanomagnetism, especially as applied to the design and syntheses and synergetic effects of multifunctional nanomaterials. With solid background in multidisciplinary sciences, he is conducting a project of the intensification of chemical process through a strong magnetic field. He is author of over 34 journal papers and 1monograph. His work was positively cited over 900 times by Nature Materials, Chem. Rev., J. Am. Chem. Soc. etc.

**Research Interests**

Energy storage and conversion materials; Magnetic field intensification technology, nanomaterials & nanoengineering; Process analysis and inspection technologies; Hybridized multifunctional materials.

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**Prof. Shimou Chen** was born in 1981 and received his BS degree from Zhengzhou University in 2002, and his Ph.D. degree from Shanghai Institute of Applied Physics, Chinese Academy of Sciences in 2007. In Apr. 2008, he moved to Nagoya University as a JSPS postdoctoral fellow. From 2011 to 2012 he was a Research Associate at National Institute for Materials Science (NIMS), Japan. In April, 2012, he joined IPE as a professor funded by “Hundred Talent Project” of Chinese Academy of Sciences. He has published more than 50 papers.
Affiliation
Guest Editor, Journal of Nanomaterials

Research Interests
Microstructure of ionic liquid; Phase behavior of ionic liquid in confined space; Ionic liquid assisted fabrication of nanostructures; Application of ionic liquid in electrolytic aluminium; Lithium-ion battery; Solar cell, etc.

Prof. Baohua Xu, born in 1980, got her Ph.D in 2008 from State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering of Nanjing University. From then to 2012, she was a postdoctoral fellow at Münster University, Germany, funded by International Research Training Group (IRTG). She has been professor of chemical engineering at Institute of Process Engineering, CAS since 2013. She is mainly engaged in organometallic catalysts and green catalytic process. She is author of nearly 20 SCI papers including the top class J. Am. Chem. Soc., Angew. Chem. Int. Ed., Chem.-Eur. J., etc., and filed for 2 patents. Her work was positively cited by Chem. Soc. Rev., Nature Chem., J. Am. Chem. Soc., Angew. Chem. Int. Ed. etc. She won the Excellent Graduate Award of Nanjing University in 2007.

Research Interests
Homogeneous catalysis; Activation and transformation of inert bonds or molecules; Related reaction methodology and green catalytic process.

Prof. Weiguo Cheng, born in 1970, earned his Ph.D. degree from Dalian University of Technology in 2005. He has been professor of chemical engineering at Institute of Process Engineering, CAS since 2014. He is mainly engaged in industrial catalysis. He focus on revealing the essential relationship between catalytic performance and the catalyst structure, by using surface analytical techniques, particularly in-situ vibrational and optical spectroscopies. He specializes in design of novel catalytic materials and catalytic process. He proposed synergistic catalytic effect of ionic liquids. A proposed mechanism based on synergistic effect provides a molecular level understanding of effect of hydrogen bond on the reaction and forms the basis of rational design of ionic liquids. He has promoted the novel technology based on ionic liquid application and industrialization, such as new technique of synthesis of ethylene glycol/dimethyl carbonate catalyzed by ionic liquids.

He is author of over 40 journal papers and 12 invention patents granted including 1 PCT patent. His work was positively cited by Angewandte Chemie International Edition, Journal of American Chemistry Society, Journal of Catalysis, Chemical Reviews, Chemical Society Reviews, Green Chemistry etc. He has been awarded Beijing Awards for Science and Technology in 2008 and Award for Scientific Progress from China Petroleum and Chemical Industry Association in 2009.

Affiliations
Member, Committee of integration of IT application and industrialization
Editorial board member, Review of Catalysts

Research Interests
Design of novel catalytic materials and catalytic process; Synthesis of ionic liquid catalysts; Mechanisms and kinetics of catalytic reaction; New catalytic process for CO₂ utilization.