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Non-line-of-sight deposition of nanoscale separator/electrolytes for 3D all-solid-state batteries

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Conventional batteries comprise two opposing electrodes that are assembled in a 2D, coplanar configuration, separated by an electronically insulating, ion conducting phase. While this general battery design is simple and amenable to mass-production, the 2D configuration leads to performance tradeoffs in terms of achievable combinations of power and energy. The limitations of 2D batteries may be overcome by transitioning to a 3D design in which the three critical battery components (anode, cathode, and separator/electrolyte) are reconstructed as 3D interpenetrating networks.[1]

In the 3D battery design, the interface between the cathode and anode is maximized, and the anode/cathode separation distance is minimized, enabling high-power operation. The retention of the interpenetrating network of interfaces as the battery thickness is increased enables the scaling of the quantity of energy without significantly decreasing the power, thus offering unprecedented combinations of footprint-normalized energy and power. Although substantial progress has been made in 3D battery design and fabrication, a common roadblock to achieving a fully functioning 3D battery is the separator/solid-state electrolyte component, which must be: (*i*) conformal to the supporting electrode architecture; (*ii*) pinhole-free; (*iii*) electronically insulating; (*iv*) ionically conducting; and (*v*) chemically and electrochemically stable.[1] These requirements, coupled with the complex geometry of most 3D battery architectures represent a significant challenge for fabrication methods that are commonly used.

Electrodeposition can circumvent the aforementioned issue with regard to the complex geometry as it is a non-line-of-sight fabrication method, and under self-limiting conditions, it can produce nanoscale, conformal to the surface, pinhole-free, electronically insulating polymer coatings. Previously, we have demonstrated the electrodeposition of ultrathin poly-(phenylene oxide)-based polymer coatings via electro-oxidation of phenol and substituted phenol monomers on ultraporous nanoarchitectures.[2,3,4] The self-limiting conditions generated conformal poly(phenylene oxide)-based films that are tens of nanometers thick and highly electronically insulating, with dielectric strengths comparable to those measured for the corresponding bulk polymer. Ionic conductivity is imparted by impregnation of the polymer film with electrolyte salts or by using monomers with pendant ionic functionalities.

Polymer formation via electro-oxidation may be incompatible with base electrode architectures that are designed to serve as the negative electrode of the ultimate 3D battery. As an alternative, we are currently exploring polymer deposition via electro-reduction (i.e., electrografting) of monomers with pendant vinyl groups. For a preliminary example, we have electrodeposited siloxane-based polymer films from 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (D_3V_3) on planar carbon substrates. Related siloxane-based polymers have been previously developed as battery electrolytes, and demonstrate such desirable attributes as low electronic conductivity, resistance to oxidation, and high dielectric strength, but must typically be modified to improve ionic conductivity.[5] In the present case, the ether groups intrinsic to the D_3V_3 monomer promote Li^+ solvation and transport in the corresponding electrodeposited polymer, adding sufficient ionic conductivity for function as a solid-state separator/electrolyte. After the initial characteristics of this new separator/electrolyte candidate are validated on a 2D substrate, we will transition to more complex 3D architectures, such as fiber-supported carbon nanofoam papers.[6]

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