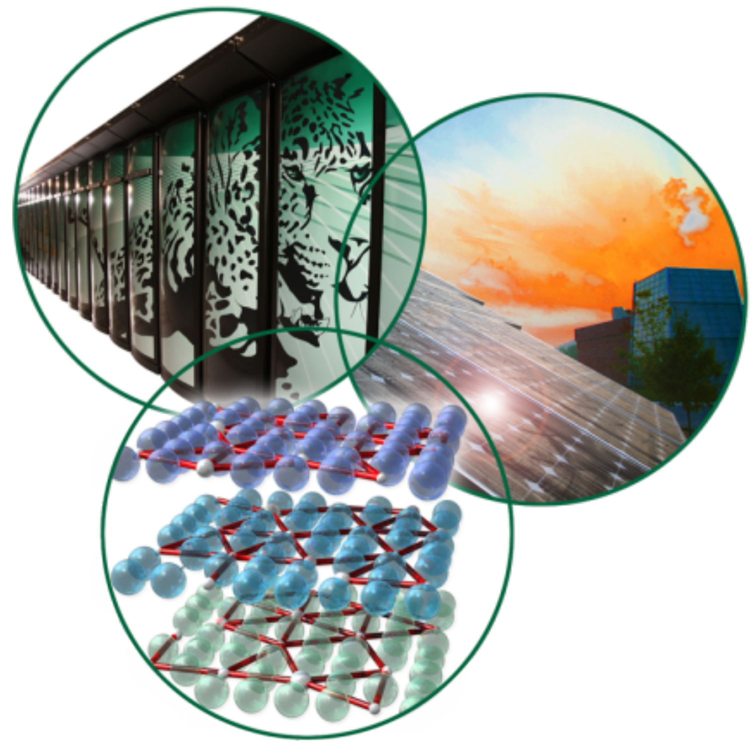
Ionic Liquids as Next Generation Anti-wear Additives
– *From Molecular Design to Engine Dynamometer Testing*

Jun Qu

Senior R&D Staff Scientist
Materials Science and Technology Division
Oak Ridge National laboratory

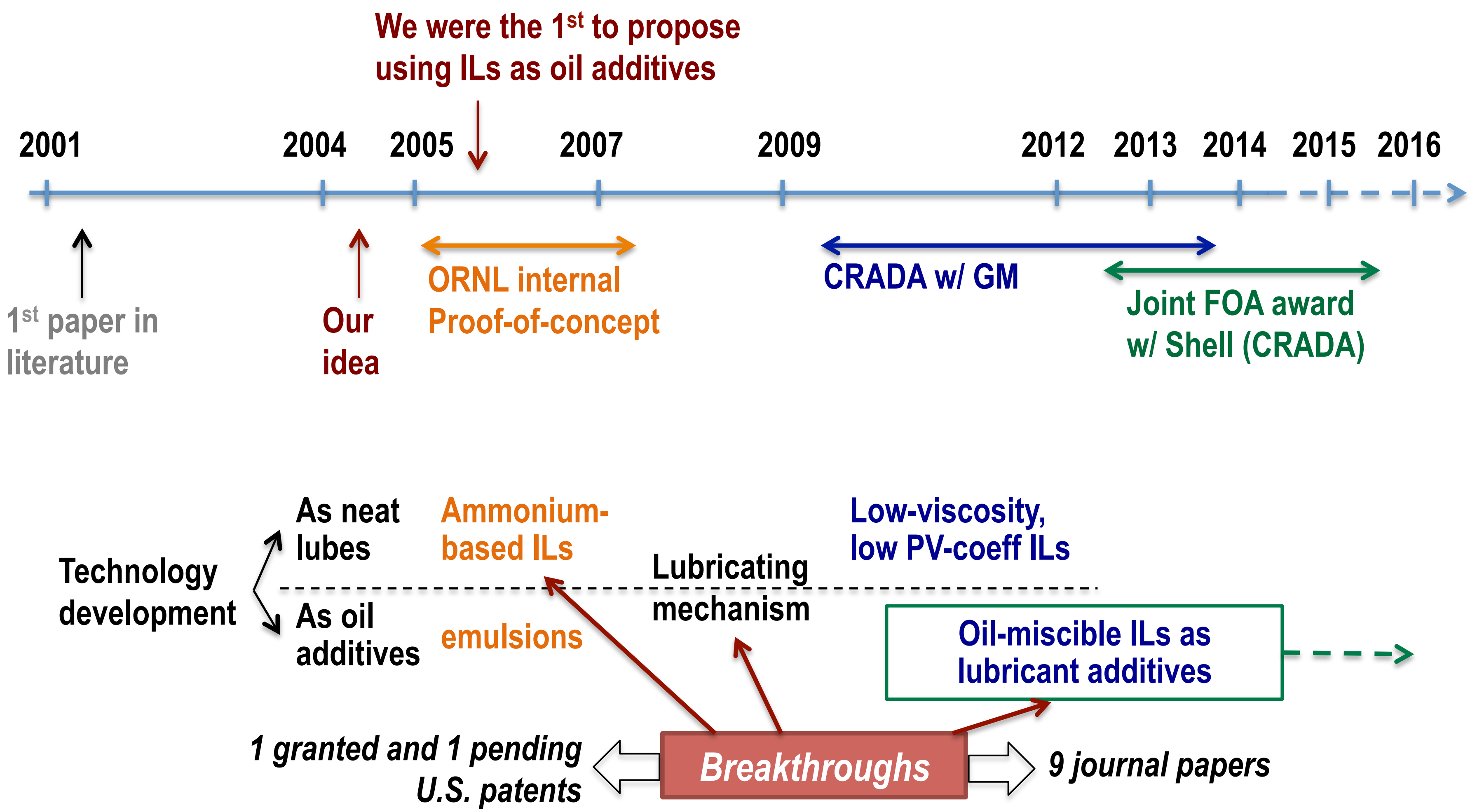


Research sponsored by the Fuels and Lubricants Program, Vehicle Technologies Office, Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy.

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

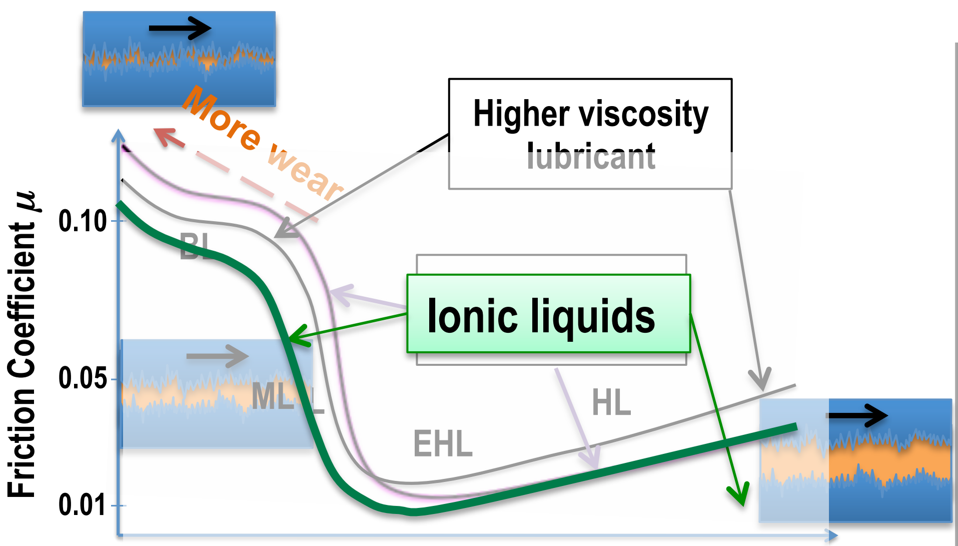
Program and technology development on Ionic Liquid Lubrication at ORNL



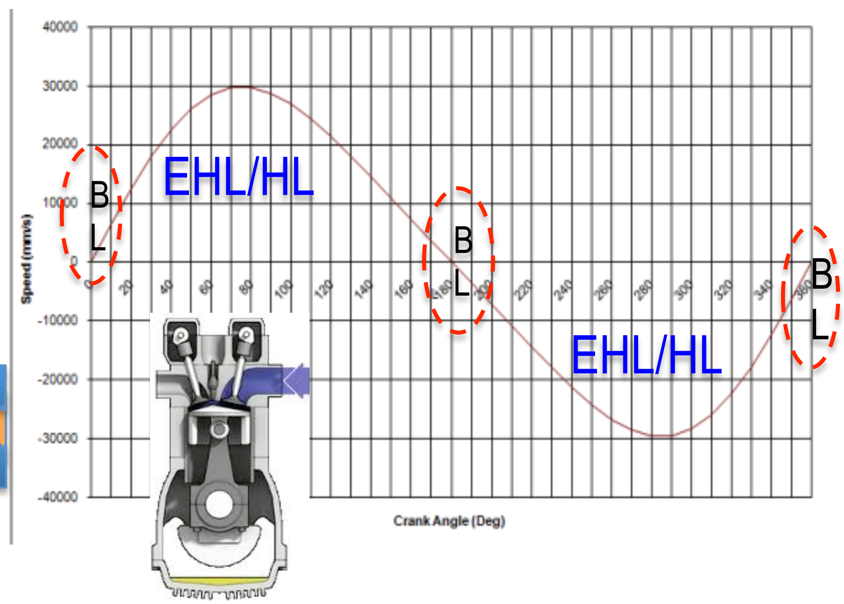
Ionic liquids for engine lubrication

- **Engine lubrication: ~80% at HD/EHD, 10-15% at ML, and 5-10% at BL**
- **Lower oil viscosity → reduced HD/EHD drag (better fuel economy) but more surface asperity collisions (wear challenge)**
- **Mitigation: more effective anti-wear (AW) additives**

- **Approach: developing ionic liquids as next-generation ashless AW additives to allow the usage of lower-viscosity engine oils.**



$$\lambda = \frac{t}{\sigma}, \quad where \quad t \propto \frac{U_e \cdot \eta}{P}$$



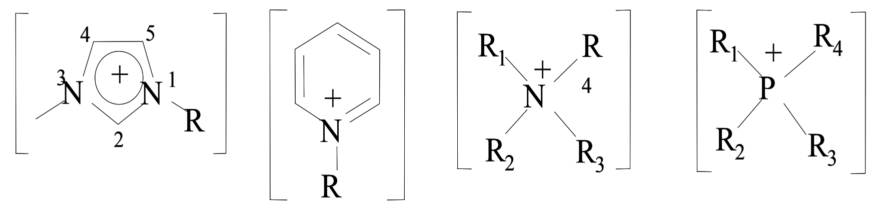
Jun Qu, 685-576-9304, qujn@ornl.gov

Ionic liquids for lubrication

- **ILs as neat lubricants or base stocks**
  - **High thermal stability (up to 500 °C)**
  - **High viscosity index (120-370)**
  - **Low EHL/ML friction due to low pressure-viscosity coefficient**
  - **Wear protection by tribo-film formation**
  - **Suitable for specialty bearing components**

- **ILs as oil additives**
  - **Potential multi-functions: AW/EP, FM,** *corrosion inhibitor, detergent*
  - **Ashless → low sludge**
  - **Allow the use of lower viscosity oils**
  - **Advantage: cost effective and easier to penetrate into the lubricant market**
  - **Problem: most ILs insoluble in oils**

Ionic liquids are 'room temperature molten salts', composed of cations & anions, instead of neutral molecules.



