NASF SURFACE TECHNOLOGY WHITE PAPERS
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The 56th William Blum Lecture
Presented at NASF SUR/FIN 2022
in Rosemont, Illinois
June 7, 2022

Polarization and Natural Order

by
Dr. Jude M. Runge
Recipient of the 2020 William Blum
AESF Scientific Achievement Award

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Dr. Jude M. Runge
(Senior SME, Principal Engineer at Apple, Retired 2023,
Cupertino, California, USA)
Recipient of the 2020 William Blum AESF Scientific Achievement Award

Editor's Note: The following paper is based on Dr. Runge's William Blum Memorial Lecture at SUR/FIN 2022, in Rosemont, Illinois on June 7, 2022. Dr. Runge was announced as the recipient of the 2020 NASF William Blum Scientific Achievement Award at SUR/FIN 2021 (Detroit) owing to a delay brought on by the cancelation of SUR/FIN 2020 (Atlanta) by the COVID pandemic.

Author's Note: I thank the NASF for honoring me with the 2020 Scientific Achievement Award. NASF is an important resource for the metal finishing industry; it connects us to one another through various conferences and publications, and thereby inspires us to be better surface finishing professionals. It is truly humbling to be recognized as one "whose outstanding contributions have advanced the theory and practice of electroplating, metal finishing, and the allied arts; raised the quality of related processes and products; enhanced the dignity and status of the profession or has been involved in their continuation", and this honor is shared in so many ways with the mentors and colleagues with whom I have had the privilege to learn and work throughout my career, which has focused on aluminum and its alloys, and finishing by way of anodic oxidation. I wish to especially thank James H. Lindsay for his recognition and support, as well as for his continued work with NASF and *Products Finishing* magazine. Lastly, I share this recognition with my colleagues in the metal finishing industry worldwide. As each of us continues with our individual efforts to research, develop, manufacture and improve new and existing metal finishing techniques and related processes, through our involvement in professional societies like NASF, we find that as colleagues, we work together and collectively learn from one another. NASF enables our work to inspire and renew interest among ourselves and young people, by providing a forum to keep our industry fresh, vibrant and relevant into the future.

ABSTRACT

Investigation of the long-range order of network structures induced by way of polarization in non-equilibrium processes, such as anodizing, reveals interesting parallels with naturally-occurring ordered equilibrium networks. Polarization, or charge separation, caused by an electric field, is important to the production of long-range network order. In non-equilibrium networks, such as anodizing, polarization sets the ordered nucleation points across the aluminum substrate. In equilibrium systems, the intrinsic energy of the network constituents set location and distance between each network member, creating a virtual energy polarization net with a fascinating hexagonal pattern. Among living systems, the polarization net sustains an integral living fabric that can move and flow with perfect synchronicity. From the smallest coral to the largest elk, network systems of all sizes exhibit similarities that connect polarization to the order that forms when same-type species assemble and move – the understanding of which is important for understanding and modifying the development of structural order in synthetic systems, and applying these concepts to actual scientific and industrial applications.

1. Introduction

There are many common industrial applications for Anodic Aluminum Oxide (AAO), and all rely on and utilize the incredible anodic oxide network, whether the application be for corrosion protection, wear resistance, dielectric resilience or decorative purposes. Polarization of the substrate as an anode by an externally applied electric field yields an ordered positive charge at the surface that drives uniform oxide nucleation, development and growth. The result is an ionic solid that provides surfaces for corrosion protection, decoration and bonding. The ordered, columnar structure also provides mechanical wear resistance and dielectric strength. Consequently anodized aluminum has been finding use in architecture, aerospace and aircraft, electronics, automotive, sporting goods and medical industries since the late 19^{th} century (Fig. 1).[1]

Figure 1 - Examples of industries that commonly use anodized aluminum; (L-R) medical sterilization containers and other devices, aircraft, architecture, automotive.

