

An *in situ* tensile tester for studying electrochemical repassivation behavior: Fabrication and challenges

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An *in situ* tensile rig is proposed, which allows performing electrochemical (repassivation) experiments during dynamic mechanical testing of wires. Utilizing the basic components of a conventional tensile tester, a custom-made minitensile rig was designed and fabricated. The maximal force that can be measured by the force sensor is 80 N, with a sensitivity of 0.5 mV/V. The maximum travel range of the crosshead induced by the motor is 10 mm with a minimum step size of 0.5 nm. The functionality of the tensile test rig was validated by investigating Cu and shape memory NiTi wires. Wires of lengths between 40 and 50 mm with varying gauge lengths can be tested. An interface between wire and electrochemical setup (noncontact) with a smart arrangement of electrodes facilitated the electrochemical measurements during tensile loading. Preliminary results on the repassivation behavior of Al wire are reported. © 2010 American Institute of Physics. [doi:10.1063/1.3292685]

I. INTRODUCTION

Among the series of biomaterials, nickel-titanium shape memory alloys are mostly sought as stents, orthodontic arch wires, and filters owing to their unique mechanical properties.¹ Application of NiTi requires knowledge about its mechanical properties and its biocompatibility. From a mechanical perspective, *in situ*-scanning electron microscopy (SEM) tensile straining investigations do provide a better picture on its fatigue characteristics, etc.² On the other hand, from a biocompatibility perspective, these materials still raise serious threat for nickel leaching. Normally, biocompatibility of the material is dictated by its surface properties. Serious efforts are being invested in order to enhance the surface properties by various surface modification methods. A systematic bottom-up approach in surface modification methods and their pros and cons was described earlier.³ Electropolishing as a starting and structuring method was described by Fushimi *et al.*⁴ Among many modifications, the growth of a thick oxide (like TiO₂) on the surface is a well established method which hinders the release of Ni ions. However, the failure of such an oxide layer during external mechanical loading cannot be discarded. Recently, Undisz *et al.*⁵ carried out an *in situ* SEM tensile straining test on thin NiTi wires to study the influence of deformation on the thermally grown surface oxide layer. They defined a complex deformation behavior with highly localized deformation as a responsible factor for crack formation in the surface oxide layer. While describing the risks related to the failure of the oxide during loading and unloading, they raised a doubt on the repassivation ability of the alloy.⁵ Hence, the corrosion performance of the implant alloys under static stress and dynamic loading-unloading conditions is quite important.

Studies have been performed to understand the effect of static stress on corrosion parameters of stainless steel, Co-Cr-Mo, Ti-Al-V.⁶ A topographic analysis performed on a Ti-Al-V alloy, suggested that the complex wear mechanisms are also related with the removal of the oxide layer causing abrasion of the alloy.⁷ Rondelli *et al.*⁸ have performed certain studies on the corrosion of NiTi under external load, but a systematic study under dynamic loading is necessary.⁹ Furthermore, studies which report on the fracture of NiTi under sustained tensile load in physiological solutions are available. These studies highlight the influence of tensile load on the localized corrosion of NiTi wires.^{10,11} Mechanical and corrosion behavior of modified NiTi surfaces were studied by Hessing *et al.*, where the effect of strain on coatings and change in surface topography were examined.¹² The substrate material retained surface integrity, whereas the coated surfaces started cracking at very low strains. A dynamic loading study on nitrided NiTi revealed higher Ni release from the surface (i.e., inability of a modified surface to withstand mechanical loading).¹³ Even though all these studies address the corrosion aspects of NiTi under tensile load in a physiological environment, they fail to directly address the electrochemical features of oxide growth and the failure of oxides.

Therefore, an electrochemical study in terms of repassivation behavior of NiTi under dynamic loading is still required. Normally, the repassivation kinetic studies performed under defined mechanical and electrochemical conditions would provide the effect of an applied stress on the failure of the protective oxides. To understand the repassivation behavior of the passive oxide, many standard methods exist. The repassivation kinetics can be understood by using the con-

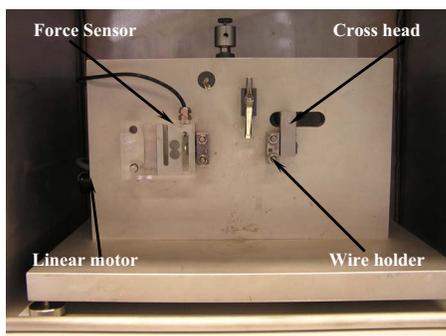


FIG. 1. (Color online) Photograph showing the parts of the fabricated tensile rig.

ventional scratch^{14,15} and indentation methods.^{16,17} Also, repassivation kinetic studies on aluminum have been reported using impingement of abrasive particle.^{18,19} However, all these methods destroy the oxide through contact.

