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14. ABSTRACT
The advancement of molecular simulation to model chemical reactions in condensed phase environments requires not only the development of new algorithms and parallelization strategies, but also access to state-of-the-art computer hardware. The transformative simulations made possible with this hardware will reveal the fundamentals of hydroxide ion solvation and transport in alkaline exchange membranes for fuel cells, currently being explored by seven PIs with a Department of Defense (ARO) MURI award. An objective of this collaboration is to examine the

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Report Title

Final Report: Specialized Computing Cluster for Simulation of Ion Transport Membranes

ABSTRACT

The advancement of molecular simulation to model chemical reactions in condensed phase environments requires not only the development of new algorithms and parallelization strategies, but also access to state-of-the-art computer hardware. The transformative simulations made possible with this hardware will reveal the fundamentals of hydroxide ion solvation and transport in alkaline exchange membranes for fuel cells, currently being explored by seven PIs with a Department of Defense (ARO) MURI award. An objective of this collaboration is to examine the ionic conductivity of the membranes, which depends on several properties, such as monomer concentration, permeability, and ionic strength across pores within the membrane. The coupling of a novel reactive MD methodology with the purchased hardware has greatly extended the accessible time and length scales of the simulations, making possible the study of hydroxide conductance as a function of the membrane morphology, in turn helping to determine optimal properties of the membrane structure that maximizes ion conductivity. The important molecular-level insight into the hydroxide transport mechanism within the membrane made possible by this computing hardware will facilitate development of key synthetic principles (a feedback loop between experiment and theory) to guide the design of new fuel cell materials.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Ulam Distinguished Scholar, Los Alamos National Laboratory

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
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Names of Faculty Supported

NAME	PERCENT_SUPPORTED
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Total Number:	

Names of Under Graduate students supported

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FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

The local structural properties of the hydroxide ion in ab initio molecular dynamics (AIMD) simulations with bulk water, benzyltrimethylammonium (BTMA) monomers, and the corresponding polymer are first carefully studied. The same AIMD data was then utilized to parametrize the first ever multistate reactive hydroxide model that accurately (and efficiently) describes both the structural and transport properties in anion exchange membranes (AEMs). These simulation results reveal important differences in the solvation structures of the hydroxide ion in bulk water vs. in AEM. Furthermore, because of the spatial heterogeneity in AEM, proton transfer reactions are particularly sensitive to the asymmetry in the distribution of water neighbors of the hydroxide ion. To obtain a reasonable reactive hydroxide model, the correct descriptions for the first water solvation shell around the hydroxide and the reaction rate for proton transfer within the first shell are crucial. Our latest reactive model shows that reactivity of the hydroxide ion in AEM is absolutely essential to explain the fast hydroxide self-diffusion constant, which would neither be attainable by any inert anions such as the fluoride or chloride ion, nor be correctly described by nonreactive models. Large simulations are currently underway to elucidate the fundamental mechanism of hydroxide transport in AEM. More details and the associated challenges are reported in the attached report.

Technology Transfer

Foreword

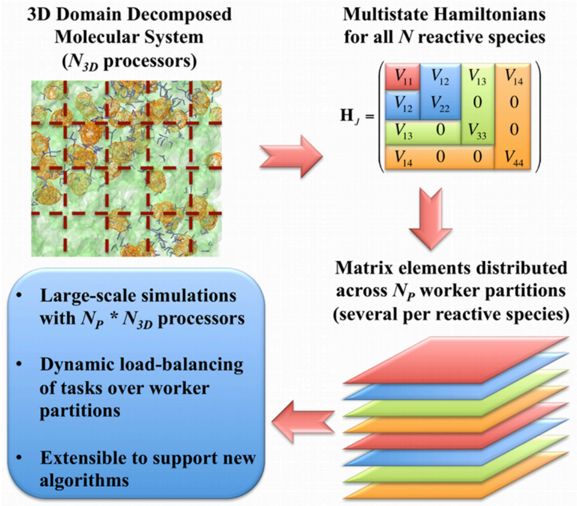

Figure 1. Scheme outlining newly developed manager/worker parallelization in RAPTOR for large-scale reactive simulations.

