Anti-Corrosion Coatings | Hot Paper

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Polyoxometalate Ionic Liquids as Self-Repairing Acid-Resistant Corrosion Protection**

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Abstract: *Corrosion is a global problem for any metallic structure or material. Herein we show how metals can easily be protected against acid corrosion using hydrophobic polyoxometalate-based ionic liquids (POM-ILs). Copper metal disks were coated with room-temperature POM-ILs composed of transition-metal functionalized Keggin anions* $[SiW_{11}O_{39}TM(H_2O)]^{n-}$ *(*$TM = Cu^{II}$, Fe^{III}*) and quaternary alkylammonium cations* $(C_nH_{2n+1})_4N^+$ *(*$n = 7$–8*). The corrosion resistance against acetic acid vapors and simulated "acid rain" was significantly improved compared with commercial ionic liquids or solid polyoxometalate coatings. Mechanical damage to the POM-IL coating is self-repaired in less than one minute with full retention of the acid protection properties. The coating can easily be removed and recovered by rinsing with organic solvents.*

Metal corrosion has a significant detrimental impact on the world's economy and an estimated 3% of the global gross domestic product (GDP) is lost through corrosion processes.[1] One major approach to prevent corrosion is the use of corrosion-protection coatings and ionic liquids (ILs) have been proposed for this purpose.[2] ILs are liquid salts (m.p. < 100 °C) which have transformed materials chemistry and led to unprecedented applications in synthesis,[3] catalysis,[4] energy conversion/storage,[5] and green chemistry.[6] Typically, ionic liquids are formed when bulky organic cations, such as alkylammonium, alkylpyridinium, or imidazolium, are combined with weakly interacting organic or inorganic anions, such as Cl^-, BF_4^-, PF_6^-, or $CF_3SO_3^{2-}$.[3a] Particularly room-temperature ionic liquids (RTILs) have become a major field of research owing to their high stability, low vapor pressure, and unique solvent properties.[3b,7]

The IL properties are typically tuned by chemical modification of the organic cation. In contrast, anion functionalization is less explored.[8] Recently, this imbalance has been addressed when anionic molecular metal oxides, so-called polyoxometalates (POMs) were introduced, giving rise to functional, polyoxometalate-based ionic liquids (POM-ILs).[9]

POMs are metal-oxo cluster anions based on early transition metals (e.g. Mo, W, V)in a high oxidation state.[10] The properties of POMs can be tuned on the molecular level by chemical and structural modification of the cluster shell, leading to a multitude of applications in academia and industry.[11] Initial studies accessed POM-ILs based on prototype clusters, such as the Keggin and Dawson anions ($[XM_{12}O_{40}]^{n-}$ and $[X_2M_{18}O_{62}]^{m-}$, respectively; X = P, Si, etc.; M = Mo, W)[10a] in combination with quaternary alkylammonium[12] or alkylphosphonium cations.[13] The potential of POM-ILs has been demonstrated by the development of self-separating epoxidation catalysts,[14] industrial catalysts for large-scale petrochemical processes,[15] or the discovery of fundamental changes in POM reactivity in ionic liquids.[16]

Herein we report the first examples of POM-ILs based on transition-metal functionalized lacunary Keggin clusters $[\alpha\text{-}SiW_{11}O_{39}TM(H_2O)]^{n-}$ ($TM = Cu^{II}$, Fe^{III})[17] as model anions with tunable cluster charge and reactivity. Tuning the cluster charge was vital as our initial studies showed that the parent Keggin anion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ does not form RTILs even when used with bulky cations, such as tetra-*n*-heptylammonium (m.p. ca. 170 °C, see Supporting Information). In contrast, when the transition-metal-substituted species $[\alpha\text{-}SiW_{11}O_{39}Fe(H_2O)]^{5-}$ and $[\alpha\text{-}SiW_{11}O_{39}Cu(H_2O)]^{6-}$ were employed with tetraalkylammonium cations Q^7 ($(n\text{-}C_7H_{15})_4N^+$) and Q^8 ($(n\text{-}C_8H_{17})_4N^+$), we found that all the compounds obtained (compounds **1**–**4**) were RTILs, see Table 1.

