Extended Abstract

Designing Ion-dipole Engineered Piezoionic Polymer Architectures for Energy Harvesting Iontronics and Multimodal Sensing

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Degree for which submitted: Doctor of Philosophy

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Abstract of the Thesis

The rapid evolution of iontronics has intensified the demand for sustainable, autonomous, and multifunctional technologies capable of operating with minimal external power requirements. This has stimulated considerable interest in mechanical energy harvesting and self-powered sensing systems for applications in wearable and implantable electronics, embedded microsystems, human–machine interfaces, and the Internet of Things (IoT).

Iontronics is a field of science and technology that combines ionic transport with electronic processes to develop devices that convert ionic interactions into measurable electrical signals. From a functional perspective, iontronic technologies can be broadly explored through two complementary approaches: (1) piezoionic energy harvesting and (2) piezoiontronic multimodal sensing.

Mechanical energy harvesting has gained considerable attention as a means of capturing ambient energy and converting it into usable electrical energy for portable and flexible electronic devices. Among various ambient energy sources, mechanical energy is particularly attractive because of its ubiquitous availability in the form of human motion, touch, vibration, fluid flow, and other mechanical stimuli. Piezoionic energy harvesting has emerged as a promising approach for mechanical energy conversion by utilizing the motion and redistribution of mobile ions in response to external stimuli. Unlike conventional piezoelectric systems, which generate electrical polarization through stress-induced changes in dipole alignment, and triboelectric systems, which rely on contact electrification and electrostatic induction, piezoionic systems exploit mechanically induced ionic redistribution to produce measurable electrical signals.

In addition to piezoionic energy harvesting, piezoiontronic sensing represents another important branch of iontronics, in which ionic materials are employed for pressure, temperature, and other multimodal sensing applications. In capacitive piezoiontronic sensors, pressure-induced ionic redistribution promotes the formation of a supercapacitive junction, known as an electrical double-layer (EDL) junction, at the ionic material–electrode interface. The formation and modulation of this junction can significantly increase the device capacitance, enabling highly sensitive pressure detection. These devices also offer the potential for a wide linear sensing range and multimodal sensing capabilities, making them promising for applications in robotics, electronic skin (e-skin), advanced human–machine interfaces, and underwater sensing.

To address these challenges, this thesis explores the rational design and development of microstructured ionic polymer-based materials using poly(vinylidene fluoride) (PVDF) incorporated with the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($[EMIM]^+[BF_4]^-$). The incorporation of mobile ionic species into the polymer matrix provides an effective means of modulating ionic transport and interfacial charge accumulation. Furthermore, engineered microarchitectures offer additional control over local stress distribution, mechanical deformation, and effective contact area during loading. These structural and ionic characteristics can work together to influence electrical output generation and enhance sensing performance. The developed materials and devices are investigated through experimental characterization, electrical measurements, and multiscale simulations to establish relationships among material composition, microstructure, ionic mobility, and device performance.

The structure of the thesis is outlined below.

Chapter 1: Introduction

This chapter introduces the fundamental principles of iontronics, focusing on piezoionic energy harvesting and piezoiontronic sensing for different applications. Both approaches involve pressure-induced ionic redistribution but utilize distinct mechanisms to achieve their respective functions. In piezoionic systems, pressure-driven ion migration generates a potential gradient, which is associated with the piezoionic coefficient and the resulting electrical output. In piezoiontronic sensors, pressure-induced changes in ionic distribution and the formation of electrical double layers (EDLs) at the ionic material–electrode interfaces produce measurable capacitive responses. The chapter discusses the working mechanisms of both systems, the role of ionic polymer electrolytes and ionic liquids in regulating charge transport, and the influence of polymer composition and microstructural engineering on device performance. It further describes the fundamental components and fabrication strategies used to develop piezoionic energy harvesters and piezoiontronic sensors. The performance parameters of piezoionic systems, including output voltage, current, and power density, are examined alongside those of piezoiontronic sensors, such as sensitivity, response time, limit of detection (LOD), and stability. Finally, the chapter reviews the materials commonly used in iontronic device fabrication, their limitations, and potential strategies to overcome these challenges. The chapter concludes by presenting the research motivation, objectives, scope, and organization of the thesis.