During Q4 2012, NVidia released the new line of K20 GPU accelerators and subsequently in March of 2013 users of the leadership computing resource Titan (Cray XK7) at the Oak Ridge Leadership Computing facility were granted access. Our research group had an allocation of computing time and used this opportunity to begin work on porting the RAPTOR code to GPUs. Given the modularity and flexibility of the LAMMPS source code, the initial port of RAPTOR to GPUs was relatively straightforward with an initial version successfully running on GPUs during the spring of 2013. As typical of porting codes to GPUs, one of the main performance challenges encountered was reducing communication costs of transferring data between the co-accelerator and host CPUs. As work on the GPU port and optimization continued, a parallel, but separate, effort to implement a new manager/worker parallelization strategy using Message Passing Interface (MPI) on CPUs was extremely successful (Figures 1 and 2). Similar in spirit to the originally planned GPU parallelization strategy, this CPU-based strategy distributes small batches of Hamiltonian matrix elements to separate worker partitions of processors for their simultaneous evaluation leading to significant performance improvements.

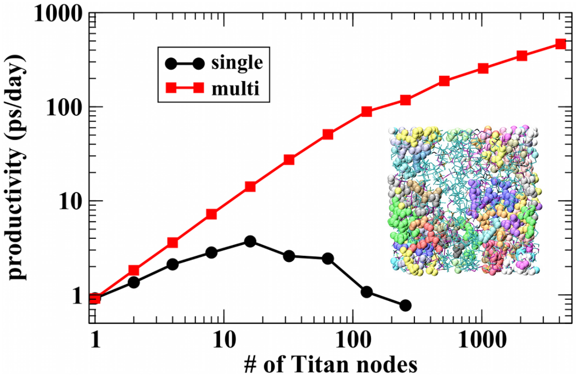

Figure 2. Performance of initial CPU-based manager/worker parallelization strategy (Q3 2013) for AEM simulation with 256 OH- using 16 cores/node.

By Q4 2013, the new NVidia K40 GPU accelerator was launched with significantly improved performance for single-precision floating-point operations and smaller increase in double precision performance. By then, Intel had already launched the new CPU-family, Ivy-bridge, to the market with the latest E5-2680v2 (dual 10-core 2.8 GHz) version available. Compared to the previous generation processor, Sandy-bridge, the newer processors were upgraded in several areas, such as clock rates and number of cores per processor. Such features intensively benefit the highly dense computing and data-transfer tasks in a molecular dynamics (MD) simulation with about 35%~40% increased productivity without any changes to source code.

Weighing all options available at the time and considering recent progress on both CPU and GPU development, the decision was made to purchase a CPU-only cluster based on the latest

Intel Ivy-bridge processors. With the same energy consumption (110 watts), E5-2680v2 gives much better performance than E5-2670. A computer cluster consisting of 38 nodes was built with each node configured with dual 10-core Intel 2.8 GHz "Ivy Bridge" Xeon E5-2680v2 processors (20 cores per node) and 64 GB DDR3 1600 MHz main memory. The interconnect is a 40 Gigabit network using non-blocking FDR10 Infiniband and high-speed GPFS shared disk space. This new cluster is housed and maintained within the newly constructed machine room operated by the Research Computing Center (RCC) at the University of Chicago. The new computational power and further algorithmic advances have shed light on the hydroxide transport in anion exchange membranes and enabled us to present our results that follow.