As the complexity in experiments increases, such as understanding mechanical behavior of micro/nanoscale fibers and superelastic materials, it becomes an absolute necessity to design and engineer novel and custom-made miniature tensile machines.^{20,21} Here, we report on a novel tensile rig which allows studying electrochemical repassivation behavior of thin oxide films. The construction of the device is described and the repassivation of an Al wire covered by a thin Al₂O₃ film under dynamic tensile loading (noncontact) is documented.

II. FABRICATION OF *IN SITU* TENSILE RIG

A. Instrumentation details

Normally, tensile properties of materials are studied using conventional tensile rigs. The basic components of a tensile rig are well known.²² Based on these principles, a tensile rig capable of working with thin wires was fabricated. Figure 1 shows the fabricated tensile rig.

The force measurement system consisted of a force sensor (ME-KD40, ME-Meßsysteme) attached to a steel block. The compact technical construction of the KD40S force sensor makes it suitable for application in quality management and material testing. The load input and output are centrally equal. The precision of 0.1% can be achieved by tuning the sensitivity to 0.5 mV/V.²³

A force sensor amplifier (GSV-2AS) was utilized to read out the force variations during loading. The maximum force limit of the force sensor is 80 N.²³ The expected force required to induce fracture of oxides would be within the maximum force limit of the force sensor. Another holder acts as the movable cross head, driven by a dc linear motor [PI 222.20, Physik Instrumente (PI) GmbH]. The linear motor was controlled using a dc motor controller [PI Mercury 862, Physik Instrumente (PI) GmbH]. The linear motor was installed onto a Newport translation stage (Parker), which induces the linear displacement. The maximum linear displacement is typically 10 mm, which is sufficient to study the tensile behavior of the wires, namely Al, Cu (500 μm diameter), and NiTi (150 μm diameter). The minimum distance resolution is better than 10 nm.

B. Data acquisition

1. Recording force versus displacement curve

An Agilent Pro-VEE program was used to record the load displacement curves. Figure 2 shows a screen shot of the VEE program. The measurements can be performed by specifying either a force limit or a distance limit. This facilitates to study the electrochemical behavior associated with incremental loading steps. Also, the cross head speed can be altered between slow and fast. Typical pulling rates are between 1 nm s^{-1} and 0.5 mm s^{-1} .

2. Interfacing with electrochemical setup

The schematic of the *in situ* tensile rig with electrochemical interfacing is shown in Fig. 3. The electrochemical interface was realized using a closely wound coil of platinum wire as counter electrode. The winding of the Pt wire is such that it holds the electrolyte of interest merely by surface tension. Such a noncontact method allows excluding other forces acting on thin wires (working electrode). The sample holders were electrically isolated from the main body of the tensile test rig to facilitate the electrical connection between the working electrode (wire) and the potentiostat. Our three electrode system used a μ -reference electrode (Hg/Hg₂SO₄). Details on the design, electrochemical fabrication, and calibration of the μ -reference electrode were reported by Lill *et al.*²⁴ The potentials of the fabricated μ -reference electrode were calibrated and the reference electrode was then inserted through the free space between two winds of the Pt coil pointing toward the working electrode, as shown in Fig. 3. With this arrangement, it is easy to perform our electrochemical experiments. The repassivation behavior was studied using a custom designed ultrafast acquisition potentiostat. Currents in the range between 100 and 10 μA can be measured at a rate of 20 MHz. The detailed electronics and features of the potentiostat are described in Ref. 19.

III. EXPERIMENT EXAMPLES

A. Mechanical testing of wires

First, the utility of the tensile rig was scrutinized by measuring tensile properties of certain metal and alloy wires. The diameter of the wires tested was restricted by the maximum force limit of the force sensor. Figure 4 is the stress versus strain curve elucidating the mechanical behavior of NiTi and Cu wire (inset), respectively. It can be seen that NiTi shows a behavior that is characteristic for a shape memory alloy. Upon loading, NiTi exhibits a linear behavior up to a certain stress and a loading plateau stress (constant stress at increasing strain). The calculated Young's modulus for NiTi in martensitic state was approximately 29 GPa. The magnitude of the loading plateau stress is approximately 450 MPa. The application of an external load beyond this results in the formation of stress induced martensite.