1-alkyl-3-methyl-imidazolium | *N*-alkyl-pyridinium | Tetraalkyl-ammonium | Tetraalkyl-phosphonium ($R_{1,2,3,4}$ = alkyl)

Common Cations

$[PF_6]^-$
$[(CF_3SO_2)_2N]^-$ (Tf_2N)
$[(C_2F_5SO_2)_2N]^-$ (BETI)
$[BR_1R_2R_3R_4]^-$
$[P(O)_2(OR)_2]^-$ (phosphate)
$[P(O)_2(R)_2]^-$ (phosphinate)

$[BF_4]^-$
$[CF_3SO_3]^-$

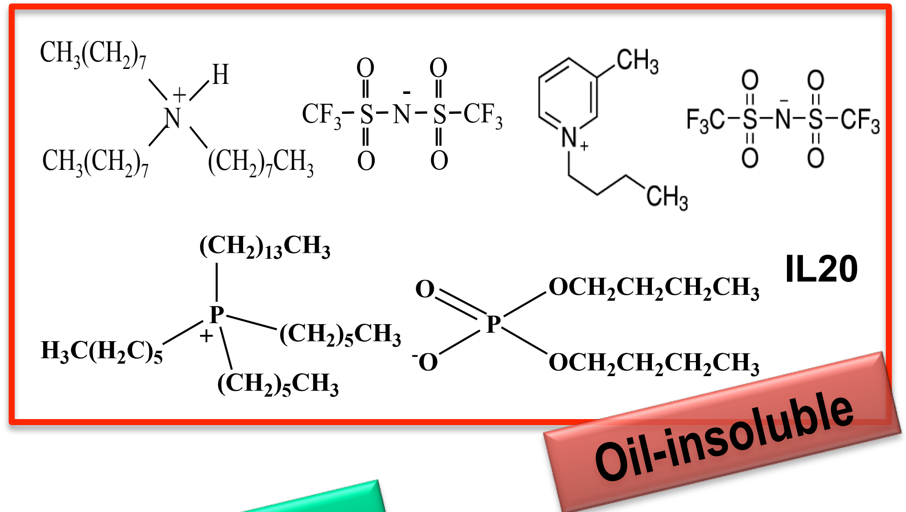
$[CH_3CO_2]^-$
$[CF_3CO_2]^-$, $[NO_3]^-$
Br^-, Cl^-, I^-
$[Al_2Cl_7]^-$, $[AlCl_4]^-$

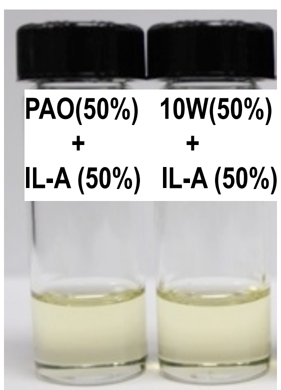
Common Anions

Jun Qu, 685-576-9304, qujn@ornl.gov

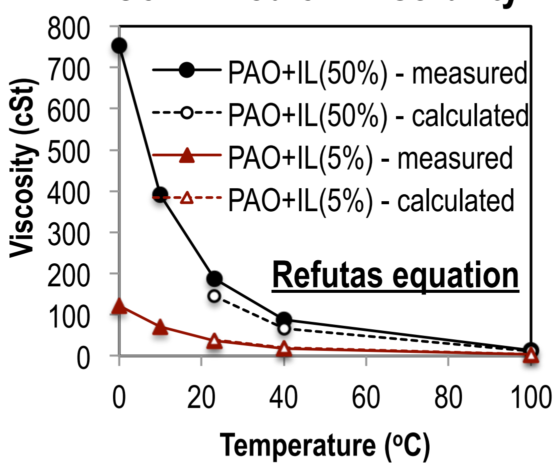
ORNL's breakthrough in oil-miscible ionic liquids

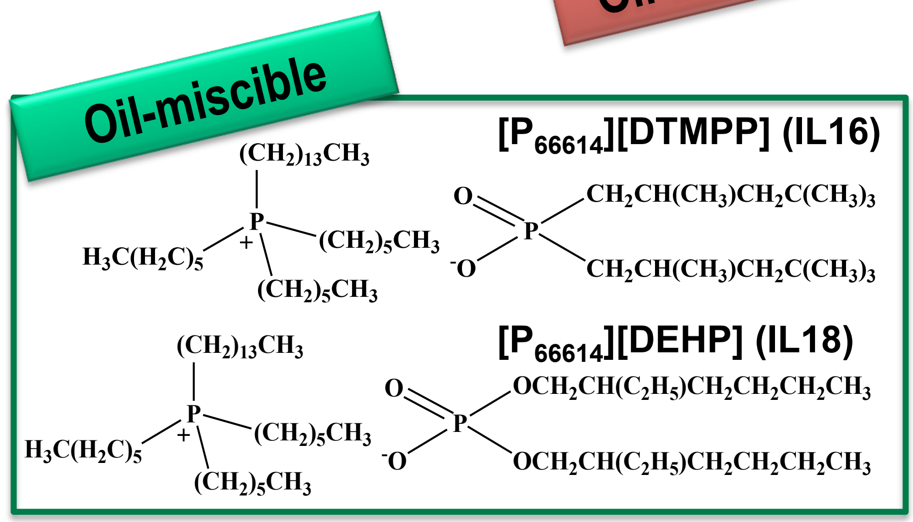
- **Most ILs have very limited oil-solubility (<<1%).**
  - 2D cations or small anions w/ intense charges
- **Molecular design criteria for oil-miscible ILs:**
  - 3D quaternary cations + surfactant anions
  - w/ long alkyls to dilute the charge to be compatible with neutral oil molecules





Confirmed oil-miscibility

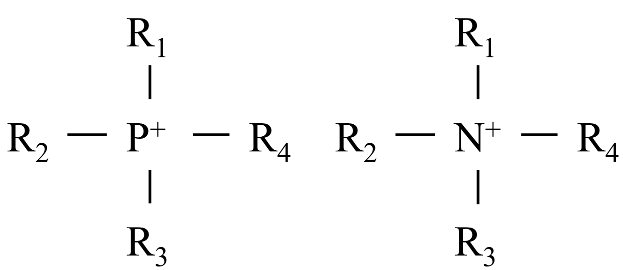




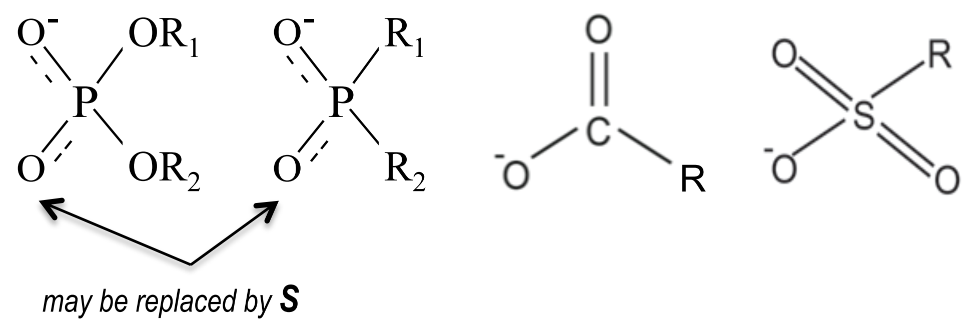
B. Yu, and J. Qu, et al., Wear (2012) 289 (2012) 58.*
J. Qu, et al., ACS Applied Materials & Interfaces 4 (2) (2012) 997.

In progress: multiple groups of oil-soluble ILs are being designed and synthesized…

Cation structures



Anion structures

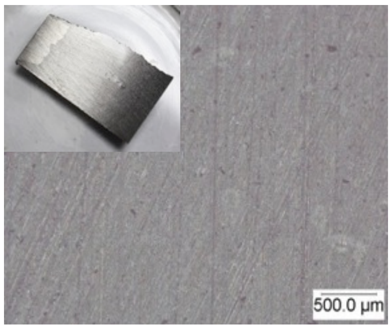


ORNL has developed more than a dozen of **ILs that are fully miscible** (>10%) in both mineral and synthetic base oils.