Statement of the problem studied

Anion exchange membrane (AEM) fuel cells have become a promising candidate to become the next generation fuel cell because of its associated low costs. In a basic environment, the oxygen reduction reaction is more facile, and it is possible to utilize non-noble metal catalysts such as iron, cobalt, or nickel. Furthermore, AEM fuel cells can theoretically operate on a more diverse selection of fuels such as the heavier alcohols (ethanol, ethylene glycol, etc.). We anticipate the hydroxide conductivity will one day be at least comparable to that now achieved with proton conductivity in proton exchange membranes. This opens the possibility of efficient and cheap fuel cells that will be readily available for civilian and military applications.

In this work, the main objective is to elucidate the fundamental molecular mechanism of hydroxide transport mechanism in AEM and understand how it differs from what we know in the bulk water situation. Computational simulations of the atomistic origins of hydroxide transport in anion exchange membranes rely on having an accurate and efficient description of hydroxide. Many details of hydroxide transport and solvation in water have been characterized with sophisticated experiments. Experiments cannot currently provide the needed resolution to understand the atomic details of AEM performance, so theoretical methods are required. To meet this objective, an improved multiscale reactive molecular dynamics (MS-RMD) hydroxide model that describes its transport accurately and efficiently for a membrane system is first formulated. In 2012, we successfully formulated a hydroxide model for bulk water,[1] but one should not just directly put this model in an AEM system in which the solvation structures of hydroxide are significantly different. As shown in the summary section below, we have achieved the new hydroxide model for AEM systems by also parametrizing against *ab initio* molecular dynamics (AIMD) data for also the solution of the monomer. Fully quantum mechanical dynamical calculations such as AIMD are computationally demanding and the collection of enough AIMD data for parametrization was only made possible by this grant.

The new MS-RMD hydroxide model is currently put to test to study poly (vinyl benzyltrimethylammonium) hydroxide [PVBTMA][OH],[2] an AEM system with a high concentration of hydroxide ions. By partitioning the calculations of the potential function into the Fourier (long-ranged) part and the (short-ranged) real part, the all-to-all inter-node message passive interface (MPI) communications can be significantly decreased and much better parallelization is achieved. With the state-of-the-art parallel algorithm, we are able to efficiently utilize the Intel Ivy Bridge nodes that were purchased with this grant for the self-consistent iterative calculations.[3] Hundreds of hydroxide ions and tens of thousands of atoms can be readily simulated with the current algorithms and computer power. With these new capabilities, an important goal of this research is to help guide experimental efforts through a complete understanding of hydroxide about its transport mechanism and its interactions with the polymer membranes is now possible.

Summary of the most important results

Different challenges are associated with constructing a physically accurate hydroxide model that works in a confined environment, such as an AEM system. The spatial heterogeneity in an AEM requires special attention in the parametrization. One should not simply put a hydroxide model that is parametrized for bulk water and use it in an AEM system to expect reasonable results for both structural and transport properties. For instance, Figure 3 shows the typical solvation structures around a hydroxide ion in both bulk water and in poly (vinyl benzyltrimethylammonium) AEM membrane (PVBTMA). In bulk water, the hydroxide ion is typically solvated by four water molecules that are hydrogen-bond donors and occasionally visited by a fifth water on the top of the hydroxide hydrogen. On the other hand, the hydroxide in PVBTMA is typically solvated by three hydrogen-bond donating water molecules and one transient hydrogen-bond accepting water that is on the top of the hydroxide hydrogen. The average water coordination number is just one of the many examples that display the differences in the hydroxide properties in bulk water and in a confined environment.