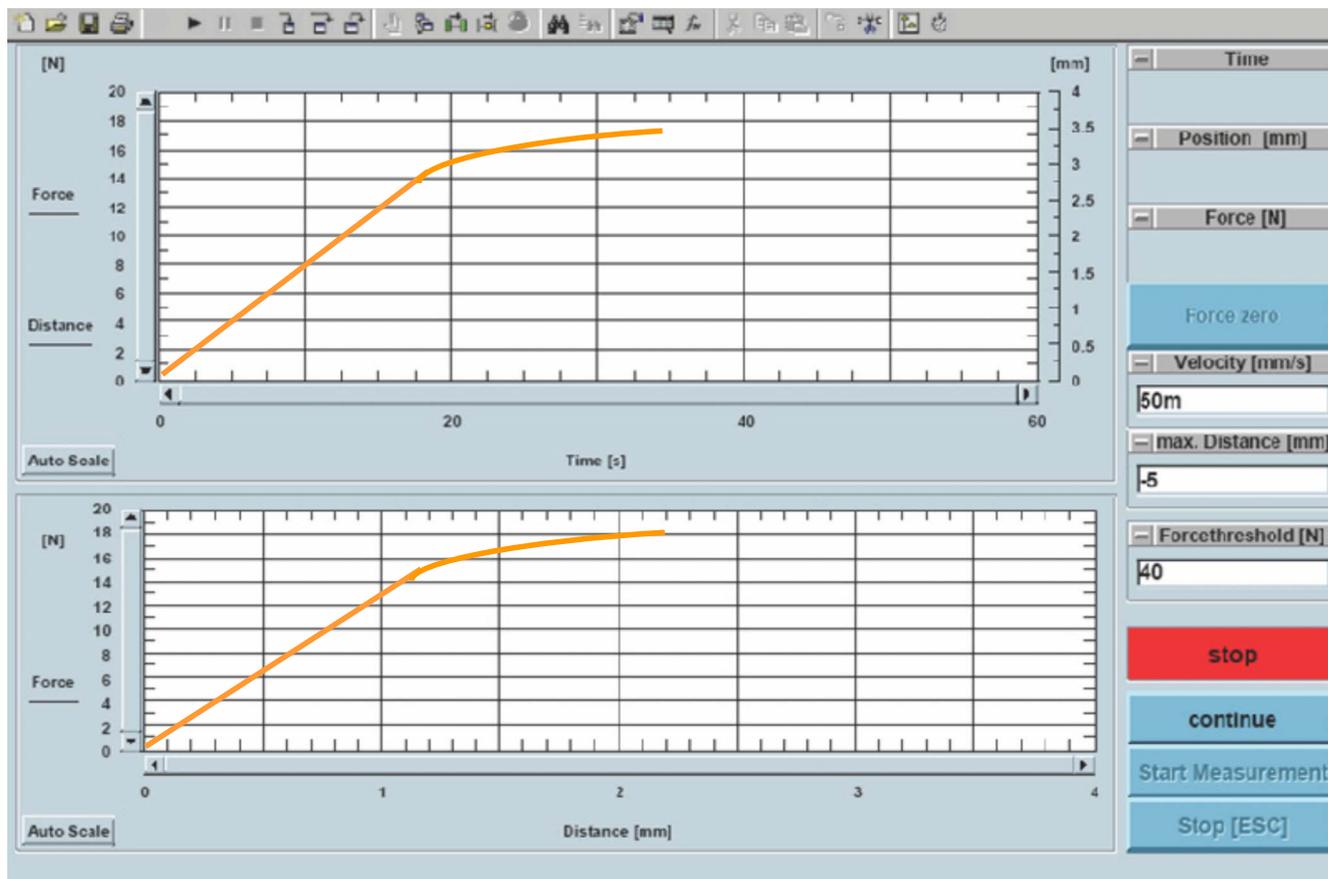


FIG. 2. (Color online) Screenshot of the VEE program, the software interface with tensile rig.

