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Oxygen diffusion in PEM fuel cell cathode catalyst layer (CCL) has been a main reaction rate determining factor at high current density region or concentration loss region. To investigate the effect of oxygen diffusion in CCL, microstructure controlled MEAs were fabricated as other electrochemical characterizations, for example, effective catalyst surface area or Pt/C contents are identical. The cell performance is higher for the large pore catalyst layer than for small pore in concentration loss region. To elucidate those experimental results, fuel cell 1D model implemented the exponential correlations between effective diffusion coefficient of oxygen and accumulated water film thickness in the simulated CCLs was suggested as a novel approach in this study. Simulated catalyst layer microstructure consisted with agglomerate particles was generated to examine the experimental results for two MEA samples of which the porosity was 0.454 and 0.644. The simulation results show reasonably similar trend with experiments and analytical discussion was followed.