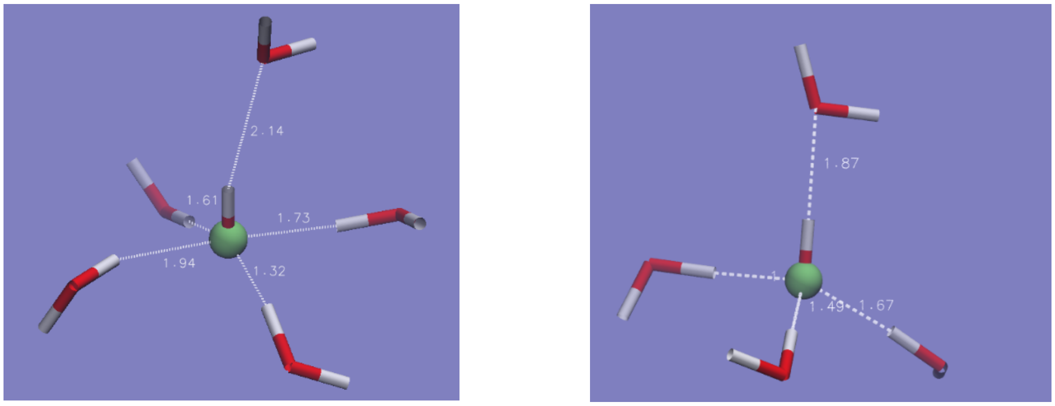

Figure 3: Typical solvation structures around a hydroxide ion in (left) bulk water and (right) in PVBTMA AEM sampled in AIMD with BLYP functional.

The hydrogen-bond donating water molecules do not all have the same distance to the hydroxide ion. The closest water that donates a hydrogen-bond to the hydroxide is called the "special pair" partner[4] because, when a proton transfer reaction happens, this special water becomes the next hydroxide ion (See Figure 4 left). However, when the special pairing is too strong, then proton rattles only between two oxygen centers. In bulk water, this problem is seldom seen because the faster water dynamics and the stronger interactions between the special water and its water neighbors will easily break this asymmetry. However, the asymmetry is a lot more stable when there is less water in an AEM system and rattling can easily become a problem. To tackle this problem in our new MS-RMD model for AEM, we have to carefully adjust the coupling strength between two valance bond states in order to weaken the asymmetry (See Figure 4 right).

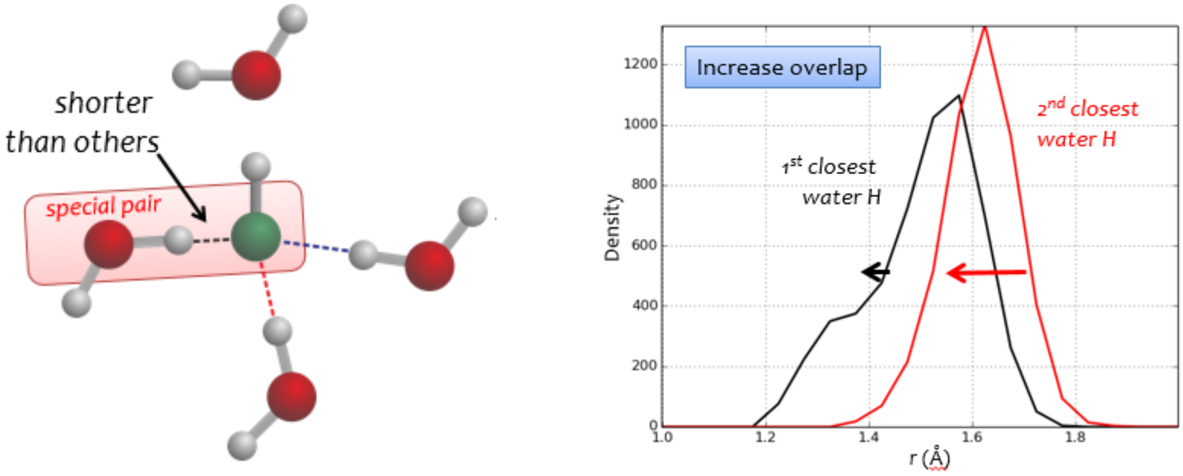

Figure 4: (Left) a schematic diagram that shows the special pair. If this pairing becomes too strong, there will be too much asymmetry in the proton transfer reaction and the proton will rattle between two oxygen centers. (Right) In the parametrization procedure in our new MS-RMD model, attention is given to decrease the discrepancy in the distances between the hydroxide and the solvating water neighbors so that a proton is more equally shared among the states.