Chapter 2: Characterization Techniques, Theoretical Methods, and Electrical Measurement Techniques

The chapter further describes the characterization techniques employed to investigate the structural, morphological, chemical, electrical, and mechanical properties of the fabricated materials and devices. These include X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy and mapping, field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), and conductive AFM using the TUNA technique. These analyses are used to examine the crystalline phases of PVDF, the distribution of ionic species, the microstructural features of the polymer electrolyte, and the surface and local electrical properties of the fabricated films. Electrochemical impedance spectroscopy (EIS) is employed to investigate ionic transport and determine the electrical resistance and ionic conductivity of the electrolyte films. Dielectric characterization is used to evaluate the frequency and temperature-dependent dielectric permittivity, dielectric loss, and electrical modulus. Small-angle X-ray scattering (SAXS) and nanoindentation-based measurements are also included where applicable to examine nanoscale structural features and mechanical properties.

In addition to experimental characterization, molecular dynamics (MD) simulations are performed using Materials Studio and the COMPASS II force field to investigate ion–polymer interactions, radial distribution functions, mean-squared displacement, and pressure-dependent ionic mobility. Density functional theory (DFT)-based geometry optimization is used where applicable to examine the optimized molecular structures and interactions. Finite-element simulations are employed to analyse stress concentration, deformation, and contact-area evolution within the microstructured sensing architecture under applied pressure. These computational approaches provide complementary insights into the relationship between ionic transport, polymer structure, and pressure-dependent sensor response.

Finally, the chapter outlines the experimental setups and measurement protocols used to evaluate the performance of the fabricated iontronic devices. Electrical characterization includes capacitance measurements using a precision LCR meter, voltage and current measurements using an oscilloscope and source meter, and force-controlled pressure testing using a force gauge. Together, these methods establish the experimental and computational framework used to investigate the structure–property relationships and multifunctional sensing capabilities of the developed ionic polymer-based devices.

Chapter 3: Ion-dipole Engineered Hierarchical Ion-gradient Piezoionic Elastomers for Enhanced Soft Energy Harvesting

This chapter presents hierarchical ion-gradient piezoionic elastomers (HiGPiE), comprising ionic-liquid-filled spherulitic microcompartments with nanoscale asymmetric ion distributions. This architecture is established through ion–dipole interactions between $[EMIM]^+[BF_4]^-$ and PVDF chains, in which $[EMIM]^+$ cations are preferentially immobilized along the polymer backbones, whereas $[BF_4]^-$ anions remain relatively mobile. This asymmetric ionic arrangement promotes selective ion migration under applied stress. The enhanced charge separation arises from two synergistic mechanisms: (i) stress amplification within the spherulitic microcompartments and (ii) intrinsically asymmetric ion organization and migration, as supported by experimental investigations and theoretical analyses. HiGPiE containing 56 wt% ionic liquid achieves a high piezoionic coefficient of 73.5 ± 8 mV kPa^{-1} and an areal power density of 54 ± 4.7 mW m^{-2}, demonstrating promising performance for piezoionic energy harvesting.

Chapter 4: Ion-dipole Engineered Hierarchical Ion-gradient Piezoionic Elastomers for Enhanced Piezoiontronic and Multimodal Sensing

The hierarchical ion-gradient piezoionic elastomer (HiGPiE) was further employed in piezoiontronic sensing mode, where pressure-induced ionic redistribution enabled a tunable interfacial capacitance of approximately 17.2 μF cm^{-2} and a high sensitivity of 44.6 nF kPa^{-1}. Proof-of-concept demonstrations included a soft piezoionic mechanotransducer for wireless robotic control, physiological signal monitoring, and a multimodal iontronic skin capable of distinguishing tactile and thermal stimuli. Furthermore, machine-learning-assisted spatial localization of touch demonstrated the potential of HiGPiE for intelligent sensing and autonomous soft electronic systems.