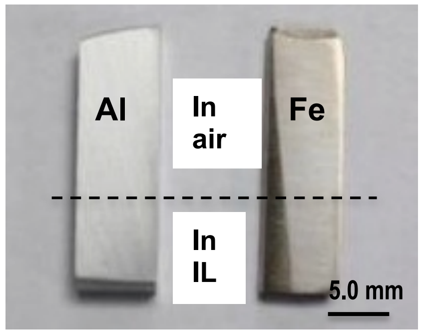
Jun Qu, 685-576-9304, qujn@ornl.gov

Non-corrosive, high wettability, and high thermal stability

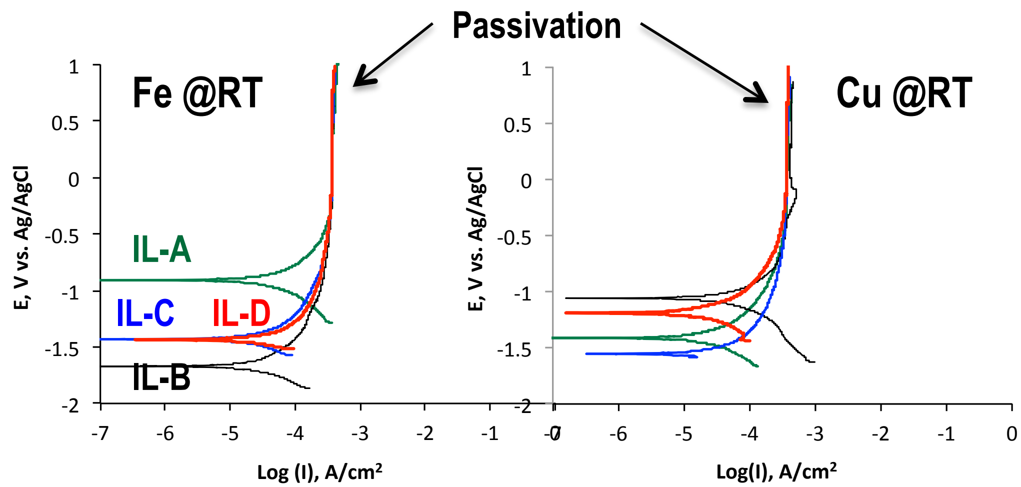
- **Non-corrosive to Fe or Al**



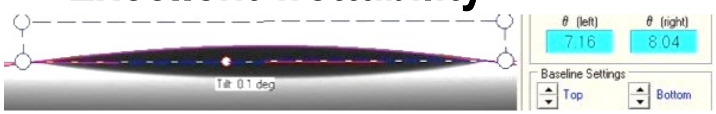
IL-A on cast iron surface in ambient for 60 days



Al and cast iron submerged in IL-A at 135 °C for 7 days



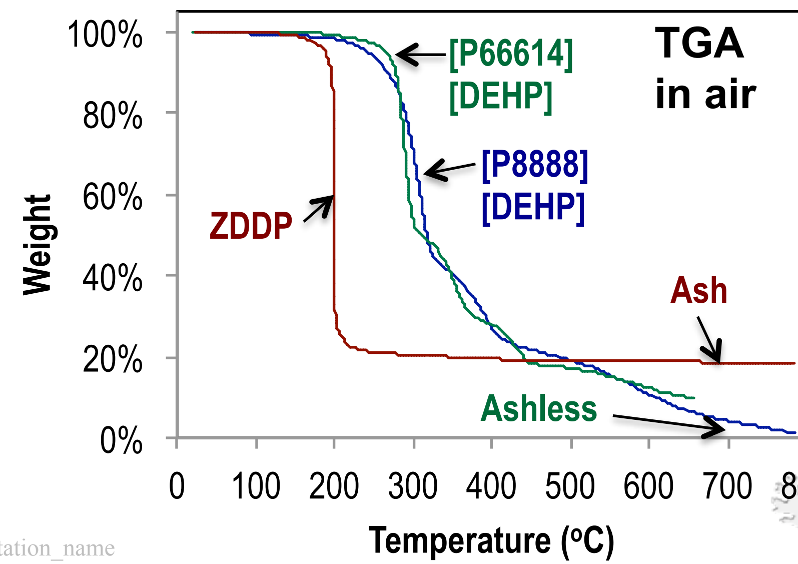
- **Excellent wettability**



	Contact angle on cast iron
PAO 4 cSt base oil	13.0
$[P_{66614}]$[BTMPP] (IL16, oil-miscible)	6.3
$[P_{66614}]$[DEHP] (IL18, oil-miscible)	7.6
$[BMIM][NTf_2]$ (oil-insoluble)	41.7

J. Qu, et al., ACS Applied Materials & Interfaces 4 (2) (2012) 997.

- **High thermal stability and ashless**



ILs' concentrations in GF-5 engine oils

ILSAC GF-5

3.a Catalyst Compatibility

Phosphorus Content, ASTM D4951	0.08% (mass) maximum
Phosphorus Volatility, ASTM D7320 (Sequence IIIGB, phosphorus retention)	79% minimum
Sulfur Content, ASTM D4951 or D2622	
0W-XX, 5W-XX	0.5% (mass) maximum
10W-30	0.6% (mass) maximum

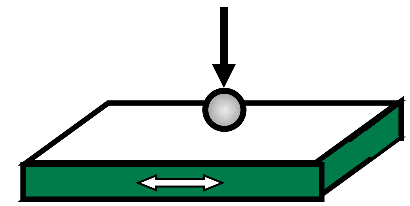
3.b Wear

Phosphorus Content, ASTM D4951	0.06% (mass) minimum

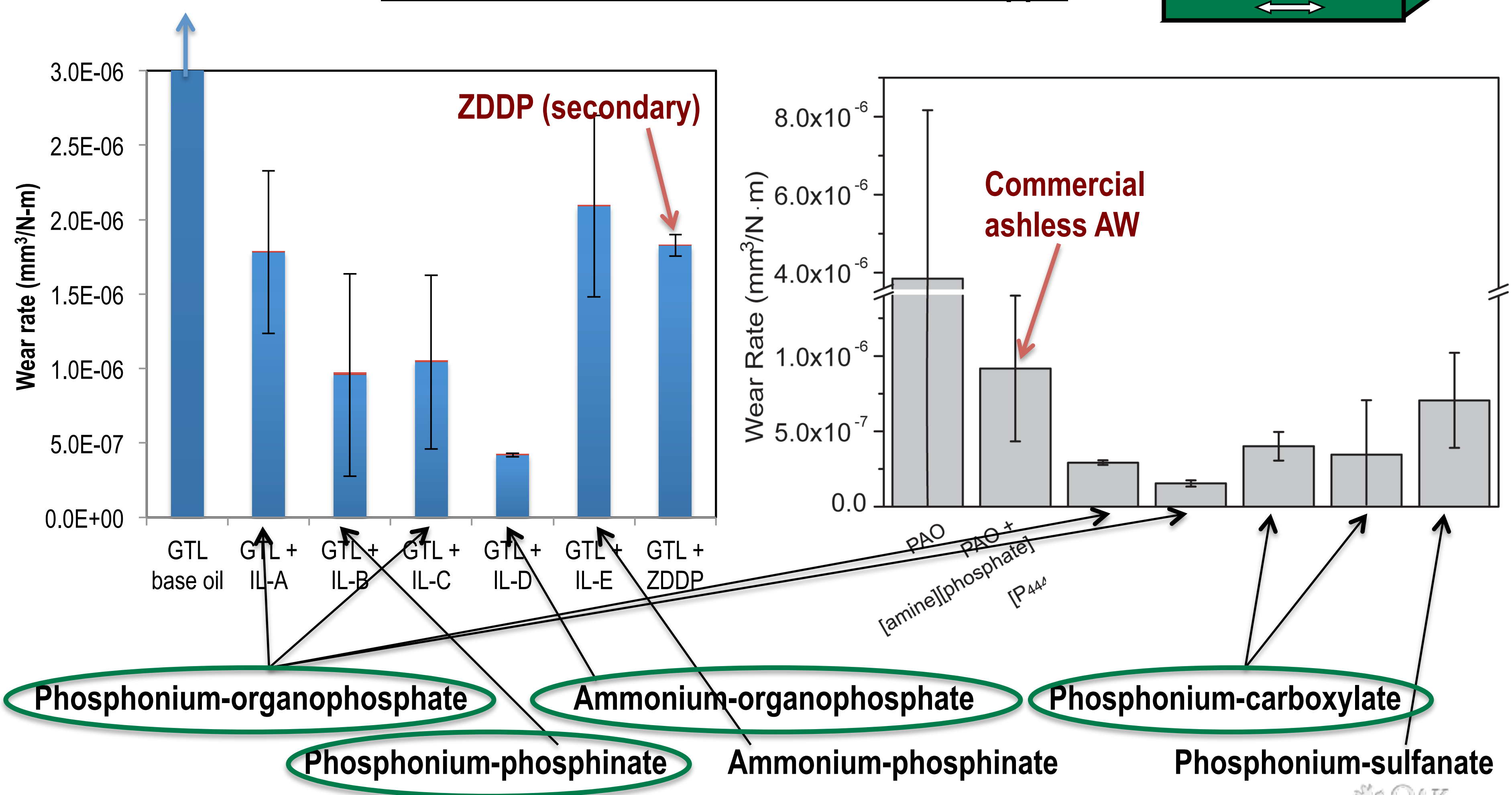
	MW	P (wt%)	S (wt%)	Zn (wt%)	Allowable concentration
ZDDP (Octyl)	771	8.04	16.6	8.43	**0.75 - 0.99 wt%**
[P_{66614}][DEHP]	804	7.71	0	0	**0.78 - 1.04 wt%**
[P_{8888}][DEHP]	804	7.71	0	0	**0.78 - 1.04 wt%**
[P_{66614}][BTMPP]	772	8.03	0	0	**0.75 - 0.99 wt%**
[N_{888H}][DEHP]	675	4.59	0	0	**1.31 - 1.74 wt%**
[P_{66614}][$C_{17}H_{35}COO$]	768	4.03	0	0	**1.49 - 1.98 wt%**

Jun Qu, 685-576-9304, qujn@ornl.gov

Tribological bench screening tests identified top-performing ILs



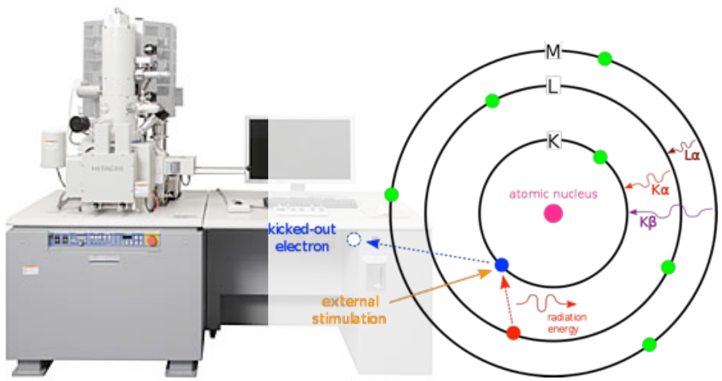
Base oil+AW at the same P content: ~800 ppm



