Exploration of new applications of inductively coupled plasma mass spectrometry (ICP-MS) to fuel cell electrochemistry

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The electrochemically active surface area of electrodes in fuel cells can be increased through the loading of nanoparticles (NPs) on the substrate. To assess their stability, the NPs mass concentration must be measured, as well as their size and the portion that is dissolved. Single particle inductively coupled plasma mass spectrometry (spICPMS) has become a convenient method for the detection and characterization of inorganic nanoparticles (NPs) in aqueous medium. In addition, if the shape, density and composition of the NPs are known, particle mass can be converted into size, and a size distribution can be obtained. To provide accurate results, the suspension should be diluted such that there is at the most one NP per droplet formed during nebulization, and the dwell time should be selected so as to measure only one NP at a time. Under these conditions, most ICPMS instruments operated in time-resolved mode can detect individual NPs as spikes in the steady-state signal. In this presentation, we will compare the performance of spICPMS to that of a simpler method involving flow injection (FI) of a discrete volume of sample or standard, i.e. FI-spICPMS.

FI-spICPMS is beneficial over spICPMS as it does not require measurement of the transport efficiency or the sample uptake rate in order to determine the injected mass of NPs [1]. Moreover, the FI mode of measuring the transport efficiency is not subject to variations in sample uptake rate as long as the entire injected volume is measured. These important advantages exist in addition to several other features of FI, including: high sample throughput, reduced matrix and memory effects from the continuous washing afforded by the carrier, etc.
In this study under identical ICPMS operating conditions, both approaches were applied to 60 nm citrate-coated monodisperse standard Au NP (nanoComposix San Diego, CA, USA) suspensions of known mass concentration. The mean particle size calculated from size distributions was $61.82 \pm 0.87$ nm ($n = 3$) and $60.23 \pm 0.60$ nm ($n = 3$) without and with FI, respectively. Both of these results are in good agreement with the vendor reported certificate value. However, no measurement of the sample uptake rate was required for the FI approach. Similar agreement between spICPMS and FI-spICPMS was achieved for the same suspension at two other dilution levels. A similar precision was also achieved by the two methods. Irrespective of the method, precision is significantly better at higher dilution levels. As the mass concentration increases at constant dwell time, precision not only deteriorates, but the particle size is overestimated. The size detection limit for Au NPs in DDW was calculated to be 20 nm without or with FI. Hence, there is no degradation of performance when using FI-spICPMS instead of spICPMS.

The validated approach was then applied to the measurement of laboratory synthesized pure platinum NPs for fuel cell, having nominal diameters of 3 and 10 nm respectively, as measured by transmission electron microscopy (TEM). With FI-spICPMS, the mean NP sizes were calculated to be $3.9 \pm 0.8$ nm and $11 \pm 2$ nm respectively ($n=3$), in excellent agreement with the TEM results. The size detection limits obtained were 2.8 and 7.8 nm, respectively. To the best knowledge of the authors, no one has ever successfully measured NPs of this size by spICPMS.