

# Potential/Charge Induced Nanoporous Metal Actuators

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**Abstract**— The mechanical response to the electrochemical charging of nanoporous metals with their pore space wetted by electrolyte have been studied in-situ using dilatometry and wide angle x-ray diffractometry techniques. The actuation strain reported in this manuscript is purely elastic and completely reversible. The capacitive double layer charging became more effective near to the potential to zero charge ( $pzc$ ) and contribute significantly to the variations of surface stress and crystal strain. In a suitable experimental setup, the actuator effect from porous metals can be amplified, where deliberate movements of the actuator parts are desirable with minimum external force, suggesting that metallic foam-like materials with high surface to volume ratio could be used to mimic natural muscles.

## I. INTRODUCTION

CERTAIN solid materials respond mechanically to external stimulus such as electric field, temperature and gas pressure and change significantly their size and shape by generating volumetric strain. The reversible expansion and contraction phenomena of such materials can therefore be exploited for use as actuators. In recent years there is a progressive improvement in the development of actuator materials for defined applications where high precision motion and high frequency operations are required. Among them, few selected materials emulate mechanical behaviour and working performance very close to natural muscles. Such materials can be used to mimic the physical movements of living creatures and for making devices operating in fluid medium.

The electric field induced actuator phenomena in solids was found at first in high modulus ferroelectric ceramics [1]. These materials derive mechanical motion from solid state crystalline effects. Actuators made from the ferroelectric materials are in use for many engineering applications. But kilovolt potentials are required to operate the ceramic actuators, and the devices should be protected from moisture and intrusions of foreign particles. Significant interdisciplinary developments have been emerged in the actuator field since 1990 the electro-active conducting polymers [2],[3] and carbon materials [4] produce actuator properties superior over to those of biological muscles. The mechanical stress-strain behaviours of these materials are quite stable in aqueous

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fluidic environments. The mechanical action for the electro-active polymers rely mostly on ion intercalation and solvent transport in to the polymer chains [3], whereas for carbon actuators, columbic electrostatic forces from charge carriers and gas (partial-) pressures in the pore spaces are important [4]. The other materials capable of producing larger strain and behave as artificial muscles are shape memory alloys and liquid crystal elastomers, but their mechanical movements are controlled mostly by joule heating, rather than electric field.

## II. POROUS METAL ACTUATORS

Porous metal actuators (PMAs) [5] are relatively new, demonstrated recently the potential/charge induced actuator phenomena in noble metals Pt and Au, Pd and their alloys in aqueous fluids. The in-situ elastic deformation results discussed in the manuscript are obtained from two different types of porous structures, prepared by consolidation of granular nanocrystalline powders and by electrochemical de-alloying. Figures 1a, b show the typical scanning electron microscopy images for porous Pt and Au specimens prepared by these respective methods. The microstructure of these porous specimens is: bi-continuous structure consisting of interconnected three dimensional pore network and inter-connected array of nanometer sized ligaments/ granular grains.

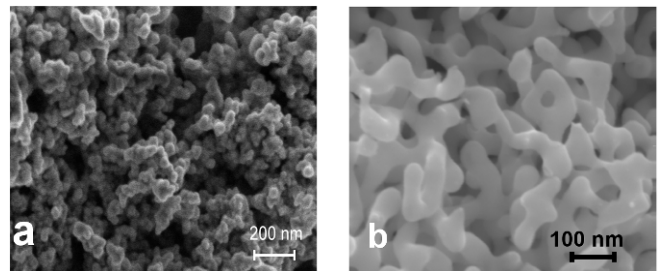


Fig. 1. Scanning electron micrographs of two different porous structures. (a) Porous Pt obtained by consolidation method and (b) Porous Au produced from electrochemical de-alloying.

The pore surfaces wetted fully with liquid electrolytes produce appreciable strain, comparable to those of ferroelectric ceramics. The performance of such PMAs is quite comparable to that of non-metallic, electrically driven systems proposed as bio-mimetic actuators. Figure 2 is the schematic view of an electrochemical set-up housed in the working place of a commercial dilatometer for the in-situ strain experiments. Figure 3 shows a typical reversible strain  $\Delta l/l_0$

result for porous Pt metal in alkaline KOH (1M) electrolyte during the cyclic current  $I$  versus potential  $E$  scan (CV) in the range of  $-0.75$  to  $+0.15$  V versus a Ag/AgCl reference electrode. Measurement cycles in different scan rates ( $1\text{mV/s} - 0.1\text{mV/s}$ ) are depicted in the figure. The strain  $\Delta l/l_0$  results were obtained from the change in dimensions  $\Delta l$  of the porous Pt. Irrespective to the scan speed, peak-to-peak strain amplitude of  $0.14\%$  was obtained from the in-situ study.