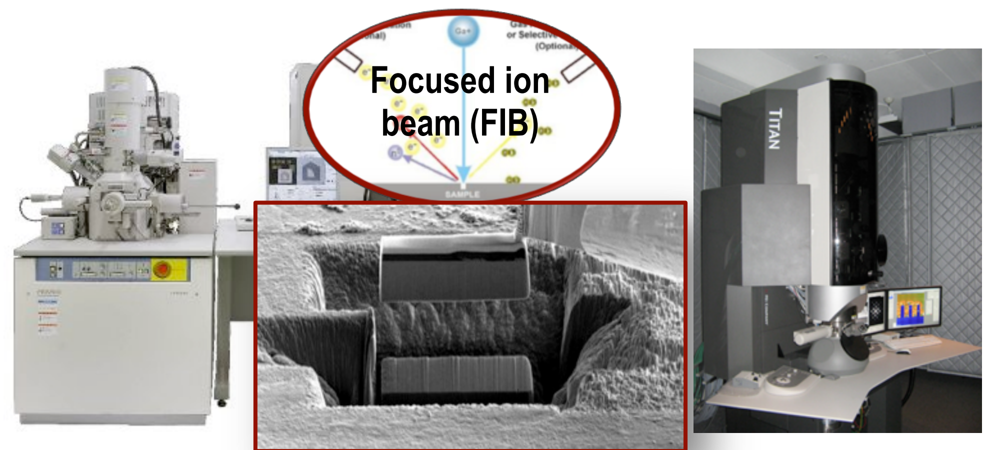
Jun Qu, 685-576-9304, qujn@ornl.gov

Fundamental understanding via comprehensive tribofilm characterization

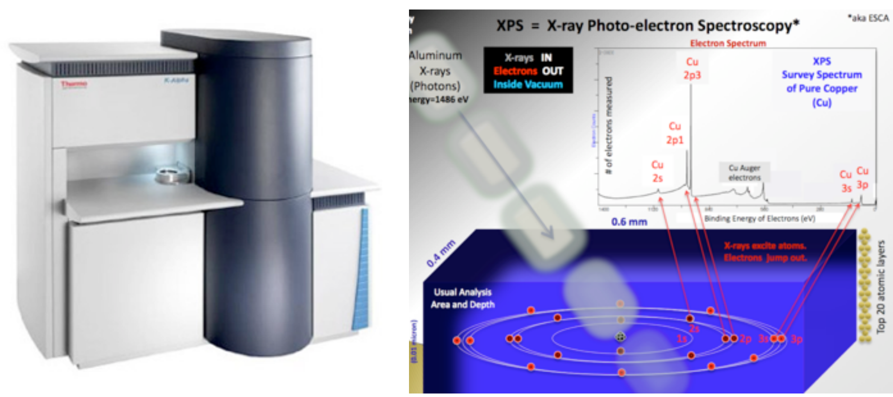
- SEM/EDS



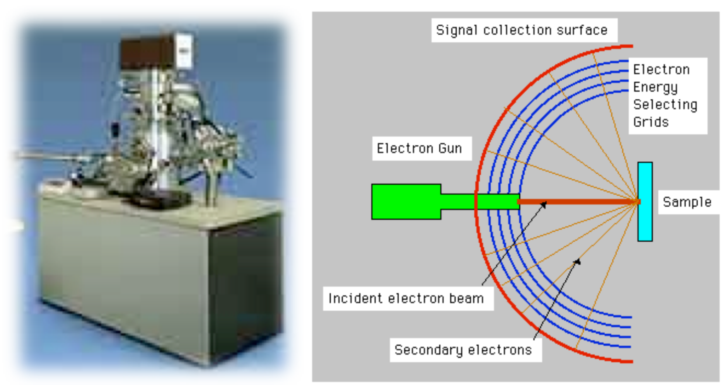
- FIB-aided cross-sectional TEM/Electron Diffraction/EDS



- X-ray photoelectron spectroscopy (XPS) aided by ion-sputtering



- Auger electron spectroscopy (AES)

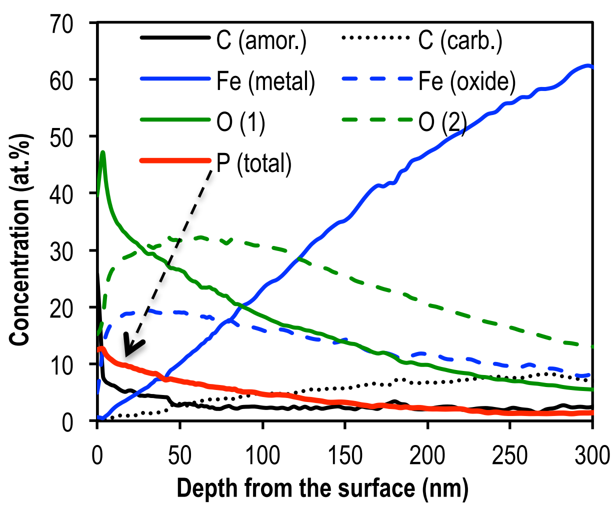


Jun Qu, 685-576-9304, qujn@ornl.gov

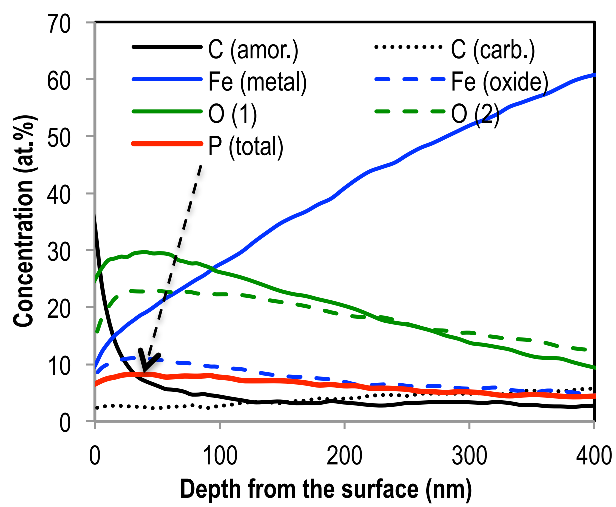
In progress: understanding the roles of cations and anions

- **Both the phosphonium cation and organophosphate anion are involved in tribofilm formation…**
- **Anions seem to be the primary contributor of IL tribofilms…**
- ***Currently correlating the IL chemistry to the tribofilm composition, nanostructure, and mechanical properties…***

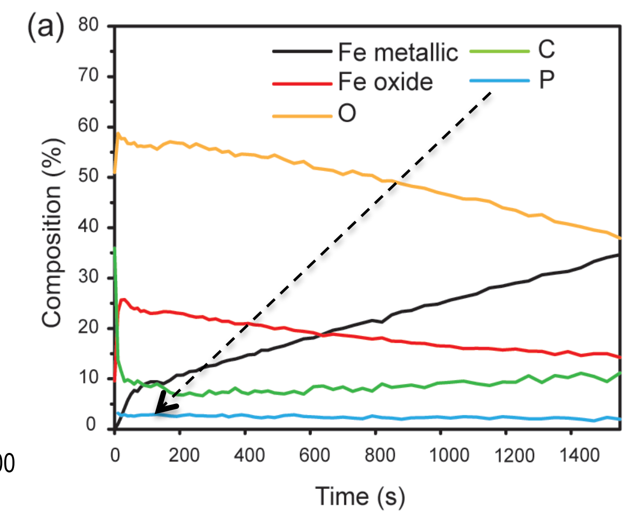
Phosphonium-organophosphate
Max P in tribofilm: 12 at%



Ammonium-organophosphate
Max P in tribofilm: 9 at%



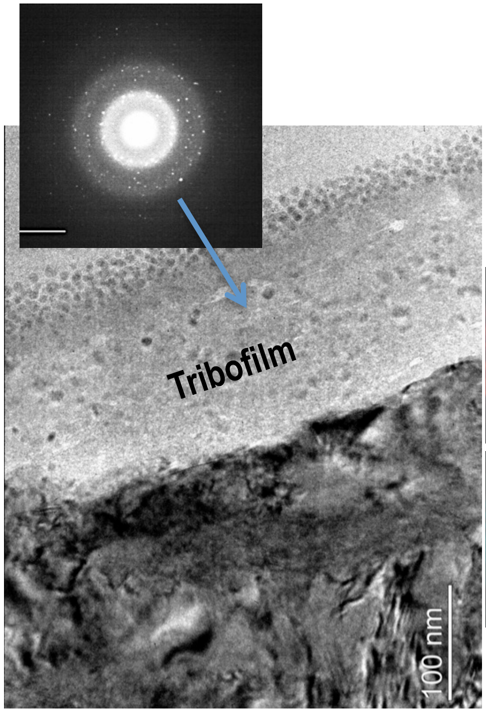
Phosphonium-carboxylate
Max P in tribofilm: 3 at%