B. Electrochemical repassivation behavior of Al

The interfacing of our electrochemical setup allows studying the repassivation behavior under tensile load. Initial tests were carried out to identify the effect of loading on the oxide formed. An aluminum wire 500 μm in diameter was passivated in acetate buffer of pH 6.0 by holding at a potential of 1.5 V (SHE). This results in an oxide, which is approximately 4 nm thick.²⁵ After passivation, subsequently the

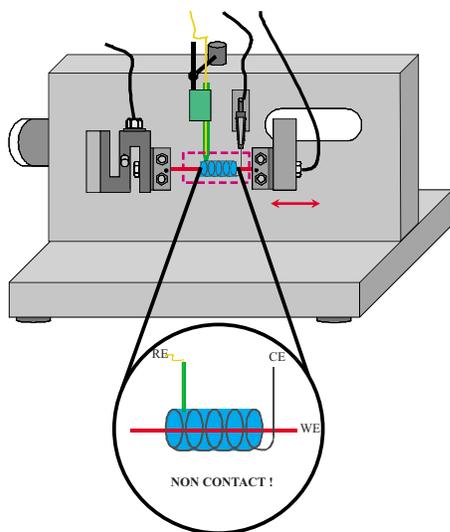


FIG. 3. (Color online) Schematic of the tensile rig interfaced with an electrochemical cell.

wire was loaded (tensile) in acidified aqueous CuSO_4 solution. Tensile loading beyond a critical force should cause brittle failure of the oxide. Upon failure, the cracks formed would expose bare aluminum which dissolves rendering electrons. These electrons would be utilized to reduce the Cu^{2+} ions in solution to form Cu, which would then deposit at cracks. This process is referred to as cementation. The SEM micrograph and EDX analysis (Fig. 5) carried out on the sample shows the deposition of Cu at cracks in oxide, which confirms that oxides can fail due to tensile loading.

To follow the repassivation behavior, experiments were carried out to record the current transients during tensile

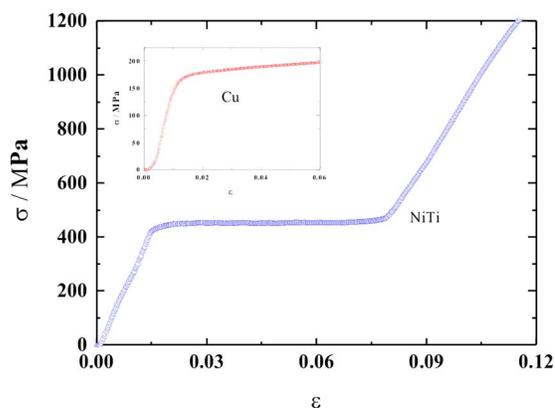


FIG. 4. (Color online) Stress vs strain curve for NiTi shape memory alloy wire. Inset shows the tensile behavior of Cu.

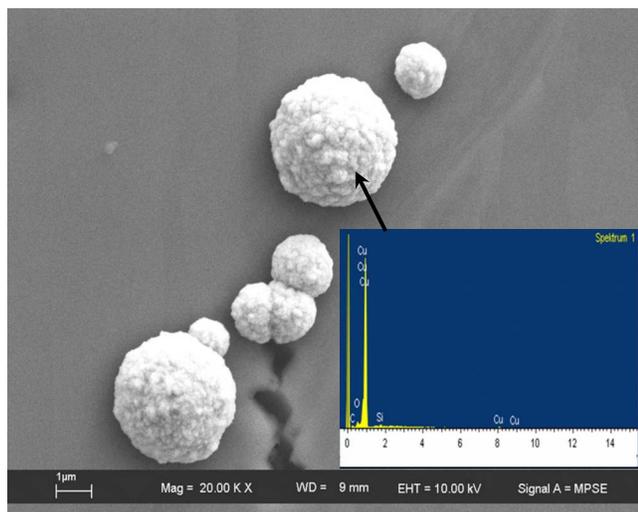


FIG. 5. (Color online) SEM micrograph of Cu deposits on the cracks of Al_2O_3 and EDX spectra confirming the presence of Cu (inset).

loading. The geometry of the wire was modified into a dog bone shape by either electropolishing or by creating a notch at its center. The narrowed zone acts as stress concentrator where the oxide would be potentiostatically grown. The passivation was carried out in an acetate buffer of pH 6.0 by holding at 1.5 V (SHE). After passivation, the specimen was loaded under tension, and, simultaneously, F (force) versus d/t (distance/time) and I (current) versus t (time) curves were recorded.