Possibly the most significant characteristic of anodic aluminum oxide (AAO), is its highly ordered structure. AAO comprises a network of thousands of nanoscale columnar cells per unit grain aluminum substrate, each with a rounded bottom and circumscribing a central pore. As-grown, with specific process parameters, the oxide structure is precise (Fig. 2); the cell walls, bottoms and pore diameters are consistent from column to column and bound together across an inter-columnar knitline. The AAO network exhibits a characteristic uniform, hexagonal pattern in plan view (Fig. 2a). Polarization of the substrate by an external power source is the key to the network order, developing an ordered charge density on the anode surface that sets points of oxide nucleation, and ultimately the precise dimensions each oxide cell.[2]

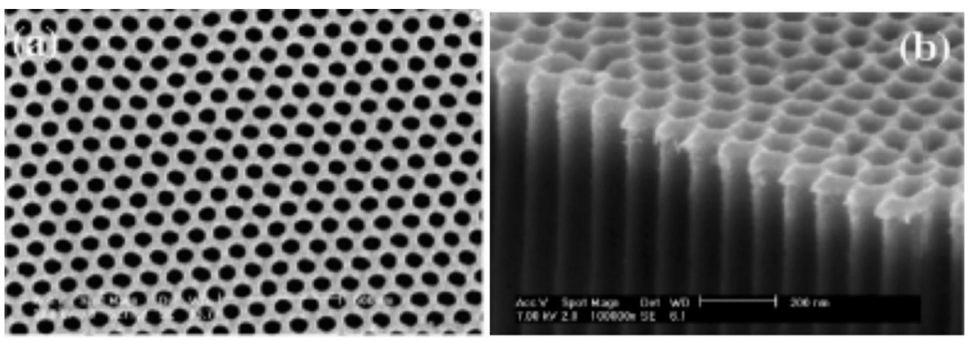

Figure 2 - Scanning Electron Microscope (SEM) image of an anodic aluminum oxide (AAO) layer showing its extraordinary structure and order. The oxide in this image was grown in a phosphoric acid electrolyte on a 1050 aluminum alloy substrate.

Similar-appearing network order that is both amazing and beautiful is commonly observed in nature. Order in self-assembled living networks, such as coral reefs, beehives, schools of fish or murmurations or birds, appears to originate at the polarized center of each network member, yielding long range order with a virtual and sometimes actual hexagonal pattern (Fig. 3). Members comprising the network are the same species, and have the same size, shape and general strength, which governs the position and spacing of each network member. No external power source drives network formation and growth. Networks connected to a substrate, such as a coral reef or a beehive continue to grow after the surface of origin is reassembled, indicating polarization is internal to the network. Many large scale natural geological networks also exhibit hexagonal order of individual elements.

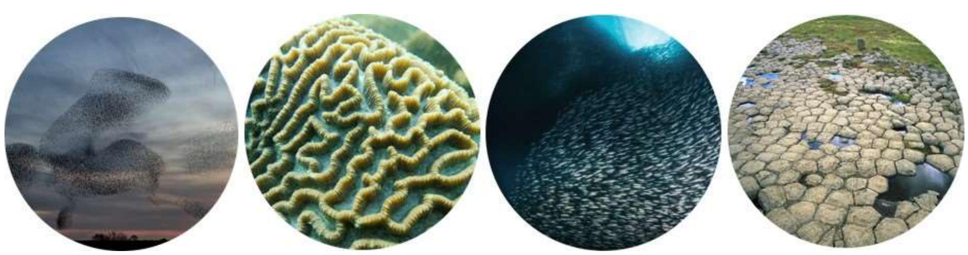

Figure 3 - Examples of equilibrium network order in nature; murmuration of starlings, a colony of coral, a school of smelt and Icelandic basalt columns in hexagonal plan view.

NASF SURFACE TECHNOLOGY WHITE PAPERS
88 (11), 1-11 (November 2024)

The 2022 Blum Lecture provides an overview of the fascinating parallels between the synthetic order established by non-equilibrium reactions, such as anodizing, which are nano-scale, and the natural order established by equilibrium reactions, many of which are on the macro-scale. Observation and recognition of the characteristics of various network types is of interest for emerging AAO applications development.

2. Polarization and Non-Equilibrium Order

The anodizing process is an electrical circuit: polarization is introduced to the aluminum anode via an external power supply, and overrides the energy of most surface phenomena on the aluminum anode while determining the points at which the oxide nucleates. *N*, the value for the magnitude of polarization, is measured in volts, sets the position for and distance between each nascent oxide column, making polarization an integral engineering component of the anodizing process. The applied current density or applied voltage, is the unique component driving the growth of the ordered anodic aluminum oxide (AAO) and enables continued oxide growth after the surface is fully reconstructed by oxide. Current is carried from the power supply and through the anode by electrons, as the oxide grows, the mode of current transport shifts from electrons to ions and continues via ions through the aqueous electrolyte to where the circuit is completed at the cathodes (Fig. 4).

