MOLECULAR DYNAMICS SIMULATION STUDIES OF STRUCTURE AND STABILITY OF MODERN ELECTROLYTES IN HYDROPHOBIC NANOSCALE CONFINEMENTS AND NEAR METAL SURFACES

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by

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Submitted

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Dedicated to

My Grandfather

Late Sh. Katar Singh Dhattarwal

Certificate

This is to certify that the thesis titled "**MOLECULAR DYNAMICS SIMULATION STUDIES OF STRUCTURE AND STABILITY OF MODERN ELECTROLYTES IN HYDROPHOBIC NANOSCALE CONFINEMENTS AND NEAR METAL SURFACES**" is being submitted by **Mr. Harender Singh Dhattarwal** to the Department of Chemistry, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**. This thesis is a record of bonafide research work carried out by him under our supervision. In our opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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Abstract

In this thesis, we report the investigation of different electrolytes for next generation energy storage devices using molecular dynamics (MD) simulations. Owing to the safety concerns associated with conventional volatile and flammable electrolytes, several new electrolytes are now being explored as their replacement. The electrolytes studied here belong to different classes including ionic liquids, solvent-in-salt electrolytes, and fluorinated solvent based electrolytes. These electrolytes exhibit properties such as a wide electrochemical window, non-volatility, high chemical and thermal stability, and high ionic conductivity, which make them suitable candidate for energy storage. These unique properties of these electrolytes have motivated us to explore the molecular-level understanding of different processes occurring in batteries using them. The liquid structures of some of these electrolytes have been reported in the past. However, the studies on important battery processes such as electrolyte intercalation and interfacial reactions, which are the focus of this thesis, are scarce in the literature. Herein, we have thoroughly studied two important phenomena with regard to battery performance. These are (i) intercalation of electrolyte species in to nanoscopic pores on electrodes, and (ii) reductive stability of electrolyte constituents at the electrode surface.

In the first part of the thesis, we have reported the intercalation/deintercalation (capillary evaporation) behaviour of 1-ethyl-3-methylimidazolium tetrafluoroborate ($EmimBF_4$) ionic liquid and Li bis(trifluoromethanesulfonyl)imide (LiTFSI) water-in-salt electrolytes (WiSE) in nanoscale carbon confinements. The effect of confinement flexibility on the process of capillary evaporation of $EmimBF_4$ is explored through enhanced MD simulations. The number density profiles and orientational order parameters are analysed to provide insight on the structural changes in the ionic liquid

confined between solvophobic carbon nanosheets. Next, the effect of electrolyte concentration and confinement separation on the intercalation/deintercalation behaviour of LiTFSI WiSE is explored. A detailed mechanism of the electrolyte deintercalation from nanoscale graphite confinement is also provided through the analysis of free energy profiles.

In the second part of the thesis, we have reported the density functional theory (DFT) based MD simulation studies on the stability of electrolytes near Li metal surface. DFT-MD studies have provided mechanistic insights on the initial solid electrolyte interphase (SEI) formation in LiTFSI based superconcentrated electrolyte in acetonitrile solvent. Time-dependent bond length and bond order variations along with vibrational density of states were computed to validate the dissociation of different electrolyte species. The structure of the initial deposition of reduced species at the Li metal surface have been examined through radial distribution function and number density profiles. Finally, the investigation of reductive stability of fluorinated and non-fluorinated ether solvent based dilute electrolytes near Li metal surface is carried out using DFT-MD simulations. Overall, this thesis is a cohesive collection of systematic investigations on the stability and structure of several electrolytes under confinement and near Li metal surface.

सार

इस थीसिस में, हम आणविक गतिशीलता (MD) सिमुलेशन का उपयोग करके अगली पीढ़ी के ऊर्जा भंडारण उपकरणों के लिए विभिन्न इलेक्ट्रोलाइट्स की जांच की रिपोर्ट करते हैं। पारंपरिक वाष्पशील और ज्वलनशील इलेक्ट्रोलाइट्स से जुड़ी सुरक्षा चिंताओं के कारण, अब उनके प्रतिस्थापन के रूप में कई नए इलेक्ट्रोलाइट्स की खोज की जा रही है। यहां अध्ययन किए गए इलेक्ट्रोलाइट्स आयनिक तरल पदार्थ, सॉल्वेंट-इन-सॉल्ट इलेक्ट्रोलाइट्स और फ्लोरिनेटेड सॉल्वेंट आधारित इलेक्ट्रोलाइट्स सहित विभिन्न वर्गों से संबंधित हैं। ये इलेक्ट्रोलाइट्स एक विस्तृत विद्युत रासायनिक विन्डो, गैर-अस्थिरता, उच्च रासायनिक और थर्मल जैसे गुणों का प्रदर्शन करते हैं

