Accelerating electrochemistry with metal nanowires
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Abstract
Scalable, solution-phase syntheses of metal nanowires are enabling their increased use in electrochemical processes. This review highlights recent results demonstrating how metal nanowires can exhibit better durability and higher activity than traditional metal nanoparticle electrocatalysts on carbon supports. Metal nanowires can also form interconnected two-dimensional and three-dimensional (3D) networks that eliminate the need for a carbon support, thus eliminating the detrimental effects of carbon corrosion. Porous 3D networks of nanowires can be used as flow-through electrodes with the highest specific surface areas and mass transport coefficients obtained to date, enabling dramatic increases in the productivity of electrochemical reactions. Nanowire networks are also serving as 3D current collectors that improve the capacity of batteries. The tunable surface structure and dimensions of metal nanowires offer researchers a new opportunity to create electrodes that are tailored from the atomic scale to the microscale to improve electrochemical performance.

Introduction
Metal nanowires are essentially sticks of metal with diameters on the order of 100 nm or less and lengths ranging from several to hundreds of microns. Some of the earliest nanowires were synthesized by electrodeposition in nanoporous aluminum oxide [1–3], but this method is difficult to scale. Around the turn of the century, researchers discovered that anisotropic, crystalline nanowires could be grown from metals with symmetric, cubic crystal structures in a liquid solution, a technique referred to as solution-phase or colloidal synthesis [4]. This innovation allowed researchers to produce nanowires at a much larger scale than was previously possible [5–7], facilitating their use in a wide variety of applications. Today, metal nanowires can be produced from 23 different metals, including Ag [8,9], Au [10–13], Cu [14–17], Pd [18,19], Pt [20,21], Ni [22], and Pb [23,24]. The structure-dependent electrical, optical, and chemical properties of metal nanowires are being explored across a wide range of applications, including transparent conductors [25–27], wearable electronics [28,29], chemical/biological sensing and imaging [30–34], cancer therapy [30–32,35–37], waveguiding [38–43], and electrocatalysis [43–43]. The purpose of this review is to highlight recent results demonstrating the role nanowires can play in the advancement of electrochemical processes.
more quickly from Cu(111) than from Cu(100) [46]. In another case, single-crystal electrochemistry and density functional theory (DFT) showed that chloride selectively displaced hexadecylamine from Cu(111), thereby increasing the rate of atomic addition to (111) facets on the ends of nanowires [45]. Additional studies are necessary to determine the facet-selective chemistry that governs the anisotropic growth of nanowires from other metals.

Metal nanowires can also grow through particle attachment [47–53], wherein the seed crystals assemble into one-dimensional structures to reduce their total surface energy. The diameter of the nanowires produced by oriented attachment is usually on the order of a few nanometers (Figure 1e) [52], whereas nanowires that grow through atomic addition usually have diameters between 10 and 100 nm. Nanowires that grow through oriented attachment are characterized by a wavy or zigzag structure, with many planar defects such as twin boundaries and stacking faults perpendicular to the longitudinal axis (Figure 1f) [53].

**Metal nanowires as electrocatalysts**

The surface-to-volume ratio of metal nanowires is smaller than that of nanoparticles with the same diameter, suggesting that the specific activity (per gram) of nanowires should be lower than nanoparticles. However, nanowires can have a higher specific activity than nanoparticles because of their unique surface structure [52,54–59]. Nanowires can also exhibit greater durability than nanoparticles because of their ability to resist Ostwald ripening, dissolution, and detachment from conventional carbon supports [52,55–57,59]. In addition, metal nanowire networks can form highly conductive, free-standing structures that do not require carbon supports. Owing to these advantages, metal nanowires are being explored as a promising alternative to conventional nanoparticle electrocatalysts for electrochemical reactions including oxygen reduction reaction (ORR) [52,54–59].
oxygen evolution reaction [63,64], hydrogen evolution reaction [58,65–67], methanol/ethanol oxidation [59,68–76], formic acid oxidation [70,77–79], and CO₂ reduction [37,80,81].