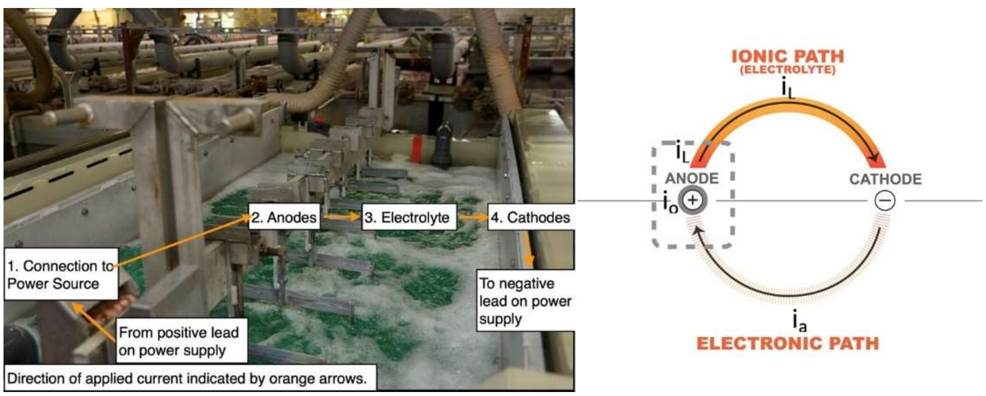

Figure 4 - Operating anodizing circuit with schematic of the current path.

The discrete features of each columnar oxide cell; the wall thickness, the pore diameter and the total oxide layer thickness, are consequently set by the anodizing parameters: polarization, the applied current density (which governs oxide growth rate), electrolyte conditions, and the amount of time reaction is allowed to proceed. The AAO network is bound across intercolumnar "knitlines", which are at the energy minima between polarized oxide centers (Fig. 5).

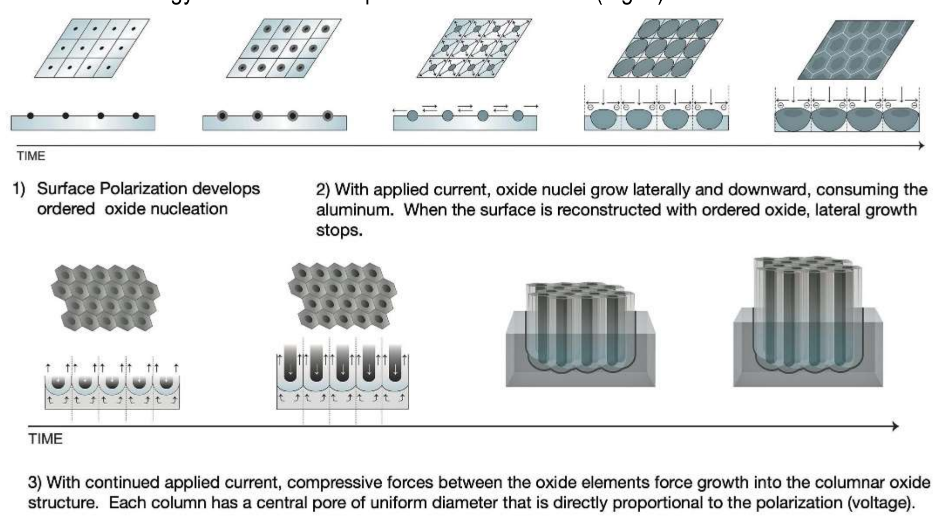

Figure 5 - Schematic for anodic aluminum oxide nucleation and growth. Uniformity of the structure is driven by polarization by an external power source.

NASF SURFACE TECHNOLOGY WHITE PAPERS
88 (11), 1-11 (November 2024)

As AAO grows and develops, it becomes a functional part of the anodizing circuit, critical for continued oxide network growth. With continued applied current density, polarization effects continue to impact how the AAO structure develops. The aluminum anode is consumed by the oxide. As the surface is reconstructed by the oxide, growth stress develops at the substrate-oxide interface, which is countered by polarization forces at the oxide-electrolyte interface. Upon impingement of the ordered oxide elements, continued oxide growth produces the unique hexagonal structure of the anodic oxide. Electrostriction forces enable each oxide element to grow in the direction of the applied current density, while polarization (voltage) forces stabilize and maintain the dimensions for all features of each developing columnar cell comprising the AAO (Figs. 6 and 7).

