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Solution spectroelectrochemical cell for *in situ* x-ray absorption fine structure

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A purpose-built spectroelectrochemical cell for *in situ* fluorescence XAFS (x-ray absorption fine structure) measurements of bulk solution species during constant-potential electrolysis is described. The new design is the result of our effort to produce a versatile, easy-to-use cell of intermediate analyte volume (ca. 5 cm^3) with separate compartments for the working and auxiliary electrodes. As added conveniences, the spectroelectrochemical cell is compatible for direct operation under anaerobic or aerobic conditions in aqueous and nonaqueous supporting electrolytes with commercially available XAFS equipment that is now in widespread use at many synchrotron radiation facilities. To realize these features, we departed from most of the previous state-of-the-art, thin-layer/parallel-plate cell designs to a parallel rod design. The cell performance was demonstrated by the collection of europium L3-edge XANES (x-ray absorption near edge structure) throughout the course of electrolysis at -0.7 V vs Ag/AgCl of an aqueous solution of $EuCl_3Ä_6H_2O$ in 1 M H_2SO_4. The europium L3-edge resonances reported here for the EuIII (4f6) and EuII (4f7) ions demonstrate that their 2p3/2-->5d electronic transition probabilities are not the same. Implications for the use of XANES in studying intermediate-valent materials and applications of the new spectroelectrochemical cell to studies of dissolved, electroactive clusters will be described.

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