स्थिरता, और उच्च आयनिक चालकता, जो उन्हें ऊर्जा भंडारण के लिए उपयुक्त उम्मीदवार बनाती है। इन इलेक्ट्रोलाइट्स के इन अद्वितीय गुणों ने हमें बैटरी में होने वाली विभिन्न प्रक्रियाओं की आणविक-स्तर की समझ का पता लगाने के लिए प्रेरित किया है। इनमें से कुछ इलेक्ट्रोलाइट्स की तरल संरचनाएं अतीत में बताई गई हैं। हालांकि, महत्वपूर्ण बैटरी प्रक्रियाओं जैसे इलेक्ट्रोलाइट इंटरकलेशन और इंटरफेसियल प्रतिक्रियाओं पर अध्ययन, जो इस थीसिस का फोकस हैं, साहित्य में दुर्लभ हैं। यहां, हमने बैटरी प्रदर्शन के संबंध में दो महत्वपूर्ण घटनाओं का गहन अध्ययन किया है। ये हैं (i) इलेक्ट्रोड पर नैनोस्कोपिक पोर्स में इलेक्ट्रोलाइट स्पीशीज का इंटरकलेशन, और (ii) इलेक्ट्रोड सतह पर इलेक्ट्रोलाइट घटकों की रिडक्टिव स्टेबिलिटी। थीसिस के पहले भाग में, हमने 1-एथिल-3-मेथिलिमिडाज़ोलियम टेट्राफ्लोरोबोरेट (EmimBF4) आयनिक तरल और लिथियमबीस (ट्राइफ्लोरोमेथेनसल्फोनील) इमाइड (LiTFSI) पानी-इंसाल्ट इलेक्ट्रोलाइट्स (WiSE) के इंटरकलेशन/डिइंटरकलेशन (केशिका वाष्पीकरण) व्यवहार की सूचना दी है, नैनोस्केल कार्बन कन्फाइन्मन्ट में। कन्फाइन्मन्ट का प्रभाव EmimBF4 के केशिका वाष्पीकरण की प्रक्रिया पर लचीलेपन को एमडी सिमुलेशन के माध्यम से खोजा गया है। सॉल्वोफोबिक कार्बन नैनोशीट्स के बीच सीमित आयनिक तरल में संरचनात्मक परिवर्तनों पर अंतर्दृष्टि प्रदान करने के लिए संख्या घनत्व प्रोफाइल और ओरिएंटल ऑर्डर पैरामीटर का विश्लेषण किया जाता है। इसके बाद, LiTFSI WiSE के अंतःक्षेपण/विघटन व्यवहार पर इलेक्ट्रोलाइट सांद्रता और कन्फाइन्मन्ट पृथक्करण के प्रभाव का पता लगाया जाता है। नैनोस्केल ग्रेफाइट कन्फाइन्मन्ट से इलेक्ट्रोलाइट विसंक्रमण का एक विस्तृत विश्लेषण ऊर्जा प्रोफाइल के माध्यम से प्रदान किया है।

थीसिस के दूसरे भाग में, हमने लिथियम धातु की सतह के पास इलेक्ट्रोलाइट्स की स्थिरता पर घनत्व कार्यात्मक सिद्धांत (DFT) आधारित MD सिमुलेशन अध्ययन की सूचना दी है। DFT-MD अध्ययनों ने एसीटोनिट्राइल सॉल्वेंट में LiTFSI आधारित सुपरकंसेंट्रेटेड इलेक्ट्रोलाइट में प्रारंभिक ठोस इलेक्ट्रोलाइट इंटरफेज़ (SEI) गठन पर यंत्रवत अंतर्दृष्टि प्रदान की है। विभिन्न इलेक्ट्रोलाइट प्रजातियों के पृथक्करण को मान्य करने के लिए अवस्था के कंपन घनत्व के साथ-साथ समय-निर्भर बॉन्ड लंबाई और बॉन्ड ऑर्डर विविधताओं की गणना की गई। लिथियम धातु की सतह पर कम प्रजातियों के प्रारंभिक जमाव की संरचना की जांच रेडियल वितरण समारोह और संख्या घनत्व प्रोफाइल के माध्यम से की गई है। अंत में, DFT-MD सिमुलेशन का उपयोग करके लिथियम धातु की सतह के पास फ्लोरिनेटेड और गैर-फ्लोरिनेटेड ईथर सॉल्वेंट आधारित तनु इलेक्ट्रोलाइट्स की रिडक्टिव स्थिरता की जांच की जाती है। कुल मिलाकर, यह थीसिस कन्फाइन्मन्ट के तहत और लिथियम धातु की सतह के पास कई इलेक्ट्रोलाइट्स की स्थिरता और संरचना पर व्यवस्थित जांच का एक समेकित संग्रह है।

Permissions

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1. **Harender S. Dhattarwal**, Richard C. Remsing, and Hemant K. Kashyap, Intercalation–deintercalation of water-in-salt electrolytes in nanoscale hydrophobic confinement. *Nanoscale*, **2021**, 13, 4195.

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