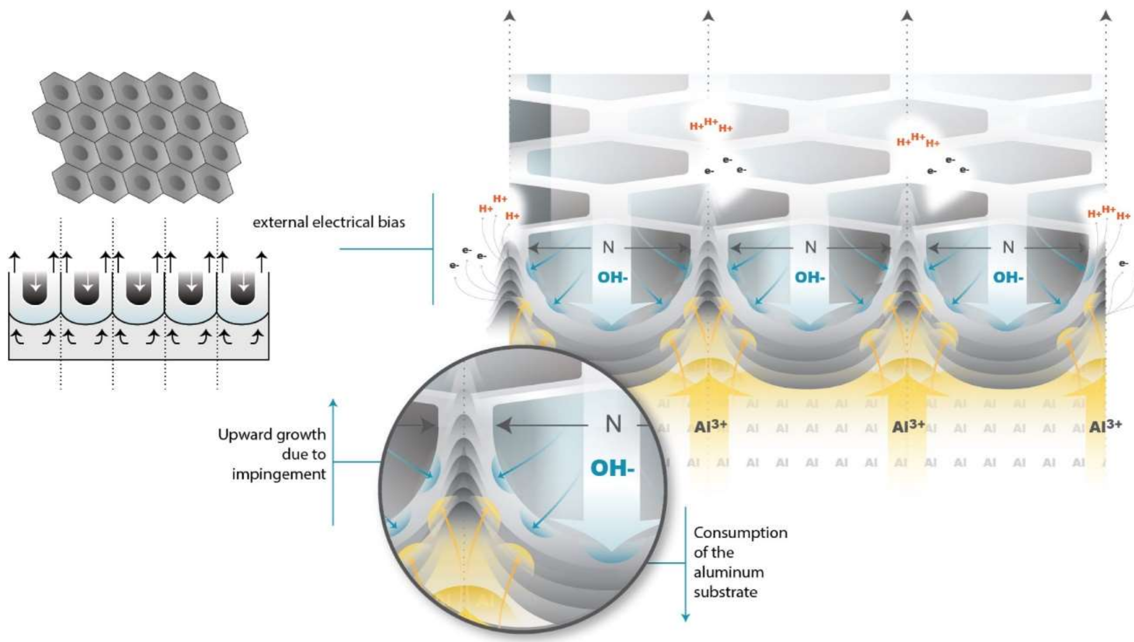

Figure 6 - Schematic of the aluminum–oxide interface during AAO growth.

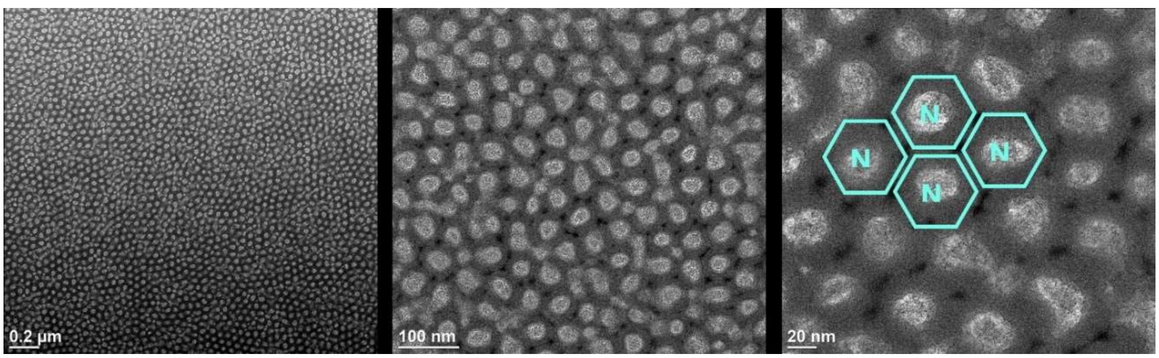

Figure 7 - TEM plan view of an anodic oxide reveals its network order. The ordered, hexagonal shape each oxide column is the result of electric field forces (polarization) within the central pore countering the mechanical forces generated at the metal-oxide interface of/by each network member. *N* is the value of polarization, measured in volts.

3. Polarization and Natural (Equilibrium) Order

In nature, polarization is also the key to network order. It can be single point, with resultant radial order, such as with the petals of a flower or the spiral of a snail shell (Fig. 8); it can also be multi-point, originating with each network member, producing an ordered network.