In the PVBTMA AEM simulations, the polymer is described by the Generalized Amber Force Field (GAFF). In order to make GAFF compatible with our MS-RMD strategy, we make use of the standard Lennard-Jones mixing rules to handle the van der Waals interactions between most atoms of the polymer and hydroxide ions. We further adjusted the remaining pair interactions by matching the nitrogen-hydroxide oxygen (N-O*) radial distribution function (RDF) against the AIMD data for a solution of the BTMA monomers. This RDF provides the crucial information about the interactions between the cationic head group and the hydroxide in AEM. Without adjustments, the original hydroxide model (JCP 2012, Figure 5 left) parametrized for bulk water does not reproduce the first solvation peak in the AEM membrane, whereas, our new MS-RMD model is able to reasonably capture the first peak.

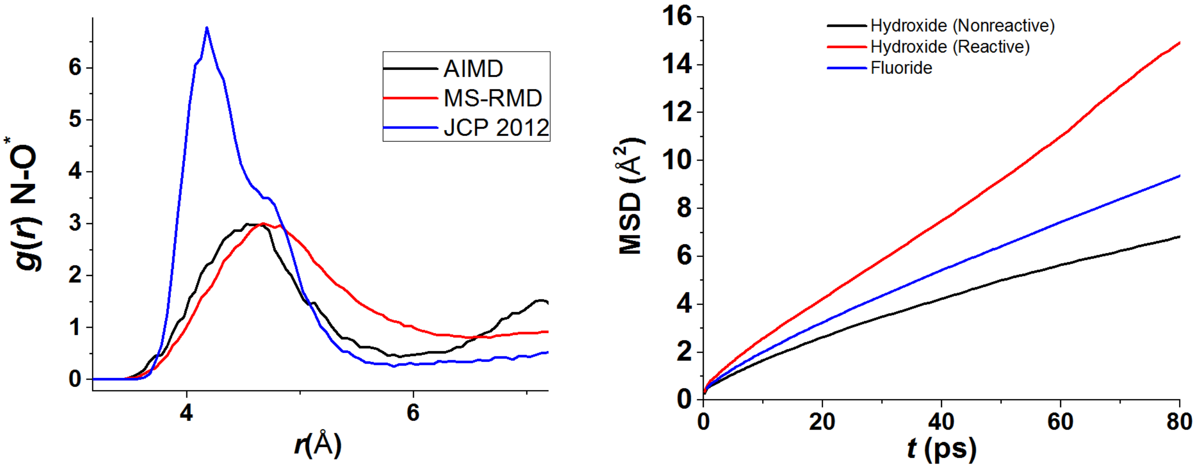

Figure 5: (Left) New MS-RMD model is parametrized to match the nitrogen-hydroxide oxygen (N-O^*) radial distribution functional so that the cationic head group and the hydroxide interactions are properly described. (Right) The mean-squared displacement (MSD) is plotted to show that reactivity is crucial for correctly describe hydroxide dynamics. Without, a nonreactive hydroxide would move slower than the fluoride ion.

After having implemented the adjustments required to handle the asymmetry problems and the N-O^* RDF, we now have a working hydroxide MS-RMD model that allows us to study hydroxide ion transport in PVBTMA AEM membrane. Our early results show that proton reactivity through the Grotthuss hopping mechanism significantly enhances the self-diffusion constant of the hydroxide. In the absence of reactivity, the self-diffusion constant of (nonreactive) hydroxide is slower than that of fluoride at the same conditions (See Figure 5 right). In the coming months, we will thoroughly study hydroxide structures and dynamics in PVBTMA AEM with this new MS-RMD model in a significantly larger setup in which there are 100 reactive hydroxide ions. This would not be possible in the past without the recent advances in our parallelism strategy for MS-RMD simulations and the recently gained computational power funded by the instrumentation program.

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