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# Morphological Instability Leading to the Formation of Self-Ordered Porous Anodic Oxide Films

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# Morphological Instability Leading to the Formation of Self-Ordered Porous Anodic Oxide Films

## **Abstract**

Porous anodic oxide (PAO) films are grown by electrochemical polarization of Al, Ti, Zr, Nb, Hf, and W in baths that dissolve the oxide. Procedures to grow films with highly ordered arrangements of nanoscale pores have led to the extensive use of PAO films as templates for nanostructured devices. The porous film geometry may be controlled precisely via the film formation voltage and bath composition (1). Recently, tracer studies and modeling showed that transport in the amorphous oxide involves both electrical migration and plastic flow (2,3). The oxide seems to behave as an incompressible material during steady-state growth of the porous film. Linear stability analysis incorporating the assumption of incompressibility predicted important features of PAO (4). These include the constant ratio of interpore distance to anodizing voltage on Al for any electrolyte composition; narrow ranges of oxidation efficiency (the fraction of oxidized metal atoms that remain in the oxide) producing ordered PAO films on Al and Ti; and the inability to produce ordered films composed of divalent metal oxides. However, the analysis did not predict the observed onset of instability at a critical oxide thickness, and the observed dependence of the interpore distance on the electrolyte composition.

## **Keywords**

Chemical and Biological Engineering

## **Disciplines**

Catalysis and Reaction Engineering | Electro-Mechanical Systems

Morphological Instability Leading to the Formation of  
Self-Ordered Porous Anodic Oxide Films

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Porous anodic oxide (PAO) films are grown by electrochemical polarization of Al, Ti, Zr, Nb, Hf, and W in baths that dissolve the oxide. Procedures to grow films with highly ordered arrangements of nanoscale pores have led to the extensive use of PAO films as templates for nanostructured devices. The porous film geometry may be controlled precisely via the film formation voltage and bath composition (1). Recently, tracer studies and modeling showed that transport in the amorphous oxide involves both electrical migration and plastic flow (2,3). The oxide seems to behave as an incompressible material during steady-state growth of the porous film. Linear stability analysis incorporating the assumption of incompressibility predicted important features of PAO (4). These include the constant ratio of interpore distance to anodizing voltage on Al for any electrolyte composition (1); narrow ranges of oxidation efficiency (the fraction of oxidized metal atoms that remain in the oxide) producing ordered PAO films on Al and Ti; and the inability to produce ordered films composed of divalent metal oxides. However, the analysis did not predict the observed onset of instability at a critical oxide thickness, and the observed dependence of the interpore distance on the electrolyte composition (1).

The present work investigated compressive stress generation during the initial stage of planar film growth, i. e. before the onset of the morphological instability leading to PAO (5). Curvature interferometry was used to measure stress evolution during Al anodizing, both during oxide growth at constant current and following growth interruptions. Elastic compressive stresses were characterized that originate from electric field-induced insertion of electrolyte oxyanions (e. g. sulfate, phosphate, and oxalate). Models of the initial anodizing period were developed. The hypothesis was evaluated that stress gradients build up during this time, and eventually produce significant rates of stress-assisted ion migration, ultimately resulting in a transition from elastic to incompressible behavior. The oxide thickness at this transition, along with the universal interpore spacing/thickness ratio revealed by the stability analysis (4), may determine the observed contaminant-dependent pore spacing.

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