NASF SURFACE TECHNOLOGY WHITE PAPERS
88 (11), 1-11 (November 2024)

Figure 8 - For single point polarization, each network member is evenly spaced at a consistent angle around a polarized center.

Equilibrium ordered networks originate from the polarized center of each member comprising the network. This is most easily called to mind by considering the coordinated flight of a flock of birds, or the ordered, circular swimming pattern of a school of fish. Each member of the network is the same species and about the same size, shape and strength. There is no fixed polarized substrate. This begs the question, what is the driving force that enables the initial formation of the network? It has been suggested in various publications on swarming behavior that the driving force behind cluster formation of living things is a basic community need such as feeding, migration or protection. A swarm of "polarized members" assembles to eat or migrate and immediately their inter-member position and distance is set.[3,4] Swarming is transient; members dissipate when the need behind cluster formation is satisfied or destroyed.

Consequently, the space surrounding members of an equilibrium network is uniform and reflects the governing characteristics. These inherent forces govern the position and inter-member spacing of the network, through which, the community of members can maintain the lowest total energy, which yields a natural "fabric" with a hexagonal pattern. The hexagonal shape enables the densest packing of network members with the lowest amount of energy, which is at its minimum at the maximum binding distance between members. In other words, inward average transfer entropy, generated by the individual network member, sets the position of each member, establishing discrete groups and inter-member order, while outward transfer entropy sets the energy minimum, or distance between each member, "knitting" the network together.[5] Networks comprised of smaller members have smaller spacing, and the opposite is also true. This is similar to the results of "tuning" AAO; oxides grown at a lower current density have columns with corresponding smaller diameter pores and thinner walls. Oxides grown at a higher current density have wider pores and thicker walls (Fig. 9).

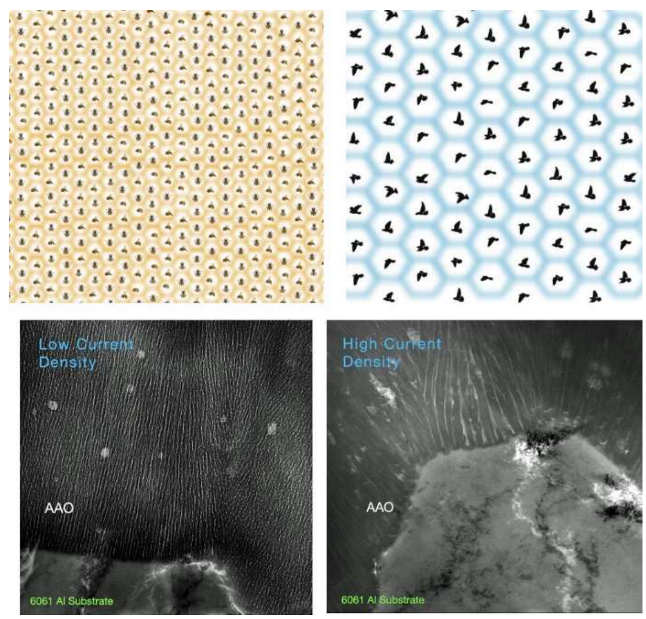

Figure 9 - Schematic showing the difference between natural order in (L) smaller (bees) vs. (R) larger species (birds) and how we can see the same trend in synthetic order in AAO produced with low vs. high current density (corresponding low vs.high polarization).

4. Discussion

4.1. Dynamic Networks, Dimension and Degrees of Freedom

Based upon the previous observations, when one considers the various ordered networks, they fall into two basic categories: non-equilibrium and equilibrium. The order of non-equilibrium networks is driven by an external power supply. Without an external power source, natural equilibrium networks rely on basic thermodynamic forces of the surface and the entropy between network members to govern how a surface layer may develop. Either type can be stationary or dynamic, exhibiting short-range or long-range order.

Dynamic equilibrium networks assemble spontaneously. An ordered swarm of several same species organisms initiates from the initial "cluster" whose need for food, protection or migration drives assembly. Assembled on a surface or in an area that is transiently polar, perhaps by the energy of the food they're about to eat, the condition of each member (size, shape and strength) produces a cluster of equidistant members. Polarization of the members sets each of 6 degrees of freedom based on each bird's geographic (x, y, and z) position and the momentum in each direction (internal transfer entropy), based on condition.[7] With order established, a virtual energy "net" develops across the group based on the position and entropy of each network member (Fig. 10).