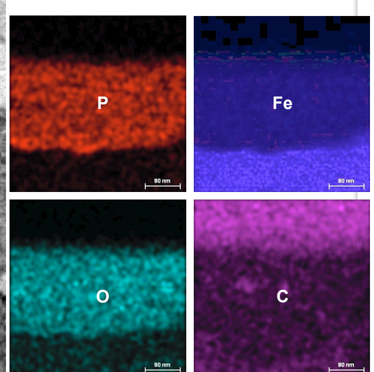


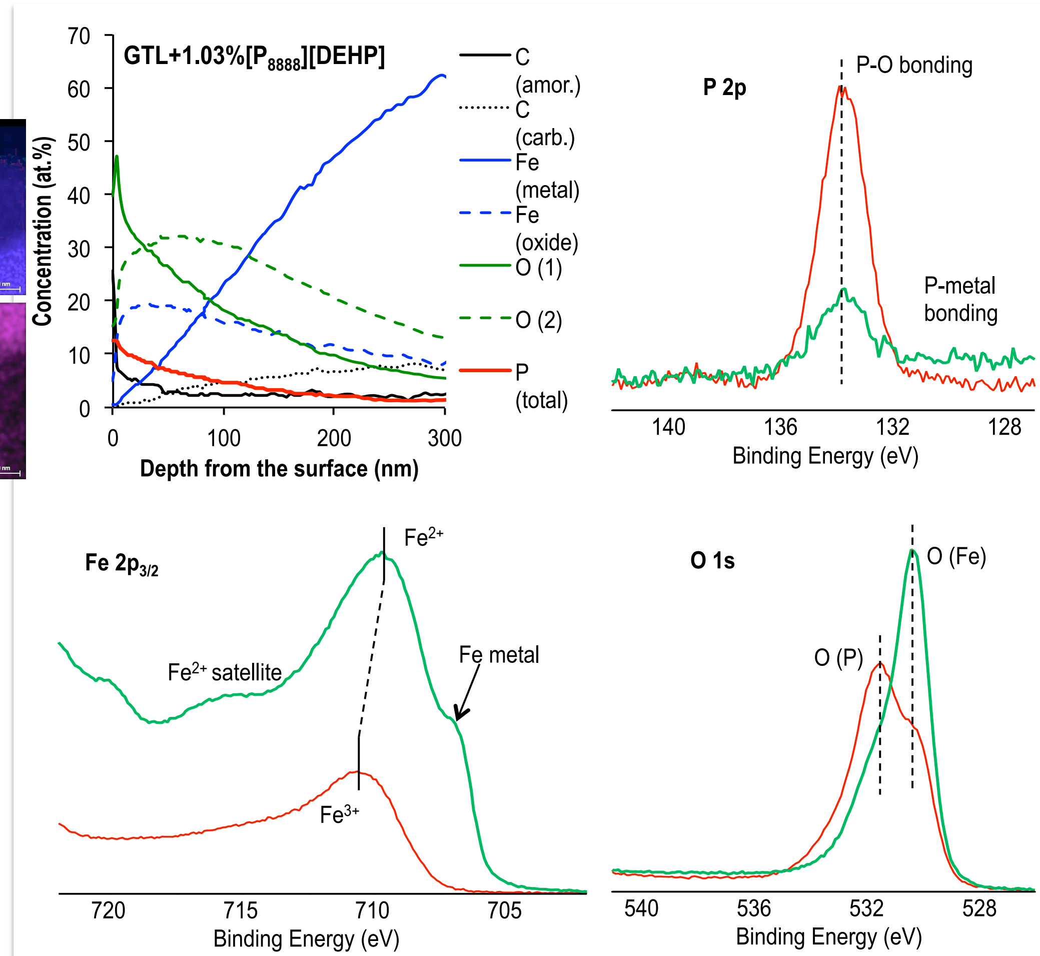
Same P content in base oil (800 ppm)

Jun Qu, 685-576-9304, qujn@ornl.gov

Tribofilm – phosphonium-organophosphate IL



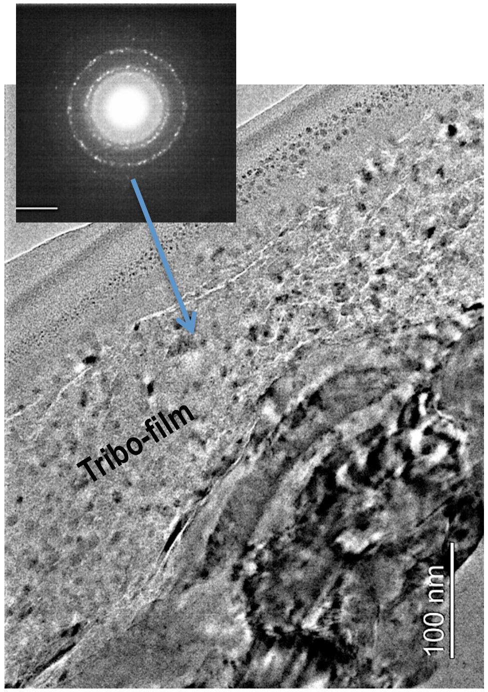


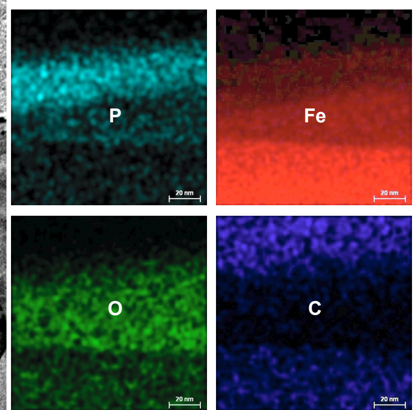


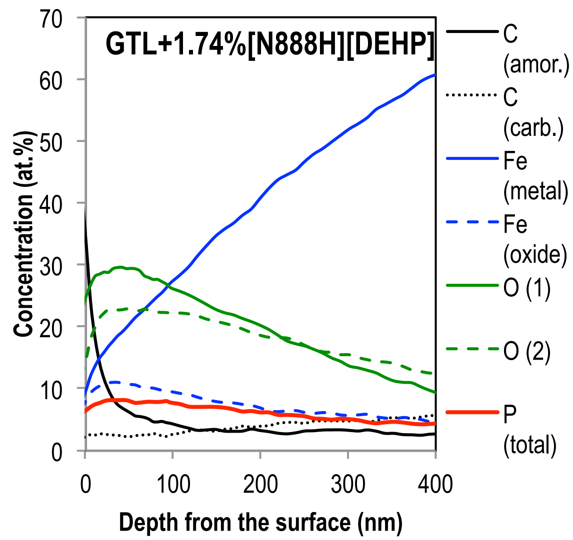
Tribofilm (up to 300 nm) on iron:

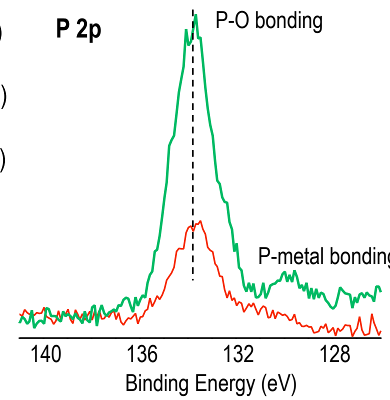
- Iron phosphates (~50 at%),
- Iron oxides (~30 at%),
- Phosphine oxides and carbonyl (~15 at%), and
- Metallic iron (<5 at%).

Tribofilm – ammonium-organophosphate IL



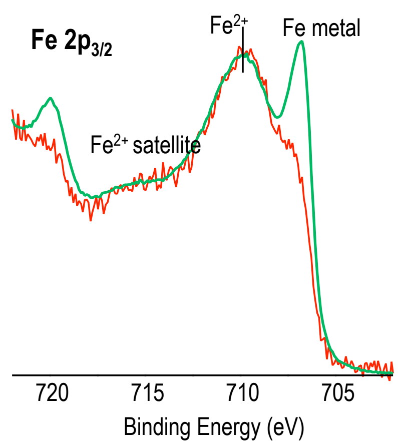


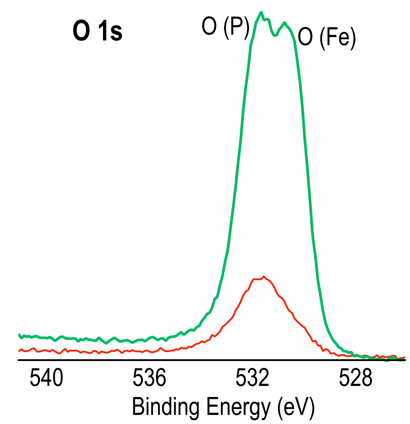




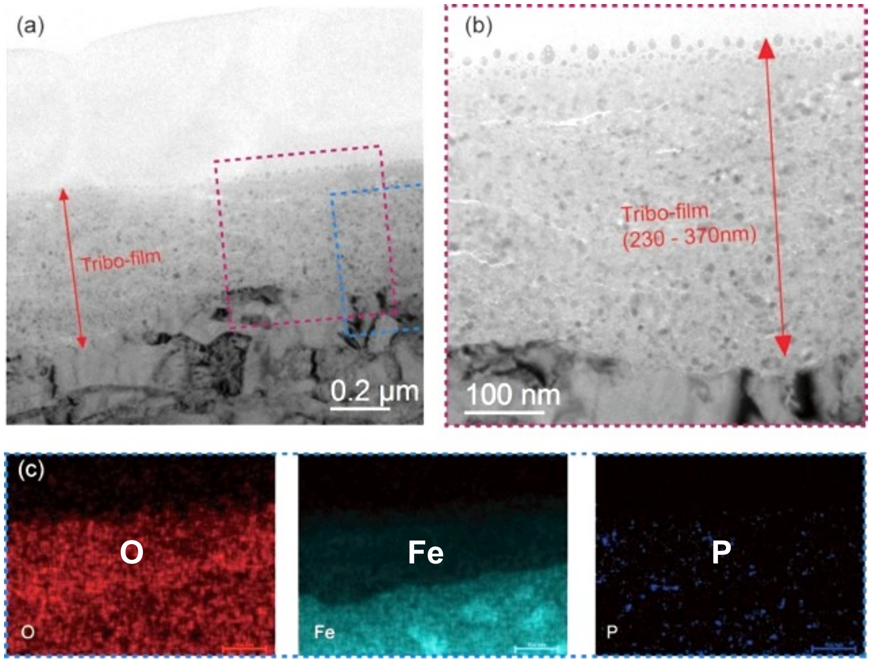
<u>Tribofilm (up to 400 nm) on iron:</u>