Compounds **1**–**4** are soluble in polar and non-polar aprotic and protic solvents as well as in halogenated solvents. In

Table 1: Overview of compounds **1**–**5**.

Compound	Compound formula	melting range [°C]
1[a]	$(Q^7)_6[\alpha\text{-}SiW_{11}O_{39}Cu(H_2O)]$	27[b] (−17)[c]
2[a]	$(Q^7)_5[\alpha\text{-}SiW_{11}O_{39}Fe(H_2O)]$	27[b] (−17)[c]
3[a]	$(Q^8)_6[\alpha\text{-}SiW_{11}O_{39}Cu(H_2O)]$	−34[d]
4[a]	$(Q^8)_5[\alpha\text{-}SiW_{11}O_{39}Fe(H_2O)]$	−59[d]/−40[d]
5 (reference)	$(Q^5)_6[\alpha\text{-}SiW_{11}O_{39}Cu(H_2O)]$[e]	200–210

[a] Room-temperature ionic-liquid. [b] Melting point; [c] Eutectic melt. [d] Glass transition. [e] $Q^5 = n\text{-}(C_5H_{11})_4N^+$.

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contrast, **1**–**4** are insoluble in water. Their hydrophobicity was investigated using the sessile drop method (see Supporting Information); for example, POM-IL **4** gave a contact angle of 60°. This is a stark contrast to classical ILs which are miscible with organic solvents and with water.[3b,7] Typically, hydrophobic ILs are based on fluorinated cations or anions which are often difficult to access synthetically or hydrolytically unstable.[18] POM-ILs might therefore be interesting candidates for biphasic synthesis, catalysis, and separation.[14]

Inspired by earlier studies in which insoluble, solid POM-salts were employed as corrosion inhibitors[19] we hypothesized that the POM-ILs are promising materials as temporary corrosion-resistant coatings. The concept was tested by drop-coating Cu metal disks ($d = 1.0$ cm) with the respective POM-IL (ca. 150 mg). Reference samples to evaluate the effects of the POM-IL were: 1) an identical, non-coated Cu disk; 2) an identical Cu disk coated with the commercial, water-soluble IL [hmim]Br (1-hexyl-3-methylimidazolium bromide); 3) an identical Cu disk coated with the solid POM salt **5**. The samples were exposed to aqueous acetic acid (50%) vapors in a closed plastic vessel for 24 h. Acetic acid was chosen as a model for volatile corrosive agents involved in the environmental corrosion of copper.[20] After the exposure, photographs of the disks were taken (Figure 1). The Cu disks were then rinsed, dried, and the weight loss was determined. Analysis of the data (Table 2) shows that significantly higher weight loss, and therefore copper corrosion (up to ca. 25 wt%) is observed for the reference samples compared with the POM-IL coated specimen (up to ca. 0.4 wt%), highlighting the protective properties of the POM-IL coatings.

Table 2: Acid corrosion tests.

Metal sample	Coating[a]	Weight loss [wt%]
Cu	–	5.2
Cu	[hmim]Br	24.9
Cu	POM-IL **1**	0.4
Cu	POM-IL **2**	0.2
Cu	POM-IL **3**	0.1
Cu	POM-IL **4**	0.3
Cu	Solid **5**	1.5

[a] Approximately 150 mg of the respective IL were used for coating, for details see Supporting Information.