Figure 10 - Clusters of two different species of birds; Avocets (larger) and Sandpipers (smaller, in the foreground).

The energy push-pull observed with the movement of a dynamic network is magnificent to consider. There is no sense of a leader - follower hierarchy within the network to maintain order, and no one member is looking at another to track position.[8] As a roving member moves, deviating from the initial ordered swarm, the nearest neighbors move collectively to maintain charge and order, hence ordered movement occurs maintaining relative long-range order. In this way, the natural fabric is "stretched" and recovers as the swarm reaches the next cluster location, and order is maintained or disperses due to lack of need or disruption. Without being fixed to a polarized substrate, the concert movement of the swarm is synchronized, but the directions of domains comprising the group are random; they can be from an edge or center position in the network. Schools of fish, murmurations of birds, swarms of bees, colonies of coral, assemble and move like a living fabric with perfect synchronicity in all directions (Fig. 11).

Figure 11 - Murmuration of starlings, a type of bird.

Figure 12 - Schematic of non-uniform spacing created by varying internal transfer energy in human networks of different size, shape and strength.

Human networks are seldom homogeneous; inter-member spacing varies with the size and shape of the individual network member. Outward transfer entropy, from one member to the rest of the nearest neighbors, is always experienced within a network, regardless of homogeneity; think of the queue at an airport, where people maintain an ordered distance, more or less, including luggage carts, or how a person reacts to another person who stands too close when they are speaking. Human internal entropy differs, depending on size, shape and strength, so our network positions to our nearest neighbors will differ, but our outward transfer entropy keeps us from colliding with our nearest neighbors.

Distances we keep vary culturally, and certainly, like our animal counterparts, equilibrium can be disrupted by threats to safety, or a welcome embrace.[9] Humans can unconsciously move in concert; consider a crowded sidewalk during rush hour; outward transfer energy between network members enables the instinctive avoidance of collisions with our nearest neighbors. However, synchronized movement with human network members can only be achieved consciously, as with the movement of a marching band or dance troupe, in which the maintenance of uniform distances must be rehearsed (Fig. 12).

4.2. Significance of understanding dynamic networks for anodic oxide formation and growth

Non-equilibrium networks such as anodic aluminum oxide (AAO) are driven by an external power source and originate at positions across the fixed, polarized substrate. In addition to the substrate being the source for polarization, the substrate is also the source of the material that comprises each network member, consequently the oxide is intimately bound to the substrate. This condition limits the degrees of freedom for anodic oxide growth from the outset, creating a stationary network. Nevertheless, oxide growth is a dynamic process. With an externally applied current density, the members grow in the spatial directions, x, y, and z, and the source momentum can be identified as the degrees of freedom that drive/hinder oxide growth: current, voltage and the conductivity of the electrolyte, which increases the degrees of freedom to six. However, once the network members impinge, reconstructing the surface with oxide, momentum in the x direction is hindered as growth in the y and z continue, effectively reducing oxide growth to five degrees of freedom. As oxide growth continues, resistance increases as oxide growth is hindered in all directions, and conductivity of the electrolyte changes, gradually inhibiting continuity of the anodizing circuit, further reducing directional degrees of freedom that occur to accommodate changes in the circuit. Network order may be disrupted as the polarization that sustains the network dielectric withstand is exceeded, which may happen local to areas of higher resistance, or across the entire metal-oxide interface.[10]

Controlling the disruption of network order externally, in a non-equilibrium system, is of interest because if the anodic oxide structure can be modified to move with more degrees of freedom, oxide networks with ordered columnar structures can be grown with patterns that exceed the confines of the fixed substrate. It is well documented that the structure of the oxide can be uniformly altered by changing polarization via current oscillation during anodizing or by turning the circuit on and off, a.k.a., pulse anodizing. Interesting properties of the anodic oxide are developed with such modifications. As an integral structure on the aluminum substrate, such structural changes improve adhesion and strength in wear applications on complex alloys, and can change the oxide light-scattering properties and appearance with interference coloring. AAO stand-alone membranes are emerging for use in a variety of applications, because modifying the AAO structure by pulse anodizing measurably changes the behavior of the ionic character within the central pore, enabling enhancement of the properties of nano-scale sensors, filters, even lenses, by changing structural order through controlling and changing polarization during the anodizing process (Fig. 13).[11,12]

