sonochemical synthesis [23], hydrothermal method [24], sputter deposition [25], pulsed laser deposition [26,27], radiation induced synthesis [28], solution reduction method [29] and chemical reduction of organometallic precursors and simple platinum salts [30,31]. Even though all these methods are efficient in producing a wide particle size range of Pt NPs, controlling the particle size continues to be the most difficult challenge because individual nanoparticles tend to agglomerate during the preparation process. Sputter deposition and pulsed laser deposition techniques though control particle size and agglomeration of the particles, their cost and non-suitability for large area deposition are their limiting factors. To overcome that, preparation of nanoparticles by simple chemical reduction of metal species at low temperatures and at room temperature has been reported for both aqueous and non-aqueous solutions. In addition, preparation of nano platinum by chemical reduction in viscous stabilizing medium has also been reported [32].

In the current work, the doping tendency of polyaniline (PANi) is exploited to incorporate platinum(IV) ion in its matrix by chemisorption followed by its reduction to metallic Platinum. PANi has the potential of a high area support material, on which platinum catalyst could be deposited. PANi was synthesized by the chemical oxidative polymerization of aniline and then platinum particles on PANi was prepared by first trapping the Pt(IV) ion onto PANi by ionic interaction, followed by chemical reduction of Pt(IV) ion to Pt^0 by sodium formate. The Pt/PANi nanocomposite was assessed in the proton exchange membrane (PEM) single cell using H_2/O_2 gases at ambient pressure. The fuel cell performance of MEA with Pt/PANi catalyst thin layer on GDL showed excellent improvement in the range of performance. The water balancing property of PANi provided the essential functionality for the support material. The Pt/PANi composite material was characterized by XRD, Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX), Infrared (IR) spectroscopy, cyclic voltammetry (CV) and AC impedance studies, density and conductivity measurements.

2. Experimental

2.1. Materials

All the chemicals used were AnalaR grade and double distilled water was used for the solution preparation. Hydrated hexachloroplatinic acid ($H_2PtCl_6\cdot6H_2O$), tetraoctyl ammonium bromide (TOAB, $N(C_8H_{17})_4Br$), toluene ($C_6H_5CH_3$), 1-dodecanethiol ($C_{12}H_{25}SH$, 98%), sodium formate (HCOONa), ammonium persulphate ($(NH_4)_4(SO_4)_2$), aniline, sodium sulphate, hydrochloric acid, sulphuric acid, acetone and absolute alcohol were used in the present study.

2.2. Synthesis of polyaniline

Polyaniline was synthesized by chemical oxidative polymerization of aniline in the presence of hydrochloric acid as a catalyst and ammonium persulphate as an oxidant by chemical oxidative polymerization method. In a typical synthesis, 25 mL of 0.2 M aniline solution was taken in a beaker and about 10 mL of 0.2 M hydrochloric acid was added to it. The beaker was kept in an ice bath maintaining a polymerization temperature of 0–5 °C. To this, 15 mL of 0.5 M ammonium persulphate ($(NH_4)_2S_2O_8$) maintained at around 5 °C was added slowly using a micro burette. The mixture was stirred continuously for an hour by an electromagnetic stirrer and the polymer precipitate was filtered in a G4 sintered crucible. The polymer was then washed with double distilled water till the filtrate became colourless. The precipitate was rinsed with 3 to 5 mL of acetone. The resultant PANi polymer was dried under vacuum at 60 °C overnight.

2.3. Deposition of platinum nanoparticles on polyaniline

About 0.1 M aqueous chloroplatinic acid ($H_2PtCl_6\cdot6H_2O$, orange coloured solution) was prepared in double distilled water and 0.2 M tetra-n-octyl ammonium bromide ($C_{32}H_{68}BrN$) (TOAB) solution was prepared using toluene as solvent. 3 mL of aqueous chloroplatinic acid was mixed with 4 mL of TOAB solution and was shaken for 30 min in a mechanical shaker at room temperature [33]. During this process, TOAB acted as the phase-transfer catalyst [34] by transferring $PtCl_6^{2-}$ ions from aqueous solution to toluene. The orange-coloured organic layer was separated, to which 2.5 g of PANi was added with constant stirring for 1 h. Thereafter, 0.65 mL of 1-dodecanethiol was added to act as the capping agent for the subsequently formed platinum particles and shaken for another 30 min. About 10 mL of 0.1 M aqueous sodium formate solution was added in drops to the above suspension and stirred continuously for another 2 h at 60 °C. The mixture was filtered through a G4 sintered crucible to remove solvent and the precipitate was thoroughly rinsed with copious amount of warm double distilled water to remove sodium formate and then with ethanol to remove the excess of 1-dodecanethiol. The scheme of preparation of Pt/PANi composite is shown in Fig. 1. The Pt/PANi product was dried overnight at 80 °C in vacuum oven and stored in dessicator. It contained 1.32% of platinum as revealed by EDX study. The density of PANi and Pt/PANi was measured by Helium Pycknometer (Pycno 30 True Density Meter, Smart Instruments Co. Pvt. Ltd., Thane, India) and the surface resistivity was measured by four probe device. Pellets of approximately 0.200 g weight were made for the studies of conductivity, cyclic voltammetry and impedance measurements.

2.4. Construction of membrane electrode assembly (MEA) and fuel cell evaluation

The gas diffusion layer (GDL) was prepared using Toray carbon paper. The carbon paper was first teflonised by 10 weight percentage of PTFE for hydrophobicity and the porous layer was provided by loading a slurry of Vulcan X (VX) Carbon and 30% PTFE, at a loading amount of 1 mg cm^{-2} of VX carbon by spraying method. The loading of 0.42 mg cm^{-2} of the Pt/PANi composite was coated on the GDL of cathode side. As PANi is a porous material, we have made the GDL without the macroporous layer (generally the GDL is prepared to consist of macro porous layer using carbon fibre in high content and a micro porous layer using VX carbon). The model of MEA prepared in this study is shown in Fig. 2.

Catalyst coatings were prepared on Nafion membrane (NRE 212) with 5 cm^2 active area by spraying catalyst ink prepared using commercial Pt/C containing 20% by weight of platinum, 5% nafion and isopropyl alcohol in nitrogen atmosphere, by the micro-spray method. The catalyst loadings on the anode and cathode catalyst layers of the reference MEA were about 0.30 and 0.50 mg Pt cm^{-2} respectively while the catalyst loadings on the anode and cathode catalyst layers of the MEA with Pt/PANi coated GDL were about 0.23 and 0.44 mg Pt cm^{-2}, respectively. The platinum loading on the reference MEA and the one prepared in this study are compared later with the data from the EDX study. The catalyst coated Nafion-212 membranes were vacuum dried at about 50 °C for 30 min before assembling in the single test cell.

The MEAs were fabricated by sandwiching the GDLs and the catalyst coated membrane inside the single cell test cell (Fuel Cell Technologies Inc., Albuquerque, NM, USA). Gas sealing was achieved using silicone coated fabric gasket and with a uniform torque of 0.45 kg m. The fuel cell performance was evaluated at 60, 70 and 80 °C at 100% RH conditions on both anode and cathode sides using Single Fuel cell Test Station (K-PAS Instronic Engineers India Pvt. Ltd., Chennai, India). The flow rates were fixed at 0.250 and 0.500 SLPM for H_2 and O_2, respectively. The steady state voltage