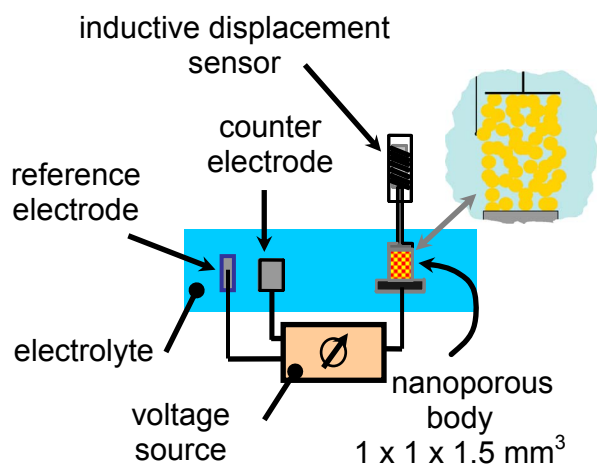


Fig. 2. Schematic view of the miniaturized electrochemical cell used for in-situ deformation experiments using a commercial dilatometer.

Figure 4 shows the potential induced variation of the lattice parameter,  $a$ , and the crystal lattice strain,  $\Delta a/a_0$ , for porous Pt in an alkaline KOH (1M) electrolyte. The variation,  $\Delta a$ , of the lattice parameter was measured from the

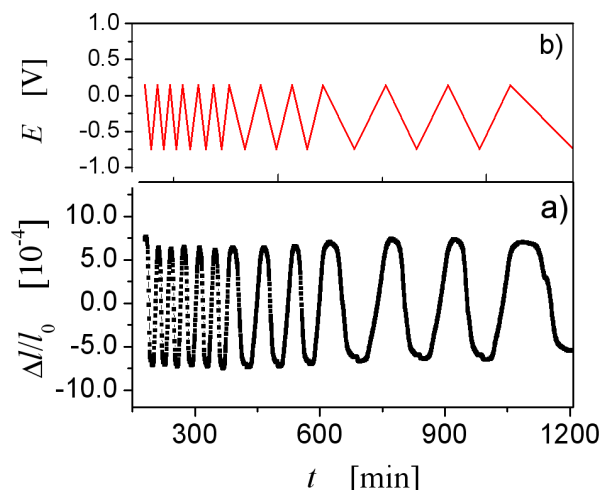


Fig. 3. In-situ strain  $\Delta l/l_0$  results for porous Pt immersed in KOH(1M) measured in a dilatometer during the potential cycling in the range  $-0.75\text{ V} < E < 0.15\text{ V}$  versus Ag/AgCl at different scan rates ( $1\text{ mV/s} - 3$  cycles;  $0.8\text{ mV/s} - 3$  cycles,  $0.4\text{ mV/s} - 3$  cycles,  $0.2\text{ mV/s} - 3$  cycles,  $0.1\text{ mV/s} - 1/2$  cycle. a) Variation of strain  $\Delta l/l_0$  and b) Variation of electrode potential applied  $E$  as a function of measurement time  $t$ .

Bragg reflections shift in an X-ray powder diffraction pattern [6] after the charge equilibration at constant Pt electrode potential,  $E$ . The experimental details are discussed elsewhere [5],[7]. The figure shows that the porous Pt underwent to a reversible lattice contraction at negative potentials of charging where excess electrons are populated in the Pt surface regions. The amplitude of the crystal strain  $\Delta a/a_0$  measured is about  $0.14\%$ , which is in close agreement with the dilatometer measured strain  $\Delta l/l_0$  from the macroscopic change in length  $\Delta l$  (fig. 3). The electrochemical features found in the measurement potential intervals (double layer charging and adsorption/desorption of OH) are overlapped partially in the  $E$  scale. Therefore, accurate determination of  $pzc$  for porous Pt in KOH electrolyte is critical. However, our in-situ X-ray diffraction results (fig. 4) show evidences for  $pzc$  around  $-0.35$  V versus Ag/AgCl, on accounting the potential  $E$  at zero strain.