A typical anodic current transient indicating the repassivation behavior is shown as an inset along with its corresponding force versus time curve in Fig. 6. Initially, the Al wire was loaded up to 20 N, without a significant rise in current. This suggests that the oxide did not fail. Also, maintaining the wire at approximately 20 N for a certain time does not result in a current increase. Further loading led to failure of the wire and in this regime, there is a significant current increase. The multiple anodic rise of the current (current transients) could be related to the multiple cracks formed during tensile loading of the wire. However, the interpretation of the observed data is not straight forward.

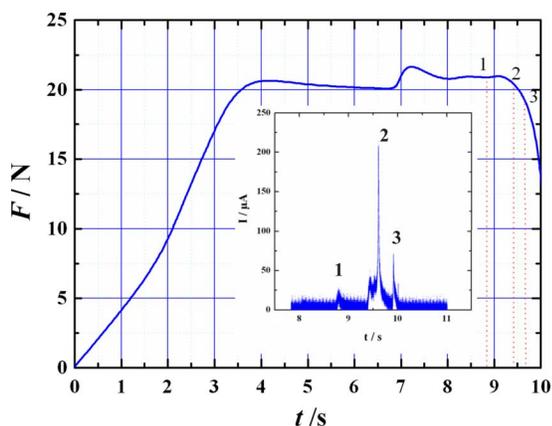


FIG. 6. (Color online) A typical current transient behavior for Al passivated at 1.5 V (SHE) in acetate buffer recorded during tensile loading. The inset shows the current transient spikes (1, 2, and 3) in correlation with the force vs time curve.

Passivation of Al at 1.5 V would lead to approximately 4 nm thick oxide.²⁵ As expected, the mismatch of mechanical properties between Al oxide and Al (brittleness of oxide compared to the Al wire) should lead to the failure of the oxide well below the elastic limit. However, the current transients were not observed for forces within the elasticity limit of Al but only at forces where Al wire plastically deforms. Hence, the origin and the critical force of the current transients are unclear. Also, this raises serious doubts whether the nanometer thick oxide fails within the elastic limit of the Al wire. Most likely, these oxides would fail well within the elastic limit but repassivate immediately and then could fail again in the plastic region. If so, basically the elasticity of oxide would be shown up as the distance between multiple current transient peaks, which could well be hidden in the background noise. On the other hand, if a crack is present, it would propagate into Al. In such a case, the strain on wire would not be completely transmitted to oxide but utilized for crack propagation. Therefore, one might not see any current transient in elastic regime.

During the plastic failure of the material, the current transient rise is multiple, with peaks of different current intensity. Also, it is well known that the plastic flow causes changes in the dimension of the wires, i.e., an increase in gauge length and decrease in cross section. However, at the point of stress concentration, where the oxide is grown potentiostatically, one would expect a current transient change only when there an exposure of the bare Al surface occurs. This is only possible when the grown oxide fails. All experiments carried out so far revealed a similar behavior. Therefore, the smaller peaks could be well related with oxide failure. The large peak (along with the associated peaks), as shown in the Fig. 6 (inset), could be due to an exposure of the fractured cross sectional area of the wire to the electrolyte after breakage. However, by knowing the charge consumption (Q), the repassivated area of oxide can be calculated by

$$A_{\text{OX}} = \frac{QM_v}{d_{\text{ox}}zF},$$

where A_{ox} is the repassivated area, M_v is the oxide mole volume, z is the number of electrons, F is the Faraday constant, and d_{ox} is the oxide thickness.

Performing this calculation for the large peak yields a repassivated area of $1.11 \times 10^5 \mu\text{m}^2$, which is comparable to the original cross sectional area of the wire of $1.96 \times 10^5 \mu\text{m}^2$ (assuming that no necking has taken place). It is normal that Al undergoes ductile failure, i.e., by necking, where there is significant reduction in cross sectional area. Therefore, it seems reasonable to assume that the current increase is related to the combined effects of oxide failure and wire fracture.

Although further work is required to fully rationalize the observed phenomena, our results show that it is well worthwhile to study the repassivation behavior of thin oxides under mechanical loading conditions. Further experiments are required to address the above issues. Overcoming these technical difficulties and normalizing the experimental procedure would be the scope of further work.