Atomic structure
The twin boundaries on the side of pentagonally twinned nanowires (Figure 1d) and surface defects of nanowires grown via particle attachment (Figure 1f) can improve electrocatalytic performance [55,59,60,78,80,82]. Li et al. [80] demonstrated how pentagonally twinned Cu nanowires improved the selectivity of CO₂ reduction (Figure 2). Unlike a polycrystalline Cu electrode that produced several products including methane, ethanol, and ethylene (e.g., ethylene: ~23%, methane: ~22%, H₂: ~21%, ethanol: ~10%, at the potential of −1.05 V vs. reversible hydrogen electrode (RHE)) [83], 95% of the product obtained using pentagonally twinned Cu nanowires was methane at a potential more negative than −1 V (vs. RHE) (Figure 2b) [80]. The Cu nanowires had a partial current for methane two times higher than Cu foils (Figure 2c). The higher methane selectivity was hypothesized to be due to a higher density of twin boundaries on the side of nanowires, which enhanced the binding of the intermediate for CO₂ reduction. When CO₂ reduction was performed for longer times, the Cu nanowires lost their selectivity for methane and produced more ethylene (Figure 2d) because of the morphological degradation of Cu nanowires (Figure 2e). A coating of reduced graphene oxide on the Cu nanowires preserved the methane selectivity (Figure 2f) by inhibiting the morphological change of Cu nanowires (Figure 2g).

In another example, the rhombic atomic structure of jagged Pt nanowire surfaces increased the electrochemically active surface area (ECSA) 1.59 times compared with conventional Pt/C [55]. Its specific activity for ORR at 0.9 V (vs. RHE) was 7.2 times higher than that of smooth Pt nanowires and 32.9 times higher than that of Pt/C.

Alloyed nanowires
Alloying noble metals with non-noble metals is an effective approach to improve electrocatalytic performance through strain and ligand effects [84–87]. The addition of a non-noble metal can modify the electronic structure of noble metal nanowires and affect the binding strength of reactants, intermediates, and products, thereby improving electrocatalytic performance. A variety of alloyed nanowires including Pt-
PtNiRh, Pd- [68,69], Ir- [62,76], and Ni-based [66] nanowires have been adopted to improve various reactions.

In one example, PtNiRh trimetallic nanowires with an atomic ratio of 3.02:1.00:0.23 (Pt:Ni:Rh) were used for ORR (Figure 3) [57]. The PtNiRh nanowires grew in the <110> direction with {111} side facets (Figure 3a–c) and had an average diameter of only 1 nm (Figure 3d). The ECSAs of Pt, PtNi, and PtNiRh nanowires were 74.7, 89.8, and 106.4 m²/gPt, respectively. These ECSAs are all larger than that of commercial Pt/C (67.9 m²/gPt) because of the thinner diameter and lower Pt−Pt coordination number of the alloyed nanowires. The specific activity, that is, catalytic activity per unit surface area, for ORR at 0.9 V (vs. RHE) was enhanced for the PtNiRh (2.71 mA/cm²) and PtNi (2.34 mA/cm²) nanowires compared with Pt/C (0.28 mA/cm²) (Figure 3e). The activity enhancement was attributed to compressive strain and ligand effects from incorporating Ni and Rh into Pt, which reduced the binding strength of oxygenated species (Figure 3f). After 10,000 cycles of accelerated durability testing, the PtNiRh nanowires lost 12.8% of their initial mass activity, PtNi nanowires, Pt nanowires, and Pt/C lost 54.3%, 21.5%, and 73.7% of their initial activity, respectively (Figure 3g). The greater durability of PtNiRh nanowires was attributed to the high energy required to form a Pt vacancy on PtNiRh(111) relative to PtNi(111) or Pt(111) (Figure 3h).

