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Potential Solutions for Creating Responsive Materials

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oceans under the icy crusts of Ganymede (*4*) and Callisto (*3*), although in the case of Ganymede the intrinsic magnetic field complicates matters (*4*). These salty oceans are likely in contact with silicate (at Europa) or ice (at Ganymede and Europa) (*5*), but their depth and detailed properties remain unknown. Because of their variety, the Galilean satellites are a fascinating target for future exploration: Europa has the ingredients for life, and Ganymede has its own magnetic field; Io's high activity and Callisto's ancient surface complete the picture.

In Saturn's system, an ocean including ammonia as an antifreeze was expected at Titan [e.g., (*6*)]. Observations of the rotation rate are consistent with this (*7*). At Enceladus, the evidence for a subsurface ocean found by the Cassini spacecraft includes the huge plumes of water and ice emanating from the southern polar region there (*8*), hinting at a large energy source and the reservoir below (*9*). Measurements of sodium in dust grains (*10*) are additional evidence for a subsurface ocean. In the case of Enceladus, the magnetic field signature, showing the field draping around the southern polar region, was the first evidence (*11*) for mass loading of the plasma nearby and led to changes in the mission profile for a closer look. Plasma (*12*) and imaging instruments (*8*, *9*) confirmed the finding, and estimates of the mass loading show that Enceladus can produce up to a third of the activity of Io. It has been found that, like Io, Europa, and Ganymede at Jupiter, Enceladus has a related auroral spot at the magnetic footprint of this active moon in Saturn's ionosphere that can be used to detect fluctuations in the activity (*13*).

Saturn's second-largest satellite, Rhea, has a simpler structure; it may have a rocky core and certainly has an icy mantle (*14*). Dione and Tethys may also have deep oceans under icy crusts, but this remains uncertain, based on data from Cassini. It has also been suggested that subsurface water-rich oceans are possible for Rhea, Titania, Oberon, Triton, and Pluto, and on the largest transneptunian objects (2003 UB313, Sedna, and 2004 DW), if even small amounts of ammonia are present (*15*).

In the case of Io, however, the results reported by Khurana *et al.* give a well-constrained picture of the interior. The ocean is not water; rather, there is a global magma ocean ("asthenosphere") at least 50 km deep, under a low-density outer crust (30 to 50 km) and surrounding a 600- to 900-km iron-rich core. An asthenosphere had been suggested earlier but was the subject of debate. This latest modeling appears to provide the answer: It exists, and it's hot; a melt fraction >20% and a temperature >1400 K provide the best fit of the modeling to the data. A magma ocean was needed to fit the multilayer modeling of the interior's conductivity, assuming reasonable conductivity values and a range of melt fractions. Modeling of the exterior plasma environment was done by means of a conducting fluid approach. Although this does not include all the individual particle kinetic effects, and plasma effects may be important, this technique is suitable for large-scale features of the interaction. The result of the coupled model gives a three-dimensional map of the magnetic field around Io and the magnetic field perturbation, including Alfvén wings, that it may produce. A simulated spacecraft fly-through at the distances of two key Galileo flybys provided a detailed comparison of the time variation of the magnetic field.

What makes Io stand out among the outer planet satellites is the global magma ocean, the source of the huge activity of this moon. Whereas the other moons have liquid water oceans, Io's contains sulfurous magma (see the figure).

The Galileo mission ended in 2003 and left many unanswered questions, especially about the Galilean satellites. The depths of the watery oceans at Europa, Ganymede, and Callisto are unknown, as are the ice shell thicknesses. Similarly, there are still many questions arising from Cassini's exploration at Saturn. Outer planet moons are tempting targets for future exploration, and recent mission studies are aimed at studying Ganymede and Europa in detail, and also Titan and Enceladus. Many questions remain about these fascinating moons. We hope the resources will be available to answer them soon.

References

1. K. K. Khurana *et al.*, *Science* **332**, 1186 (2011).
2. M. G. Kivelson *et al.*, *Science* **289**, 1340 (2000).
3. K. K. Khurana *et al.*, *Nature* **395**, 777 (1998).
4. M. G. Kivelson *et al.*, *Icarus* **157**, 507 (2002).
5. C. Sotin, G. Tobie, *C. R. Phys.* **5**, 769 (2004).
6. O. Grasset, C. Sotin, F. Deschamps, *Planet. Space Sci.* **48**, 617 (2000).
7. R. D. Lorenz *et al.*, *Science* **319**, 1649 (2008).
8. C. C. Porco *et al.*, *Science* **311**, 1393 (2006).
9. J. R. Spencer *et al.*, *Science* **311**, 1401 (2006).
10. F. Postberg *et al.*, *Nature* **459**, 1098 (2009).
11. M. K. Dougherty *et al.*, *Science* **311**, 1406 (2006).
12. R. L. Tokar *et al.*, *Science* **311**, 1409 (2006).
13. W. R. Pryor *et al.*, *Nature* **472**, 331 (2011).
14. J. Castillo-Rogez, *J. Geophys. Res.* **111**, E11005 (2006).
15. H. Hussmann, F. Sohl, T. Spohn, *Icarus* **185**, 258 (2006).