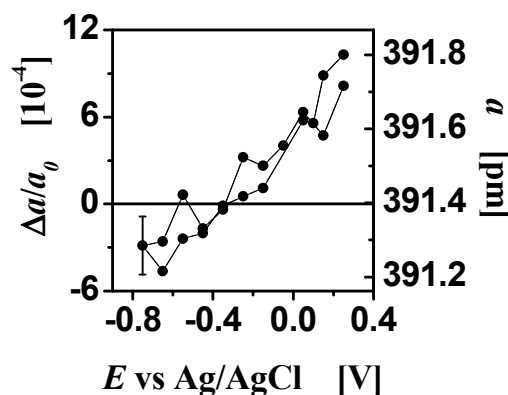


Fig. 4. Results of in-situ powder X-ray diffraction for Pt immersed in aqueous KOH(1M) The figures in the right ordinate shows the lattice constant  $a$ , and in the left ordinate shows the crystal strain  $\Delta a/a_0$  versus the electrode potential  $E$ . The variation of  $a$  and  $\Delta a/a_0$  are found reversible upon variation of  $E$ . The uncertainty in the lattice constant determination is with in  $\pm 0.3\text{ pm}$  [5].

### III. AMPLIFICATION OF MECHANICAL ACTUATION

Besides the potential- or charge-induced displacement observed on porous metals, the foam-like metal specimens have large yield strength, in the range of  $10\text{-}200\text{ MPa}$ , [8]. The values reported are larger than those for bio-mimetic, polymer actuator materials. While the porous metals produce reversible crystal strain in excess of  $0.1\%$ , resulting from the atomic bond rearrangements in response to charge transfer, the displacement can be enhanced or bending movement can be accelerated by optimizing the geometry and surface microstructure [9]. Figure 5 illustrates a demonstration experiment in an electrochemical cell showing the mechanical amplification of the porous Au in  $1\text{M HClO}_4$ . Two composite bi-layer metal strips of thickness about  $30\text{ }\mu\text{m}$  (sandwich of  $6\text{ }\mu\text{m}$  thin layer of solid Au cold-welded

with 24  $\mu\text{m}$  thick porous Au) were used as working and counter electrodes. The pore surfaces were obtained by dealloying [10]. By switching the electrode potentials between +1 V and -1 V, the tips of the sandwich cantilevers move by roughly 3 mm, which is by a factor of  $10^6$  larger than the planar electrodes used as samples in previous surface stress studies. The switching response time for the porous bi-layer Au strips as measured was 25 ms. Due to the large reversible bending action and its fast switching response, which is visibly seen from the naked eye, the noble porous metals may be potentially considered as commercial actuator material to use in Bio-engineering field, where it is desirable that the actuator parts moves deliberately with minimum force.

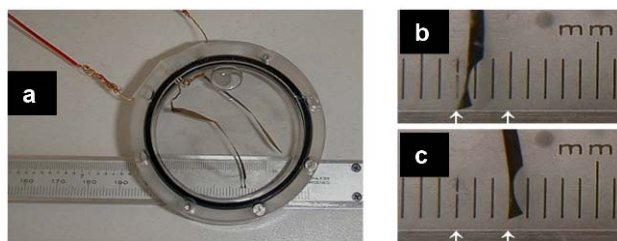


Fig. 5. Illustration of a demonstration electrochemical cell used for showing the mechanical amplification of potential/charge induced porous Au strips. a) The cell consist of two identical metallic strips (one side porous Au and other side solid Au) immersed in aqueous 1M  $\text{HClO}_4$  electrolyte. b), c) The enlarge view of the cell in a) showing the tip of one of the Au strip moves approximately 3 mm on switching the potential by +/- 1V [9].