Chapter 5: Microstructured Ionic Polymer-Based Multifunctional Iontronic Skin for Pressure Sensing, Object Recognition, and Underwater Environmental Monitoring

This chapter presents a multifunctional iontronic skin based on a microstructured ionic polymer (MSiP) comprising PVDF and $[EMIM]^+[BF_4]^-$ ion pairs. The MSiP layer is fabricated using maskless photolithography to produce a highly ordered micropillar array with a diameter of 30 μm, a height of 5 μm, and an interspacing of 20 μm. The iontronic skin is assembled by sandwiching the MSiP layer between flexible PDMS/PEDOT electrodes. Under applied pressure, the migration of highly mobile $[BF_4]^-$ anions, as elucidated by

molecular dynamics simulations, promotes electrical double-layer formation at the MSiP–electrode interface, thereby enhancing the capacitive response. Finite-element simulations further demonstrate that the microstructured architecture concentrates local stress, increases the effective contact area, and amplifies deformation during compression, contributing to the sensor's exceptional pressure sensitivity. The resulting sensor exhibits an ultrahigh pressure sensitivity of 833 kPa^{-1}, a highly linear response (R^2 = 0.98), and excellent mechanical durability over 20,000 loading–unloading cycles, while detecting pressures as low as 3 Pa. Integration with a robotic arm enables a tactile interface for real-time object grasping, lifting, and releasing in response to forces applied to the sensor surface. In addition, the sensor can be attached to the human body to monitor physiological signals and various body movements. When coupled with machine learning, it distinguishes objects with different mechanical properties, ranging from soft cloth to a rigid steel bottle, with a classification accuracy of 95–97%. Beyond on-land applications, the sensor demonstrates underwater multifunctional sensing, enabling depth monitoring over 0–35 cm, temperature detection from 20 to 80 °C, and salinity measurement across 0–8 ppt. Overall, this work establishes a versatile iontronic sensing platform with potential applications in wearable electronics, intelligent robotics, human–machine interfaces, and underwater environmental monitoring.

Chapter 6: Conclusion and Future Scope

This chapter summarizes the results and outlines the future scope of the work.

Research Publications:

1) Microstructured Ionic Polymer-Based Multifunctional Iontronic Skin for Pressure Sensing, Object Recognition, and Underwater Environmental Monitoring, ***Shubham***, Naman Patel, Hemant, Dileep Kumar, Tanish Maheshwari, Abhishek Kumar Singh, Vipin Amoli, ***ACS Applied Materials & Interfaces - ACS Publications, 2026. (Published)***
2) Ion-dipole Engineered Hierarchical Ion-gradient Piezoionic Elastomers for Enhanced Soft Energy Harvesting and Multimodal Sensing, ***Shubham,*** Hemant, Dileep Kumar, Naman Patel, Tanish Maheshwari, Prasanjit Kumar Dey, Amandeep, Vipin Amoli, ***(Revision submitted)***
3) Enhanced Dielectric Properties of Ionic Poly (vinylidene fluoride). ***(Manuscript under preparation)***

4) Highly Asymmetric Cu_{SA}-O_v-Ti_{3c} Atomic Sites Catalyst for Unprecedented Solar Hydrogen Generation, D. Kumar, A. Mishra, ***Shubham***, Hemant, S. Bhattacharjee, R. R. Urkude, B. Ghosh, A. Bhaumik, A. K. Sinha*, A.S.K. Sinha and V. Amoli* ***Advanced Energy Materials, 2024, 14, 2401964***
5) Highly Deformable and Durable PEDOT:PSS Printed Electrodes via Tailored Chemistry and Fabrication Synergy for Scalable Wearable Electronics, Hemant, ***Shubham,*** D. Kumar, C. Yadav, P. Raj, Amandeep, V. Amoli* ***Advanced Materials Technologies, 2025, 0:e01625.***
6) Defect-Induced Band Bending Mitigation Enables Bias and Photo-assisted Cathodic Response in Cu Single Atom Doped Faceted TiO_2 Thin Films Electrodes. D. Kumar, Hemant, A. K. Verma, S. Agrawal, J. S. Bhati, ***Shubham***, S. Singh, V. Amoli*. ***Chem Cat Chem,18,10,2026.***
7) Spray-Pyrolyzed PTAA/PVDF Flexible Gas Sensor for Selective NO2 and NO Detection with Machine Learning–Assisted Repeatability Analysis, Akash Chaurasia, Berj Kishor Jha, ***Shubham,*** Vipin Amoli, Abhishek Kumar Singh, Vijay Kumar Singh, ***IEEE Transactions on Electron Devices***. (Révision submitted)

Research publications 1 and 2 are included in the Thesis