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MATERIALS SCIENCE

Potential Solutions for Creating Responsive Materials

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Plastic deformation of a nanoporous material can be altered by changing its surface via an electrochemical potential.

Structural materials are often engineered for toughness—an ability to withstand sudden impact and avoid brittle failure. If these materials could sense their surroundings and if their properties could be "tuned" with an external stimulus, then it might be possible to engineer materials that can self-repair the damage they may incur. Some composite polymeric materials have been developed with such capabilities (*1*). However, for many applications, we are still years away from knowing how to create and tune the properties of other useful materials. On page 1179 of this issue, Jin and Weissmüller (*2*) describe in situ tuning of a two-phase composite structure formed from nanoporous gold infiltrated with a perchloric acid ($HClO_4$) electrolyte solution. They demonstrated "reversible" tuning of the flow stress—the pressure needed to maintain plastic deformation—by changing the composition of absorbed molecules on the gold surface with an applied electrochemical potential (*3*).

The solid phase was made by selective leaching of silver from a silver-gold alloy. A connected network of gold ligaments formed, roughly 10 to 20 nm in diameter, that contained pores of similar dimensions (see the figure, panel A). The network was bicontinuous; that is, both the solid phase and the void space were continuous, and there were no isolated porous regions. The changes that

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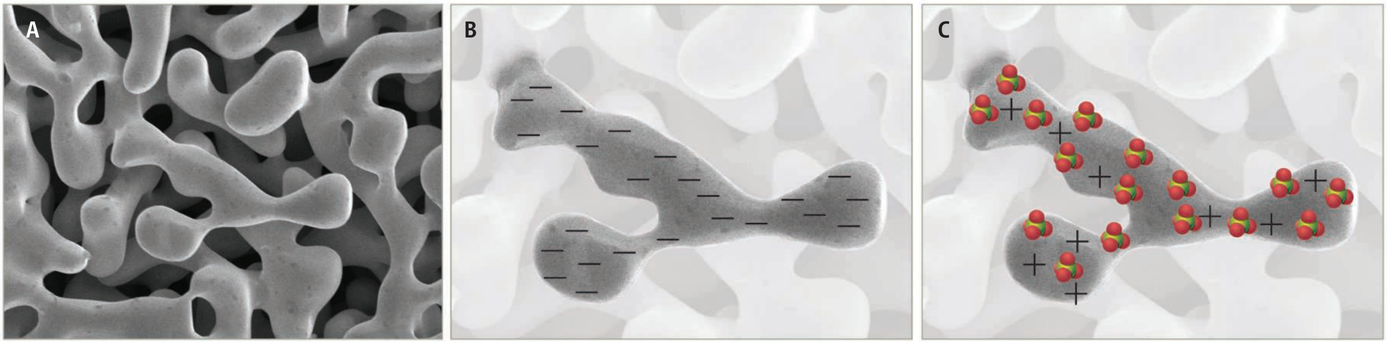

Tuning mechanical properties. Jin and Weissmüller examined changes in flow stress of a nanoporous gold structure (**A**) filled with a 1 M $HClO_4$ electrolyte. Application of electrochemical potential changes the nature of the surface and its mechanical response. (**B**) Between 0 and 0.5 V, the surface builds up a negative charge like a capacitor. (**C**) Between 0.5 and 1.2 V, the positive charge in the surface is compensated by an adsorbed layer of anions from the electrolyte.

occurred on a gold surface when an electrochemical potential was applied with $HClO_4$ as the electrolyte fell into three regimes (*4*). Between 0 and 0.50 V (*5*), the surface charged like a capacitor (see the figure, panel B). Between 0.50 and 1.20 V, anions were attracted to the positive charge and adsorbed (see the figure, panel C). Between 1.20 and 1.50 V, a monolayer of oxidized gold formed. The monolayer oxidation process began with hydroxide (OH^-) adsorption into surface sites unoccupied by adsorbed ClO_4^-; as the potential became more positive, more OH^- was incorporated and correspondingly ClO_4^- desorbed. Finally, the surface underwent a reconstruction in which the oxygen atoms were incorporated into the gold surface atoms to create a layer of gold oxide.