IV. CONCLUSIONS

A tensile rig interfaced with an electrochemical system was designed and fabricated. The applicability of the fabricated tensile rig is validated by studying the tensile properties of Cu and NiTi wires. Also, the equipment in principle, allows studying the repassivation behavior of wires covered with thin oxides. The tensile loading of the passivated specimen leads to the failure of the oxide. Tensile loading of a passivated surface in acidified CuSO₄ led to Cu deposition at oxide cracks. However, failure of the oxide did not merely occur in the elastic regime of Al. Multiple anodic current spikes (current transients) were observed during the plastic deformation of the wire. The origin of the current transients during plastic deformation is most likely due to oxide failure.

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¹T. Duerig, A. Pelton, and D. Stöckel, *Mater. Sci. Eng., A* **273**, 149 (1999).

²M. Frotscher, K. Neuking, R. Böckmann, K. D. Wolff, and G. Eggeler, *Mater. Sci. Eng., A* **481**, 160 (2008).

- ³A. W. Hassel, *Minimally Invasive Ther. Allied Technol.* **13**, 240 (2004).
- ⁴K. Fushimi, M. Stratmann, and A. W. Hassel, *Electrochim. Acta* **52**, 1290 (2006).
- ⁵A. Undisz, F. Schrepel, W. Wesch, and M. Rettenmayr, *J. Biomed. Mater. Res. Part A* **88A**, 1000 (2009).
- ⁶K. Bundy, C. Williams, and R. Luedemann, *Biomaterials* **12**, 627 (1991).
- ⁷J. Black, R. M. Graham, M. Laberge, T. E. McGovern, and J. J. Jacobs, *J. Biomed. Mater. Res.* **32**, 447 (1996).
- ⁸G. Rondelli and B. Vicentini, *J. Biomed. Mater. Res.* **51**, 47 (2000).
- ⁹S. A. Shabalovskaya, *Biomed. Mater. Eng.* **12**, 69 (2002).
- ¹⁰K. Yokoyama, K. Kaneko, K. Moriyama, K. Asaoka, J. Sakai, and M. Nagumo, *J. Biomed. Mater. Res. Part A* **69A**, 105 (2004).
- ¹¹K. Yokoyama, T. Ogawa, A. Fujita, K. Asaoka, and J. Sakai, *J. Biomed. Mater. Res. Part A* **82A**, 558 (2007).
- ¹²C. Heßing, J. Frenzel, M. Pohl, and S. Shabalovskaya, *Mater. Sci. Eng., A* **486**, 461 (2008).
- ¹³T. Peitsch, A. Klocke, B. Kahl-Nieke, O. Prymak, and M. Epple, *J. Biomed. Mater. Res. Part A* **82A**, 731 (2007).
- ¹⁴F. P. Ford, G. T. Burstein, and T. P. Hoar, *J. Electrochem. Soc.* **127**, 1325 (1980).
- ¹⁵H. J. Pearson, G. T. Burstein, and R. C. Newman, *J. Electrochem. Soc.* **128**, 2297 (1981).
- ¹⁶K. S. Tan, A. W. Hassel, and M. Stratmann, *Materialwiss. Werkstofftech.* **36**, 13 (2005).
- ¹⁷K. Fushimi, K. Takase, K. Azumi, and M. Seo, *Electrochim. Acta* **51**, 1255 (2006).
- ¹⁸E. Akiyama, M. Stratmann, and A. W. Hassel, *J. Phys. D* **39**, 3157 (2006).
- ¹⁹A. W. Hassel and A. J. Smith, *Corros. Sci.* **49**, 231 (2007).
- ²⁰E. P. S. Tan and C. T. Lim, *Rev. Sci. Instrum.* **75**, 2581 (2004).
- ²¹K. I. Dragnevski, T. W. Fairhead, R. Balsod, and A. M. Donald, *Rev. Sci. Instrum.* **79**, 126107 (2008).
- ²²W. Callister, *Materials Science and Engineering*, 7th ed. (Wiley, India, 2007).
- ²³See <http://www.me-systeme.de/> for details.
- ²⁴K. A. Lill and A. W. Hassel, *J. Solid State Electrochem.* **10**, 941 (2006).
- ²⁵A. W. Hassel and M. M. Lohrengel, *Mater. Sci. Forum* **185**, 581 (1995).