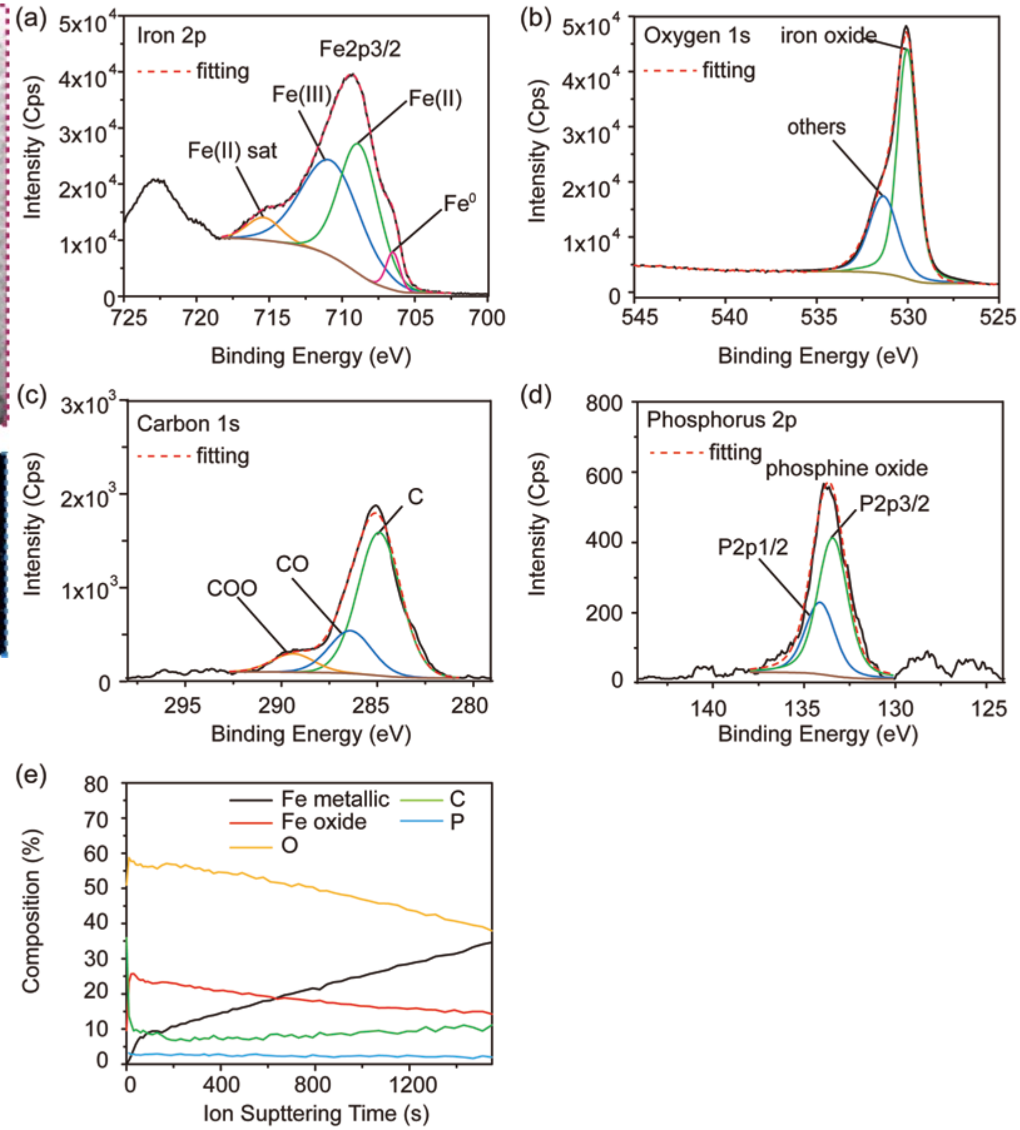
- Iron phosphates (~50 at%),
- Iron oxides (~20 at%),
- Carbonyl (~10 at%),
- Carbide (~5 at%), and
- Metallic iron (~15 at%).





Tribofilm – phosphonium-carboxylate IL



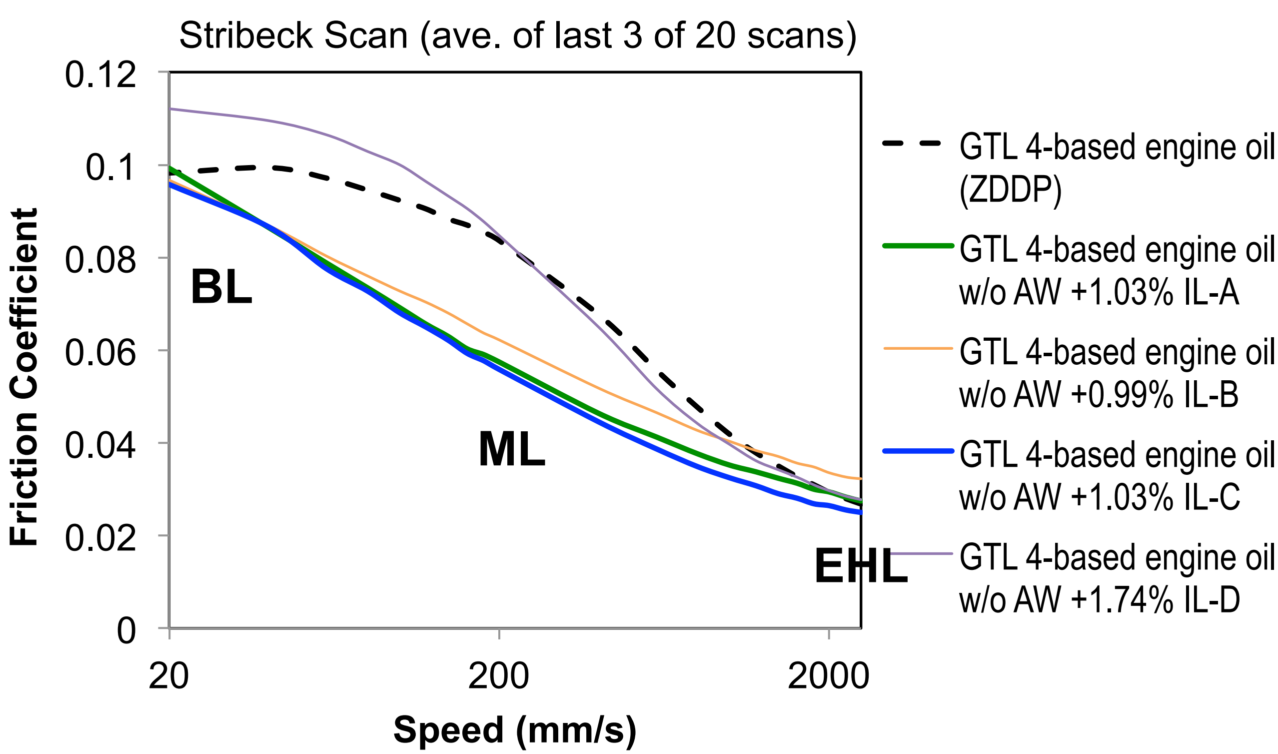


Tribofilm (up to 400 nm) on iron:

- Iron oxides (~55 at%),
- Iron carboxylates (~20 at%)
- Phosphine oxides (~15 at%), and
- Metallic iron (~10 at%).

ILs showed lower friction than ZDDP in mixed lubrication (FM-like behavior)

- **Formulated w/o AW + ILs compared with fully formulated oil**
- **25-50% friction reductions in mixed lubrication when IL-A, IL-B, or IL-C replacing ZDDP.**
- ***Hypothesis: smoother, lower-friction IL tribofilm***



Rolling-sliding bench tests on MTM2 at Shell

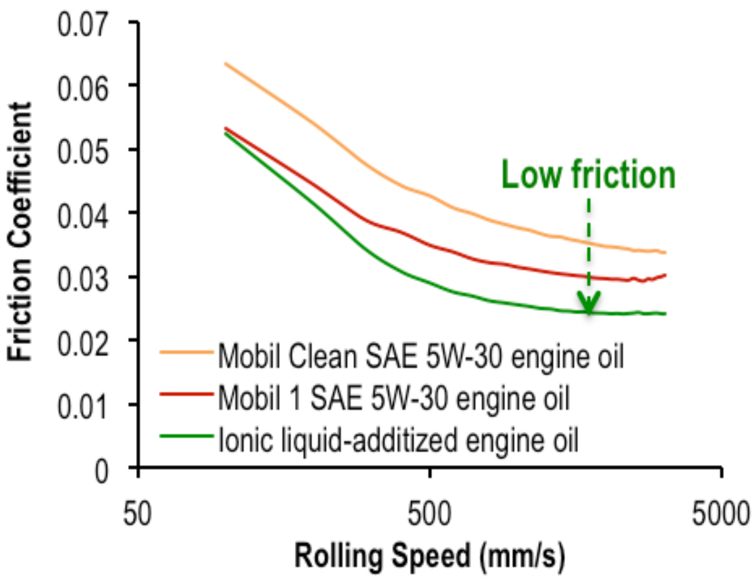
Jun Qu, 685-576-9304, qujn@ornl.gov

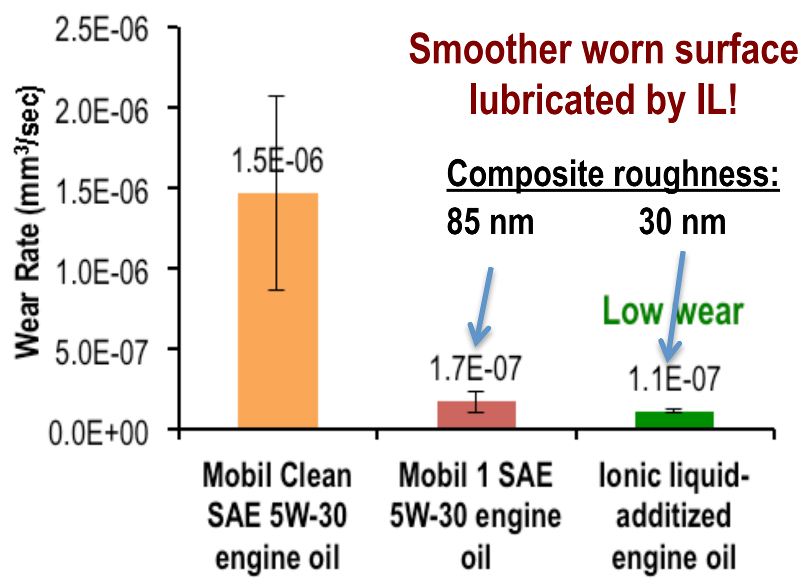
1st prototype IL-additized fully-formulated low-viscosity engine oil