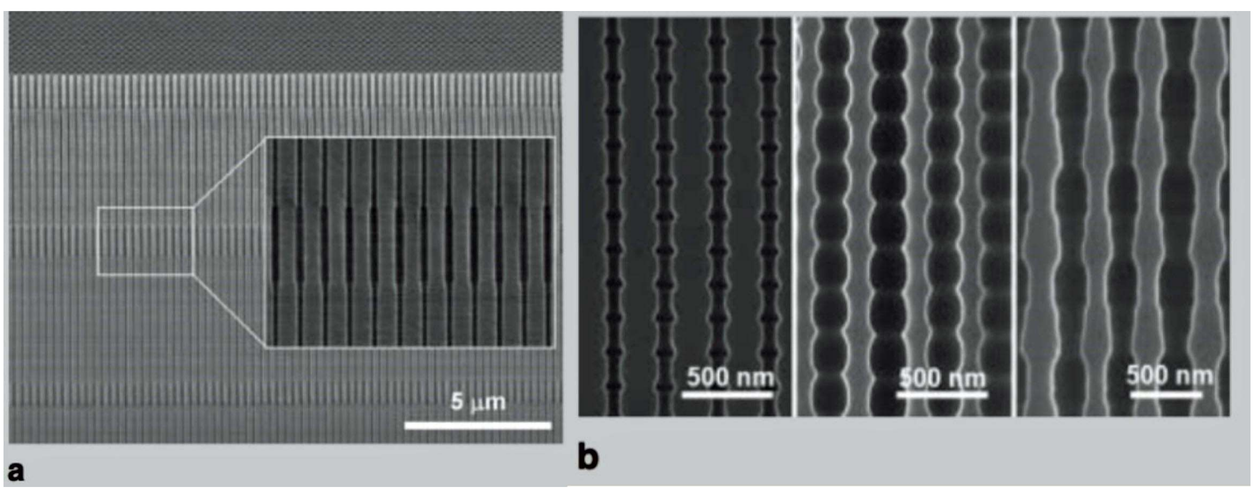

Figure 13 - Examples of the impact of changing polarization the ordered network structure from an integrally attached aluminum (alloy) substrate: (a) SEM photomicrograph showing a cross section of AAO grown by combining Mild Anodizing (MA) or Type II anodizing parameters with Hard Anodizing or Type III anodizing parameters; (b) SEM photomicrographs of various AAO structures grown with oscillating current during hard (Type III) anodizing. Oscillating current profiles (pulse anodizing) determine the internal pore geometry of the nanoporous AAO.[13]

Changing the AAO structure is also possible by modifying the substrate from which the oxide is grown. Interesting oxide structures, which integrate single-point polarization with the general polarization of the primary substrate, have been grown from substrates with defects that support unique oxide growth from discrete locations.[2] The utility of such structures has yet to be investigated, showing the need for continued research and development to find applications as well as consistent manufacturing methods, should such structures prove beneficial (Figs. 14 and 15).

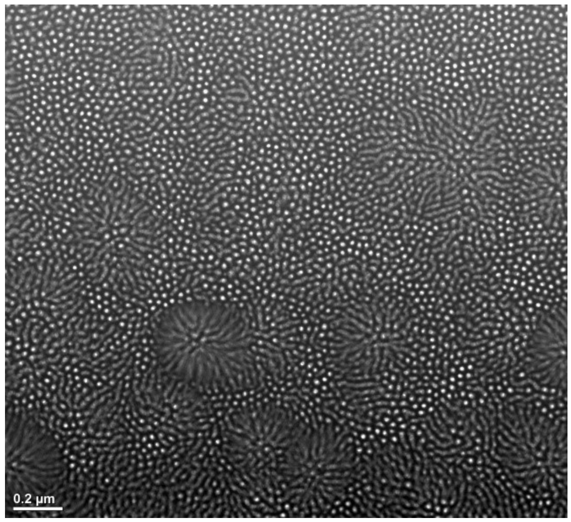

Figure 14 - TEM Plan view of anodic oxide grown on 6063 T6 aluminum alloy. Long-range order is affected by discrete areas of single-point polarization developed from defects in the primary substrate from which the AAO was grown.