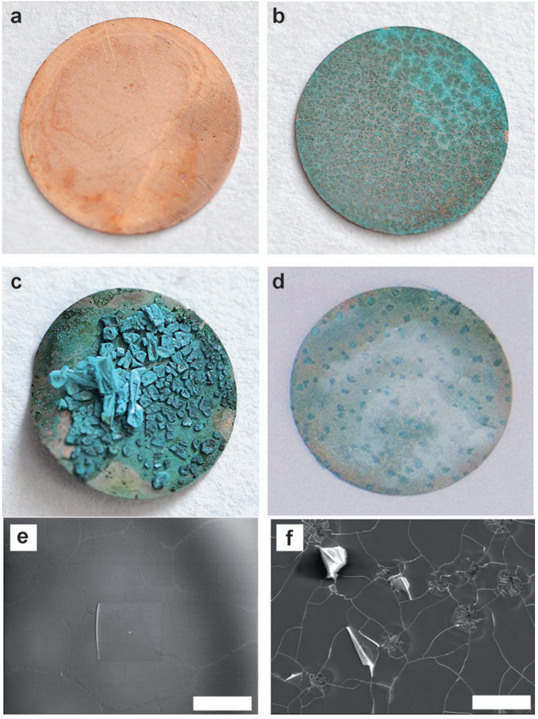

Figure 1. Cu disks ($d = 1$ cm) exposed to aqueous acetic acid (50%) vapor for 24 h. a) coating: POM-IL **3**; b) non-coated Cu disk; c) coating: commercial IL [hmim]Br; d) coating: solid compound **5**. e) scanning electron micrograph of the surface of disk (a) coated with POM-IL **3**; f) scanning electron micrograph of disk (d) coated with the solid **5**. Scale bars: 200 μm.

Scanning electron microscopy was performed on the POM-IL coated copper disks (Figure 1; POM-IL **3**). It can be seen that the POM-IL forms a smooth surface film with only superficial cracks which do not reveal the underlying Cu metal surface; therefore, virtually no corrosion was observed upon acid exposure. In contrast, the solid **5** coated sample shows significant cracking with deep cracks which fully penetrate the coating and reveal the underlying Cu metal. Thus, after acid exposure of the solid **5** coated disk, increased corrosion was observed, see Figure 1 and Table 2.

To test the long-term stability of the POM-IL coating under relevant environmental conditions, an "acid-rain simulator" was constructed where aqueous acetic acid (50%) was dropped from a height of ca. 2 cm onto a Cu disk coated with POM-IL **3** for 24 h (flow rate: ca. 12 mL min^{-1}), see Figure 2. After the procedure, the sample was rinsed with acetone, dried, and a weight loss of 0.2 wt% was observed, showing that the coating is both chemically and mechanically stable over prolonged periods and is not washed off.

Based on rheological analyses (see Supporting Information) we hypothesized that the POM-ILs should be able to essentially self-repair upon mechanical damage (e.g. scratching) so as to re-seal the hydrophobic coating and thereby

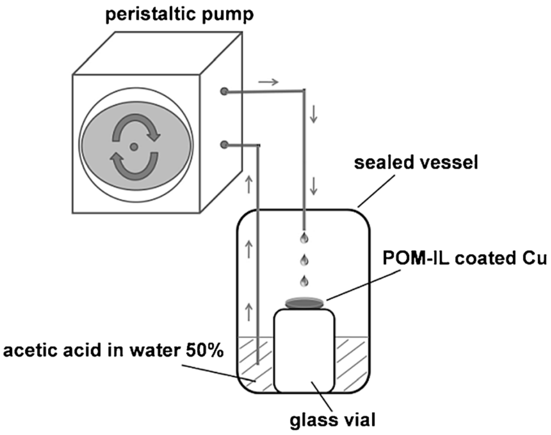

Figure 2. "Acid-rain simulator" to determine the mechanical stability of a POM-IL coating. Aqueous acetic acid (50%) was dropped from a height of ca. 2 cm onto the coated Cu disk for 24 h (flow rate: ca. 12 mL min^{-1}).