**Hollow nanotubes**

Another approach to boost electrocatalytic performance is to use hollow nanotubes which present more specific surface area for electrochemical reactions. Hollow nanotubes can be synthesized via galvanic displacement of nanowire templates [38,39,75,77,88]. In one recent report, PtRuTe and PtPdRuTe nanotubes were synthesized via galvanic displacement of Te nanowires [75]. The atomic composition of the nanotubes was easily controlled by changing the ratio of Pt and Pd precursors. The mass activity of the optimal PtPdRuTe nanotubes for methanol oxidation was 1261.5 mA/mgPt, which was 2.2 times higher than that of Pt/C. The ratio of the peak currents from the forward and backward scans was 20% higher for PtPdRuTe nanotubes than Pt/C, indicating the PtPdRuTe nanotubes were more resistant to poisoning from carbonaceous species [75].

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**Figure 3**

PtNiRh nanowires for the oxygen reduction reaction. (a–c) TEM images of PtNiRh nanowires. (d) The diameter and length of the PtNiRh nanowires. (e) Polarization curves for Pt/C, Pt nanowire/C, PtNi nanowire/C, and PtNiRh nanowire/C in O₂-saturated HClO₄ solutions. (f) The binding energy of OH on Pt(111), PtNi(111), and PtNiRh(111). (g) The changes in the mass activity after durability testing. (h) The energy required for the formation of a Pt vacancy for Pt(111), PtNi(111), and PtNiRh(111). Reprinted with permission from Ref. [57]. Copyright 2018 American Chemical Society.
Self-supporting metal nanowires

Carbon is widely used as a conductive support for nanoparticle catalysts. However, carbon supports can be corroded during electrochemical processes, leading to the detachment of the electrocatalysts from the support [73,89,90]. The degradation of carbon supports can also produce CO when the electrode potential is more positive than 0.5 V (vs. RHE), accelerating the poisoning of the electrocatalysts [73,89,90]. Because metal nanowire networks do not require carbon supports to achieve high electrical conductivity, these problems can be avoided and better durability can be achieved [39,43,73,77,91,92]. In one example, a free-standing Pt nanowire membrane without carbon supports retained 82% of its initial ECSA, whereas Pt/C and Pt black catalysts retained only 5% and 39% of their initial ECSAs, respectively, after 3000 cycles of cyclic voltammetry [91]. The better stability of the Pt nanowire membrane was attributed to the absence of electrochemical carbon corrosion and the greater resistance of the Pt nanowires to Ostwald ripening compared with Pt/C.

Three-dimensional nanowire networks

The high aspect ratio of metal nanowires enables the fabrication of highly porous three-dimensional (3D) structures via filtration [28,93], ice-template freezing [94], electrodeposition [95,96], and drop casting [97]. In our experience, one of simplest ways of fabricating a nanowire-based porous electrode is filtration. The porosity ($\varepsilon$) of the nanowire felt made via filtration of stiff nanowires is determined by the aspect ratio of the nanowires, as described in the following equation [98].

$$
\varepsilon = 1 - \frac{2 \ln(\text{Aspect ratio})}{\text{Aspect ratio}}
$$

Parkhouse and Kelly [98] and Kim et al. (M.J. Kim et al., ChemRxiv https://doi.org/10.26434/chemrxiv.7468703.v1) validated this equation experimentally using uncooked spaghetti and Cu nanowires, respectively. This equation predicts that nanowires with an aspect ratio of 100 will have a porosity of 91%. The large void fractions of nanowire felts, coupled with the small diameters of the nanowires, suggest they can be used as flow-through electrodes. Flow-through electrodes are used in redox flow batteries [99,100], water treatment [101], and chemical production [102–104] because of their high mass transport coefficients and large surface areas per unit volume. As the flow-through electrodes currently in use (e.g. carbon paper) were all introduced over 40 years ago, there may be room for improvement.