- **Fully-formulated engine oil using PAO 4 cSt as the base oil and containing 1 wt.% IL18 (by Lubrizol)**

	cSt @ 40 °C	cSt @ 100 °C	HTHS (cP @150 °C)
Mobil 1™ 5W-30 engine oil	**64.27**	**11.38**	**3.11**
Mobil Clean™ 5W-30 oil	**56.1**	**10.1**	**3.06**
SAE XW-20 engine oil		>6.9, <9.3	>2.6
SAE XW-16 (newest)		>6.1, <8.2	>2.3
proposed SAE 12			*>2.0*
proposed SAE 8			*>1.7*
IL-additized engine oil	**25.53**	**5.38**	**1.85**

← **'SAE 8'**

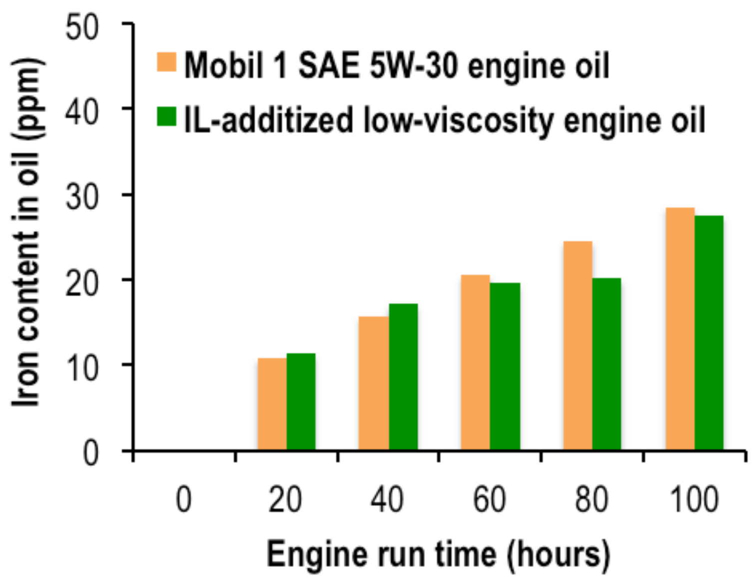




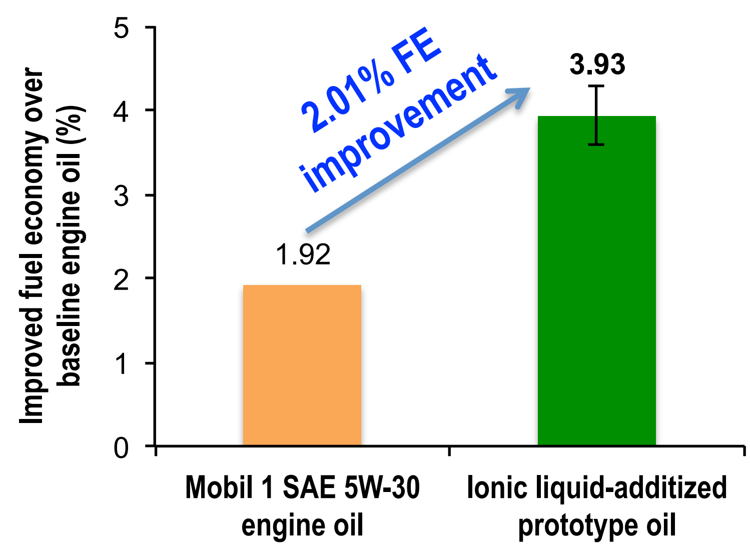
Rolling-sliding bench tests on MTM2 at GM

Engine dyno tests demonstrated good wear protection and 2% improved fuel economy

- High-temperature high-load engine test (GM)
  - LSX 6.2L Gen4 small block engine, rated at 450 HP
  - 100 hrs at 2700 rpm, 120 N load, 145 °C oil sump temp
- Oil consumed: 41.2 oz for IL-additized oil and 41.9 oz for Mobil 1™ 5W-30
- HTHS viscosity after 100 hrs: 1.85→2.03 cP for IL-additized oil and 3.11→3.17 cP for 5W-30



- GF-5/ Sequence VID (ASTM D 7589) test (InterTek)
  - 2008 Cadillac SRX 3.6L HF V6, 4-cycle engine
  - 200-2250 rpm, 20-110 N-m torque, 35-120 °C oil sump temp
  - Two aging stages: 16 hrs + 84 hrs
  - Baseline oil: SAE 20W-30 w/o FM or VII

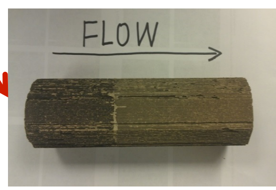


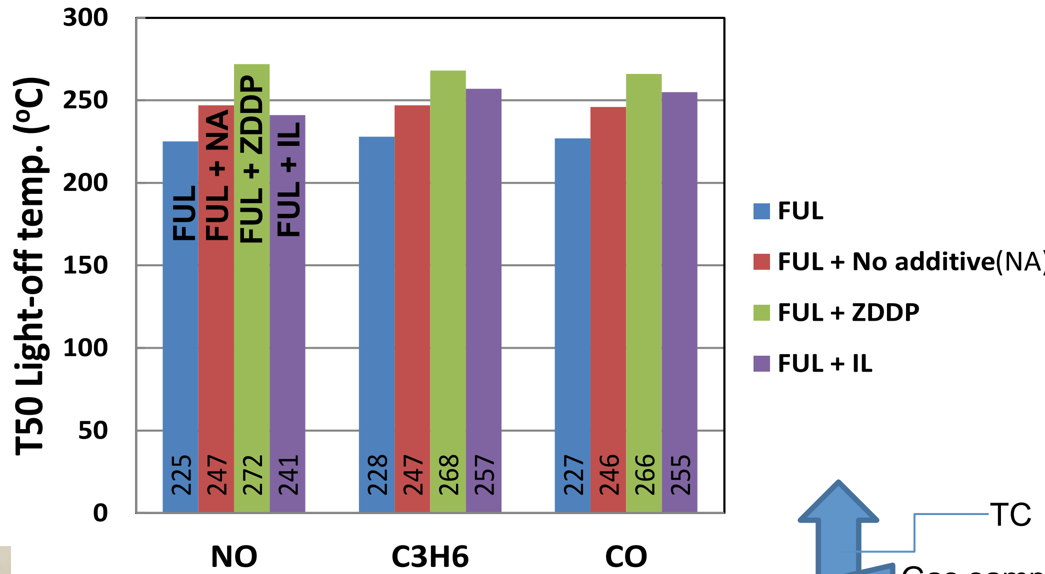
Jun Qu, 685-576-9304, qujn@ornl.gov

IL18 demonstrated potentially less adverse effects on TWC compared to ZDDP

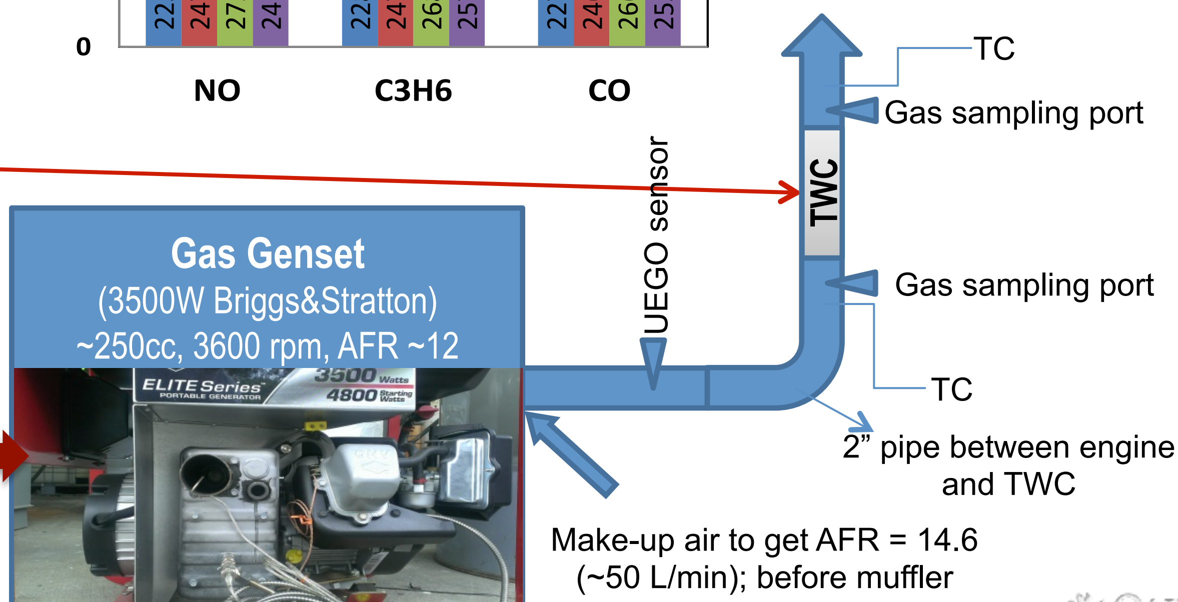
Close-coupled TWC from GM: aged to 150K miles, or the equivalent of full useful life