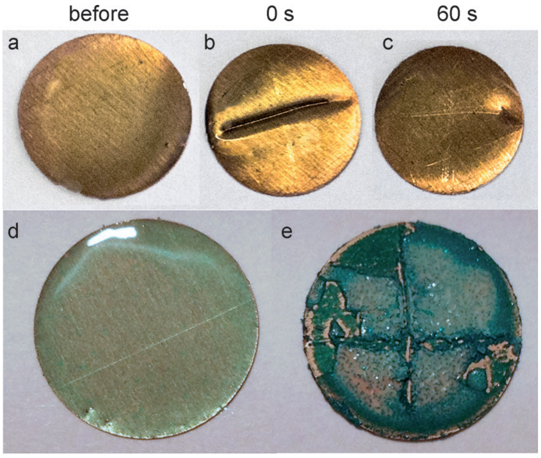

Figure 3. Top: Self-repair of the POM-IL coated Cu disk ($d = 10$ mm) upon scratching. a) sample before scratching; b) sample immediately after scratching; c) sample 1 min after scratching. Bottom: Acid corrosion test of the scratched samples coated with d) POM-IL **3** (weight loss 0.2 wt%) and e) solid **5** (weight loss 1.1 wt%).

recover their protective properties. To this end, Cu disks were coated with POM-IL **3** and solid **5**. Both samples were then scratched using a knife blade, the results are illustrated in Figure 3. For the POM-IL coated sample it can be seen that upon scratching, the coating is temporarily removed; the viscous POM-IL subsequently self-repairs and re-seals the scratch, giving the fully repaired surface after approximately 60 s. In contrast, in the sample covered by the solid POM salt **5** the scratches cannot re-seal. The samples were then tested using the standard acid corrosion procedure (see above) and it was shown that the POM-IL-coated sample only showed marginal corrosion (weight loss: 0.2 wt%) whereas the sample coated with solid **5** showed significantly higher corrosion (1.1 wt%). The weight loss observed for the POM-IL coated sample is in line with the results observed for the non-scratched sample (see Table 2), demonstrating that the scratching did not permanently damage the coating and the self-repair process fully recovered the acid protection properties.

In conclusion, we present the first examples of POM-ILs as acid-resistant corrosion protection. The hydrophobic and highly viscous materials can easily be accessed and handled. They offer promising chemical and mechanical corrosion protection of Cu metal against acetic acid. In addition, the POM-ILs can easily be removed and recovered by rinsing with organic solvents, enabling their sustainable recycling. The POM-ILs can self-repair mechanical damage (e.g. scratches) in a short time, and full recovery of the acid-protective properties is observed. In addition, this is also the first systematic report of POM-ILs based on transition-metal-functionalized Keggin anions $[\alpha\text{-SiW}_{11}O_{39}TM(H_2O)]^{n-}$, thus opening new avenues for the design and reactivity tuning of redox-active, POM-based ionic liquids.

Future work will broaden the application range of POM-ILs by investigating their performance as coatings for other acid-sensitive materials (e.g. marble). Further, task-specific tuning of the properties (e.g. viscosity, oxidative resistance, etc.) will be addressed by anion and cation chemical modification with particular focus on in situ conversion of the POM-IL into a permanent coating.

Experimental Section

Synthesis of compounds **1–4** is a modified version of a literature method:[17] An aqueous solution of $K_8[\alpha\text{-SiW}_{11}O_{39}]\cdot 13\,H_2O$[21] was treated with the heterometal salt of choice (see Table 1) for 1 h at ca. 50–60 °C. The cluster was transferred into the organic phase by anion metathesis using a toluene solution of the desired tetraalkylammonium bromide salt. The organic phase was separated and the solvent removed under vacuum. The product was thoroughly dried under high vacuum and lyophilized several times. For synthetic and analytical details see Supporting Information.

Cu disk coating: The Cu disks were sonicated for 5 min in acetone and thoroughly rinsed with acetone. After air-drying, ca. 150 mg of the corresponding POM-IL was drop-coated onto both sides of the disks and the thus prepared disks were heated in a glass vial to $T = 60$ °C for ca. 30 min to allow the POM-ILs to spread evenly over the sample.

Acid corrosion tests: The Cu disks were exposed to vapors of aqueous acetic acid (50 vol%) in a closed plastic vial ($V = 250$ mL) for 24 h. After exposure, the samples were sonicated and rinsed with water and acetone, thoroughly dried and weighed.

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