Jin and Weissmüller determined the mechanical properties of this composite material by applying pressure and measuring deformation while an electrochemical potential was applied. The largest changes in material properties occurred when the applied potential was jumped from the region of ClO_4^- adsorption (about 1 V) to the monolayer oxidation region (about 1.5 V). In this case, the flow stress increased by as much as a factor of 2. They also observed smaller increases in flow stress when the potential was pulsed from the region of ClO_4^- adsorption (about 1 V) into the capacitive charging region (about 0.1 V). The flow stress was smallest in the vicinity of the potential of zero charge (about 0.5 V).

One can conceive of several possible mechanisms by which a two-dimensional gold oxide layer could increase the flow stress of nanoscale structures. The movement of atoms that allows a crystalline material to deform actually occurs via the movement of dislocations—line defects that run through the material. The rate of this process depends on how easily dislocations move and their density. A surface oxide could reduce the surface mobility of a dislocation by pinning it at the point where it emerges on the surface (*6*), making it immobile. The oxide could also create an elastically stiff barrier that impedes a dislocation from escaping through the surface.

The mechanical properties reported by Jin and Weissmüller are connected to various observations of surface effects on crystal plasticity often generically termed Rehbinder effects (*7*). This effect originally referred to the adsorption-induced reduction in hardness or flow stress of a material caused by a concomitant lowering of the surface energy (*8*). These quantities are related because a portion of the work of plastic flow is associated with the creation of new surfaces as the material stretches. However, Jin and Weissmüller observed a minimum in the flow stress in the range of potentials such that the surface is free of adsorbates.

Their results are also connected to more recent reports of sample size effects on the yield and flow strength of solids (*9*). Because the surface-to-volume ratio in a nanostructure is relatively large and the bulk dislocation content is likely small, the importance of surface effects is magnified. For potentials that oxidized the surface, the amplitude of the variation in flow stress increased with decreasing gold ligament size. Similar results have been reported for flow stress of nanoscale gold pillars (*10*), although the cause of this behavior is unclear.

One intriguing aspect of the results reported by Jin and Weissmüller relates to the brittle behavior of the composite structure in the oxidative region and the connection of this behavior to stress-corrosion cracking of metal alloys. In some cases involving noble metal alloys and stainless steels, stress corrosion has been linked to the selective dissolution of an alloy component and the consequent formation of a nanoporous structure (*11*). In the case of silver-gold alloys, the nanoporous structure initially forms at length scales on the order of 2 to 3 nm (*12*). The magnitude of the behaviors reported by Jin and Weissmüller increased with decreasing gold ligament size, so it seems quite plausible that at yet smaller length scales, these effects will be larger and therefore possibly relevant to certain forms of stress-corrosion cracking.

A timely application of the concepts presented in the report by Jin and Weissmüller may be connected to mitigating damage evolution that occurs in rechargeable batteries when metal ions intercalate in and out of electrode materials. The associated volume change can crack the material and electrically isolate parts of it. Such mechanical failure of intercalation materials is believed to be a possible mechanism of capacity loss in lithium-ion batteries (*13*). It may be possible to design intercalation electrodes with nanoscale morphologies that, under suitable voltage conditions, make use of electric charge or surface-active agents that modify the plastic properties of the electrode structure. Such approaches may relieve, at least to some extent, fatigue damage created by cycles of intercalation and de-intercalation.

References and Notes

1. R. P. Wool, *Soft Matter* **4**, 400 (2008).
2. H.-J. Jin, J. Weissmüller, *Science* **332**, 1179 (2011).
3. Reversibility is used here not in the thermodynamic sense, but to indicate that the flow stress behavior is recoverable during potential cycling.
4. H. Angerstein-Kozlowska, B. E. Conway, A. Hamelin, L. Stoicoviciu, *Electrochim. Acta* **31**, 1051 (1986).
5. Voltages are measured relative to a standard hydrogen electrode.
6. A. R. C. Westwood, *Philos. Mag.* **7**, 633 (1962).
7. F. R. N. Nabarro, *Theory of Crystal Dislocations* (Oxford Univ. Press, London, 1967), p. 294.
8. P. A. Rehbinder, E. D. Shchukin, *Prog. Surf. Sci.* **3**, 97 (1972).
9. M. D. Uchic, D. M. Dimiduk, J. N. Florando, W. D. Nix, *Science* **305**, 986 (2004).
10. J. R. Greer, W. C. Oliver, W. D. Nix, *Acta Mater.* **53**, 1821 (2005).
11. K. Sieradzki, R. C. Newman, *J. Phys. Chem. Solids* **48**, 1101 (1987).
12. S. G. Corcoran, D. G. Wiesler, K. Sieradzki, *Mater. Res. Soc. Symp. Proc*. **451**, 93 (1997).
13. W. H. Woodford, Y.-M. Chang, W. C. Carter, *J. Electrochem. Soc.* **157**, A1052 (2010).

10.1126/science.1206856