

Anomalous ionic conduction within nanoporous metals

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It is not a new observation that ionic conduction in extremely confined gaps is affected by the proximity of the double layers on either side of the gap, but nanoporous metals prepared by electrolytic dealloying of metallic solid solutions offer an unusually elegant opportunity to study such effects. The pore/ligament size can be varied by adding less surface-mobile metals (e.g. alloying Pt into AgAu), or by varying the temperature of the electrolyte, or by post-heating of the nanoporous material. The range of pore/ligament sizes available is from roughly 2.5 nm to the micron scale.

We have estimated pore electrolyte resistances for nanoporous metals based on dealloyed AgAu(Pt). The method relies on a deLevie type of analysis of impedance spectra. For the binary AgAu alloy, which has a pore/ligament size in the 15-20 nm range after dealloying, the dealloyed material conducts almost like a normal aqueous solution. Pore resistance, other things being equal, is proportional to the resistivity of the bulk electrolyte. At the other extreme, a dealloyed AgPt alloy with pore size around 2-3 nm shows very peculiar behaviour, even showing a kind of inverse ohmic behaviour (higher pore resistance for higher ionic strength of the bulk solution) under certain conditions. However this material dealloys in a very local manner at grain boundaries, so we do not rely too strongly on such data for quantitative characterization. A good compromise is the ternary AgAuPt system, which gives nearly the same pore/ligament size as the AgPt alloy, but with less localization at grain boundaries. Ongoing measurements show behaviour more similar to AgPt than to AgAu.

Some explanations of the observed behaviour are offered, based partly on existing literature and partly on novel concepts of conduction within very narrow channels.