#### IV. SURFACE STRESS – SURFACE CHARGE RESPONSE (CAPACITIVE DOMINATING DOUBLE LAYER REGION)

The mechanical actuation phenomena demonstrated on the porous metals are highly remarkable because the analogous effect was previously been reported only in ionic and covalent bonded solids [1]-[4]. The in-situ deformation results (fig. 3 and fig. 4) show that the externally injected excess electrons lead to the tendency of the metal surfaces to contract the underlying crystal lattice, while excess holes result in expansion. The surface atomic layers will thus experience more tensile stress (positive stress) at negative electrode potentials, while at the same time the compensating stresses in the bulk are compressive. The plausible explanation for these important finding from metals are as follows: When excess electrons are localized in the surface regions, the surface layer tends to stretch outwards. The immediate reaction would be an increase of in-plane bond strength due to charge redistribution, similar to the transverse elastic response that is commonly found in bulk solid matter. For a detailed explanation, the reader is referred to Refs. [11,12]. Such an intrinsic surface effect observed from the porous metals can be quantified accurately in the double layer potential regime near *pzc* where Coulomb forces—an alternative, but very much weaker part of the capillary forces at charged surfaces—are considerably reduced. For a discussion two cyclic voltammograms for porous platinum in NaF (0.7M) measured in two different potential intervals are as shown in fig. 6a. The voltammogram recorded in a

wider potential interval,  $-0.85\text{V} < E < +0.9\text{V}$ , showed typical electrochemical characteristic features for Pt in aqueous electrolytes, namely adsorption/desorption of hydrogen at negative potentials and adsorption/desorption of oxygen ad-species ( $\text{OH}^-$ ,  $\text{O}^-$ ) at positive potentials. The cyclic voltammogram plotted in the narrow potential interval,  $-0.4\text{V} < E < +0.2\text{V}$ , showed a constant current passed capacitive dominating double layer regime.

The results from the in-situ experiments show that the forces developed at the electrode surfaces are transferred coherently into the matter underlying the electrode surfaces for creating matching inter-atomic spacing between the surface and the bulk. Since surface stress  $f$  can be defined via the action of these forces, the elastic response of solids to the changes in the surface charge density  $q$  can be verified. The variation of  $f$  with  $q$  is found to be a linear function  $f = f(0) + \zeta q$  with  $\zeta$ , a constant known as surface stress-charge coefficient [12]. The slope of the  $f(q)$  linear plots gives the value  $\zeta$ . It is to note that the surface stress  $f$  discussed here is by definition different to the charge dependence of pressure  $P$ , in fluid droplet, which is primarily quadratic in nature [13], [14]. The surface stress  $f$  for solids can be computed from the volumetric strain data and bulk modulus  $K$ , of the material, using the generalized capillary equation for solids [15].

On determining  $\zeta$  as a function of electrolyte concentration  $X$ , the relative contribution of anion adsorption to the capacitive charging effect can be studied [16]. Figure 6b shows  $\zeta$  versus the electrolyte concentration  $X$  of NaF in the ideal capacitive potential intervals  $-0.05\text{V} < E < +0.12\text{V}$  versus Ag/AgCl, which is around the *pzc*. The value  $\zeta$  is found to become independent to the electrolyte concentration at the highest dilution. Between  $X = 0.02$  and 1, the value  $\zeta$  varies by a factor of 2. The value of  $\zeta$  ( $= -1.9\text{V}$ ) obtained in the diluted electrolytes is in close agreement with those reported for (111) textured Au in NaF and  $\text{HClO}_4$

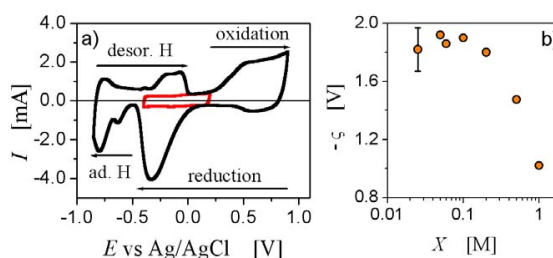


Fig. 6a. Cyclic voltammograms for porous Pt in NaF electrolyte recorded in two different potential intervals  $-0.85\text{V} < E < +0.9\text{V}$  and  $-0.4\text{V} < E < +0.2\text{V}$  versus Ag/AgCl.

Fig. 6b. Surface stress-charge coefficient  $\zeta = \Delta f / \Delta q$  versus concentration  $X$  of NaF electrolyte [12].

electrolytes [17]. These studies are suggesting strongly that the surface stress is an important driving source influences significantly to the actuation properties for solid metals.

## V. CONCLUSION

In conclusion, the porous metals are promising candidate for actuator devices operating in fluidic environments. The porous metals produce competing actuator properties (large actuation strain in low operating voltages, mimic natural muscles, fast switching response) similar to other non-metallic materials used/proposed as actuators.

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