To quantify the performance of a flow-through electrode, one can measure its mass transport-limited current, $I_L$, by Eq. (1) [105–107].

$$
I_L = nF A_L C_0 \left[ 1 - \exp \left( -\frac{L k_m A_r}{u} \right) \right]
$$

Here $n$ is the number of electrons required for the reaction, $F$ is the Faraday constant, $A_r$ is the cross-sectional area of the porous electrode, $u$ is the superficial velocity, $C_0$ is the concentration of reactant at the inlet, $L$ is the thickness of the porous electrode, $k_m$ is the mass transport coefficient of the electrode, and $A_r$ is the specific surface area of the electrode. $I_L$ increases as $k_mA_r$ increases, so the higher the $k_mA_r$, the better the electrode.

Recent results demonstrate that replacing carbon fibers with Cu nanowires in a flow-through electrode increased the $k_mA_r$ up to 53.9 times at a superficial velocity of 0.5 cm/s (M.J. Kim et al., ChemRxiv https://doi.org/10.26434/chemrxiv.7468703.v1). At an electrode thickness of 1 cm, Eq. (2) predicts that the nanowire felt can accommodate a $10^3$ times faster flow rate than carbon paper and obtain the same single-pass conversion of 0.9. However, a reaction will likely be limited by charge transfer kinetics before such high productivities can be achieved. Even with the current limited by charge transfer, a 278-fold increase in productivity for Cu ion reduction and a 4.24-fold increase in intramolecular cyclization were achieved with Cu nanowire felt relative to carbon paper.

Metal nanowire felts can also be used to improve the performance of Li batteries [94,97,108–110]. Active materials with a large capacity for lithium ions usually suffer from a volume change that quickly degrades the capacity. The large voids in a nanowire composite electrode of Cu and Si nanowires could accommodate the volume change of the Si active material upon Li intercalation while retaining electrical contact, thereby improving the retention of capacity [109]. In Li metal batteries, a current collector made of metal nanowires [94,97,108] has shown to suppress the growth of Li dendrites, which often results in short circuiting and irreversible consumption of Li [111]. In one example, Li deposition mainly took place in the voids of a 3D Cu nanowire network, preventing Li dendrite formation [97]. As a result, a stable cumbic efficiency over 200 cycles (~98.6%) was achieved with the nanowire network, while the cumbic efficiency for Cu foil dropped to 50% in 40 cycles.

Conclusion and outlook

This review introduced ways in which the unique structure and morphology of nanowires can be used to improve electrochemical processes. Metal nanowires can improve electrocatalytic activity and durability because of their ability to host numerous surface defects and resist degradation. Further improvements in their properties would be greatly aided by computer
simulations that can guide experiments to produce a desired alloy composition and defect structure, as well as the ability to synthesize such structures with high precision at large scales. There remains a huge number of electrochemical reactions in which the properties of nanowires have not been tested. Most metal nanowires from solution-phase syntheses are produced in the presence of shape-directing agents, but there is little research on how such agents affect the electrochemical performance of nanowires. It is likely that the performance of nanowire catalysts would be improved by a cleaning step that is similar to that which is used for cleaning nanoparticles [112]. Nanowires can also be filtered from solution to create 3D flow-through electrodes with the highest specific surface areas and mass transport coefficients reported to date. Future work can focus on creating nanowire felts from more durable materials that can withstand the oxidizing conditions widely used in electro-organic syntheses. The large pore volume of 3D nanowire electrodes has facilitated improvements in capacity retention for lithium ion and lithium metal batteries. Further improvements may result from examining how the aspect ratio of metal nanowires, and thus the porosity of the electrode, impacts battery performance. Overall, metal nanowires offer a new opportunity for researchers to design and synthesize optimal electrode structures from the atomic scale to the microscale, but the design rules have yet to be written.

Conflicts of interest statement
Nothing declared.

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References
Papers of particular interest, published within the period of review, have been highlighted as:
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