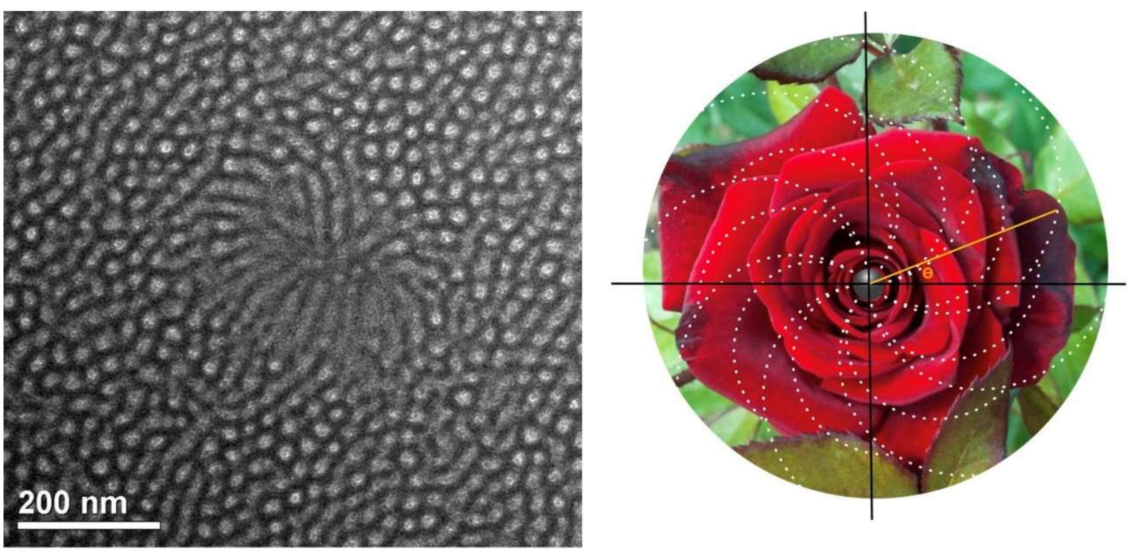

Figure 15 - Comparison of (L) an AAO single-point polarization nano-scale structural feature with (R) that of a naturally-occurring single point polarization.

5. Conclusion

Observation and study of equilibrium natural processes has often been the basis for scientific development and engineering ideas for non-equilibrium processes. For this paper, the opposite approach, the observation and study of a non-equilibrium process - anodizing, that yields ordered networks at the nano-scale - was used to develop interesting insight for natural equilibrium spacing and order in macro-scale networks. During the process of preparing the paper for the lecture, the review came full circle, connecting the macro-scale occurrence of single-point polarization in nature to nano-scale AAO "defects" that cause single point polarization in AAO. Understanding the influence of polarization on network order can drive useful changes on how to influence the structure and properties of ordered structures.

Interest in employing the order of Anodic Aluminum Oxide (AAO) for various industrial applications has gained interest in the scientific community since the late 1990s.[14] Since then, AAO membranes, with their highly ordered columnar structure, and central pore, with its "tunable", precise diameter and intrinsic ionic character, have been the source of research and development for a variety of nano-scale technologies. AAO membranes are used as templates for producing arrays of nano-dots, nano-tubes and nano-wires in developing sensors, filters, lenses and other applications for the biomedical, photonic, food/beverage and chemical industries.[15-18] Additional research and modeling are necessary to fully develop equilibrium/non-equilibrium order concepts for new synthetic network systems.

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NASF SURFACE TECHNOLOGY WHITE PAPERS
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7. About the author

Dr. Jude Mary (Judy) Runge has more than forty years of industrial, government and academic experience, specializing in the areas of metallurgical engineering and interfacial science; specifically, in anodizing, component and assembly-level failure analysis, manufacturing processes and process evaluation, coatings and coating processes, and dissimilar materials joining. She is known for her expertise in analytical methods for materials, component and assembly characterization. A graduate of the University of Illinois at Chicago, she is recognized internationally as an author, lecturer and teacher. She is the author of **The Metallurgy of Anodizing Aluminum**, published by Springer Nature in April, 2018 and the Division Editor to **ASM Handbook, Volume 2A: Aluminum Science and Technology**, published in December, 2018. Judy was honored with the National Association of Surface Finishers NASF Scientific Achievement Award in 2020. At the time of her award lecture, in 2022, she was employed by Apple as Principal Subject Matter Expert for Metal Finishing. After 12 years of working for Apple as a contractor and full-time employee, she retired in July, 2023.