Catalyst core for engine aging





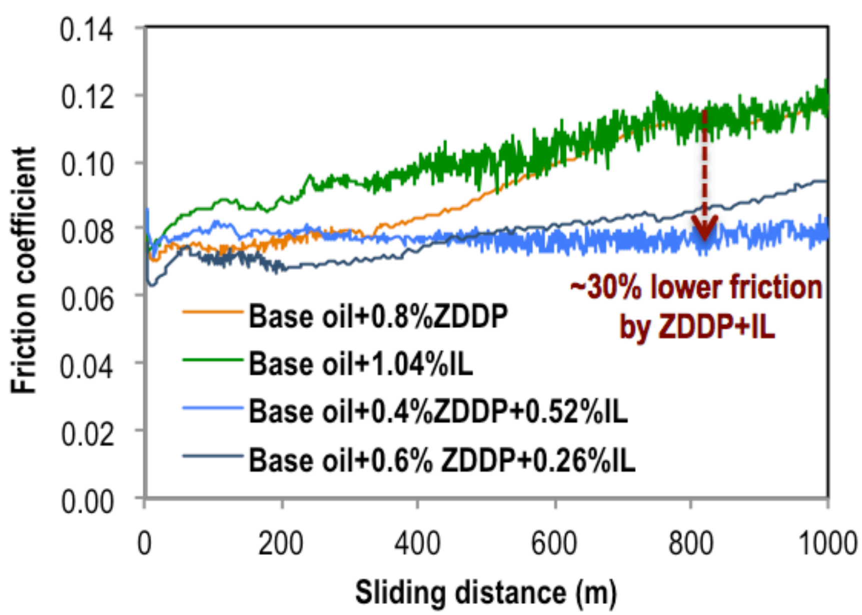
35 g of IL18 or ZDDP blended into the gasoline to simulate the maximum lifetime AW additive consumption in a modern automotive engine

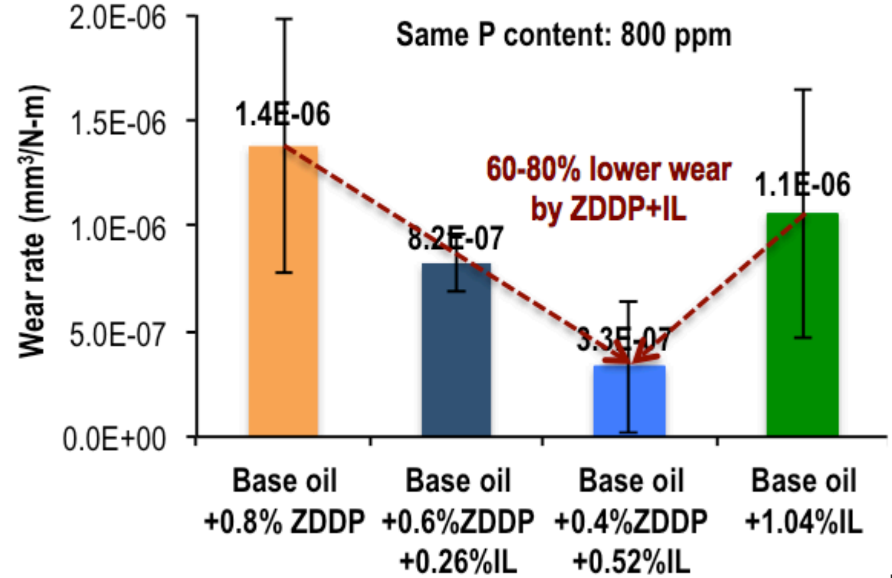


Jun Qu, 685-576-9304, qujn@ornl.gov

In progress: synergistic effects between IL and ZDDP

- Substantial friction and wear reduction by mixing IL (from a certain group) and ZDDP into a oil compared to either the IL or ZDDP alone at the same P content.
- Strongest synergistic effects at 1:1 molar ratio for IL:ZDDP.
- No such a synergy for two other groups of oil-miscible ILs (one different in cation and another different in anion).
  - Again suggest important roles for both the cation and the anion.

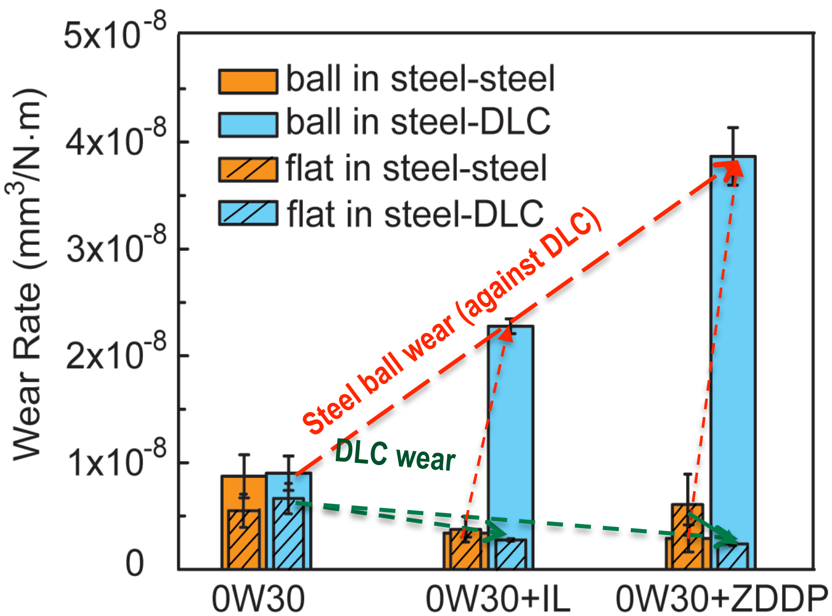


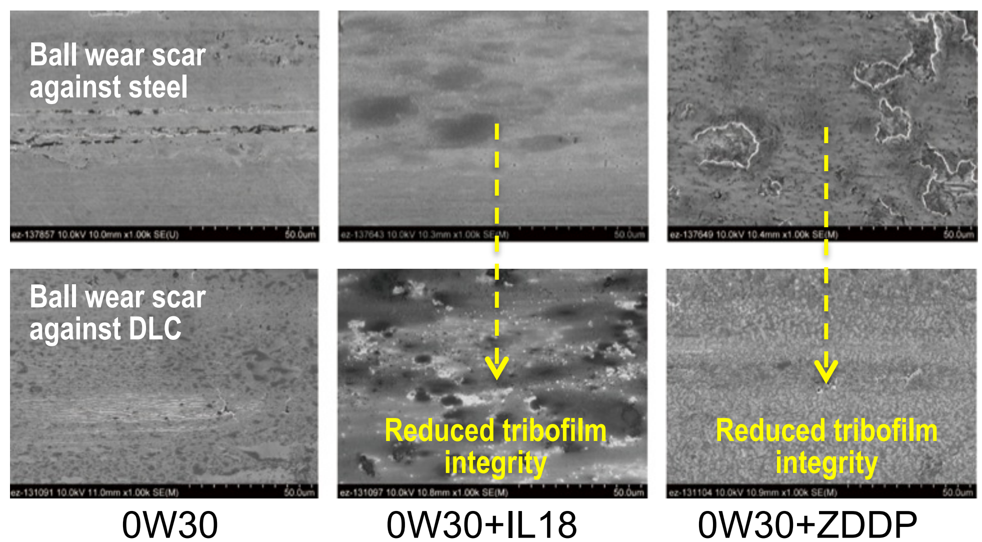


Jun Qu, 685-576-9304, qujn@ornl.gov

In progress: ZDDP or IL with hard coatings

- AW additive (either ZDDP or IL18) alone (w/o DLC) reduced the wear rates for both the ball and flat in the steel-steel contact, as expected;
- Diamond-like-carbon (DLC) alone showed no negative impact on wear or friction;
- Combination of AW (ZDDP or IL18) and DLC further reduced the flat wear, however surprisingly increased the counter steel ball wear!
  - ZDDP+DLC produced 8X and 4X higher wear on the counter steel ball than using the ZDDP and DLC alone, respectively!
- *Hypothesis: competition between AW tribofilm formation and graphite transfer→ poor tribofilm integrity→ higher wear rate of the steel ball.*





Jun Qu, 685-576-9304, qujn@ornl.gov

Summary

- Accomplishments
  - A series of oil-miscible ionic liquids have been developed as candidate ashless additives for engine lubricants with potential multiple functionalities including AW, FM, detergent, antioxidant, etc.
  - 1st prototype IL-additized, low-viscosity engine oil has been formulated.
  - Engine dynamometer tests of the IL-additized engine oil demonstrated >2% improved fuel economy with comparable engine wear protection compared to Mobil 1 SAE 5W-30 engine oil.
  - Ionic liquids have potentially less adverse impact on TWC compared to ZDDP.
  - The ORNL-GM CRADA project had been successfully concluded in Sept. 2013, and a new joint FOA proposal was recently submitted to DOE for follow-on R&D.
- On-going activities
  - Further developing and optimizing the IL molecular structures for lubrication
  - Deeper fundamental understanding the mechanisms of IL lubrication
  - Seeking synergy between ILs and other oil additives
  - Investigating compatibilities between ILs and hard coatings

Acknowledgements

- DOE VTO Fuels and Lubricants Program for funding
- DOE HQ program managers (Kevin Stork and Steve Przesmitzki) and ORNL program managers (Ron Graves and Robert Wagner) for strong support to this research
- ORNL team
  - Co-PIs: Peter Blau (retired), Huimin Luo, Sheng Dai, Bruce Bunting (retired), Brian West
  - Key technical personnel: Todd Toops, Jane Howe (left ORNL), Harry Meyer III, Miaofang Chi, Donovan Leonard, John Storey, Samuel Lewis Sr.
  - Postdocs/students: Bo Yu (left), William Barnhill, Chao Xie, Cheng Ma, Dinesh Bansal (left), and Yan Zhou
- GM: CRADA partner
  - Co-PIs: Michael Viola, Gregory Mordukhovich (left GM), and Donald Smolenski (retired)
  - Key technical personnel: Tasfia Ahmed, Meryn D'Silva, Paul Harvath, and Ngoc-Ha Nguyen
- Shell: FOA/CRADA partner
  - Co-PIs: Brian Papke and Cheng Chen (left Shell)
  - Key technical personnel: Hong Gao and Bassem Kheireddin
- Lubrizol: lubricant formulator
  - Key technical personnel: Ewa Bardasz (retired)
- Cytec: IL feed stocks supplier
  - Key technical personnel: Jeff Dyck and Todd Graham (left Cytec)

Jun Qu, 685-576-9304, qujn@ornl.gov