3
Synthesis and Characterization of Cathode Materials

This chapter describes about the synthesis method and characterization techniques which are adopted during the thesis work. The chapter is composed of four sections and thirteen sub-sections. The section 3.1 presents rationale of the chapter. The procedure of cathode materials synthesis is elaborated in the section 3.2. The basic principle about the physical characterization techniques is expressed in the section 3.3. The principle and instrumentations, which are implemented for electrochemical characterizations, are presented in the section 3.4 and the section 3.5 covers closing remarks.

3.1 INTRODUCTION

The synthesis method is playing an important role in determining physical and electrochemical properties of cathode material. The distinct synthesis methods are available in literature which are falling into two broad categories- solid state reaction and sol-gel method. The sol-gel method is followed during the research work due to its peculiar features, for intance low temperature and easy to control on particle morphology, over solid state reaction method. The sub-section 3.2.1 contains the details about analytical grade chemical utilized to synthesize cathode materials. The organic solvent based sol-gel method is described with schematic flow chart. The physical properties are evaluated by employing physical characterization techniques and the electrochemical characterization techniques are executed to evaluate battery performance parameters.

3.2 CATHODE MATERIAL SYNTHESIS

The details about analytical grade reactants and sol-gel method are discussed as follows:

3.2.1 Analytical Grade Chemicals*:* The $LiMn_2O_4$ (LMO) and its different rare-earth element doped derivative cathode materials are synthesized via organic sol-gel method. The analytical grade chemicals in stochiometric ratios are weighted to synthesize cathode material. The details about reagents are tabulated in Table 3.1. The mostly analytical grade chemicals are acetate salts.

Table 3.1: Analytical Grade Chemical, Formula and Supplier

Chemical Description	*Chemical Formula*	*Physical State*	*Product Code*	*Supplier*
Lithium Acetate Di hydrate (99%)	$LiOOCCH_3.2H_2O$	Solid	LOT: 10172281	Alfa Aesar, USA (A17921)
Manganese (II) Acetate Tetrahydrate (Mn 22% typical)	$Mn(OOCCH_3)_2.4H_2O$	Solid	LOT: J07X035	Alfa Aesar, USA (12351)
Nickel Acetate Tetrahydrate (98%)	$Ni(OOCCH_3)_2.4H_2O$	Solid	LOT: MKBJ0243V	Sigma Aldrich, USA (101171181)
Gadolinium Acetate Dihydrate	$Gd(OOCCH_3)_2.4H_2O$	Solid	LOT: 24192	Alfa Aesar, USA (89518)
Dysprosium Acetate Dihydrate	$Dy(OOCCH_3)_2.2H_2O$	Solid	LOT: MKBL6999V	Sigma Aldrich, USA (1001411551)

Terbium Acetate Dihydrate	$Tb(OOCCH_3)_2 . 4H_2O$	Solid	LOT: 24667	Alfa Aesar, USA (A17338)
Ytterbium Acetate Dihydrate	$Yb(OOCCH_3)_2 . 4H_2O$	Solid	-	Alfa Aesar, USA
Neodymium (III) Acetate Dihydrate (99.9 %)	$Nd(OOCCH_3)_2 . xH_2O$	Solid	LOT: G20X057	Alfa Aesar, USA (44587)
2-Ethylhexanoic Acid, (99%)	$C_8H_{16}O_2$	Liquid	LOT: 10174867	Alfa Aesar, USA (A12644))
Carbon (Acetylene) Black	C(SA = 75 m^2/g) and bulk density 170-230 g/L	Solid	LOT:F24X016	Alfa Aesar, USA (45527)
Poly(vinylidene fluoride) ;PVDF	$(-CH_2-CF_2-)_n$	Solid	-	Alfa Aesar, USA (44080)
1-Methyl-2-Pyrrolidinone; (NMP)	C_5H_9NO	Liquid	LOT:10171980	Alfa Aesar, USA (A12260)
Electrolyte	1 M $LiPF_6$ in EC+DMC (1:1)	Liquid	LOT:SHBF8219V	Sigma Aldrich, USA (1001941969)
Al-Metal Foil	Al (Thick: 0.025 mm)	Solid	LOT: C26W005	Alfa Aesar, USA (10558)
Li-Metal Foil	Li	Solid	LOT:K291055	Alfa Aesar, USA (10769)

3.2.2 Organic Sol-gel Synthesis Method: The analytical grade chemical reagents are weighted in stoichiometric ratios. The organic sol-gel method is adopted to synthesize the cathode material. The flow chart of synthesis method is presented in Figure 3.1. The amount of material obtained in single batch was in rage of 6.6 – 7.9 g.

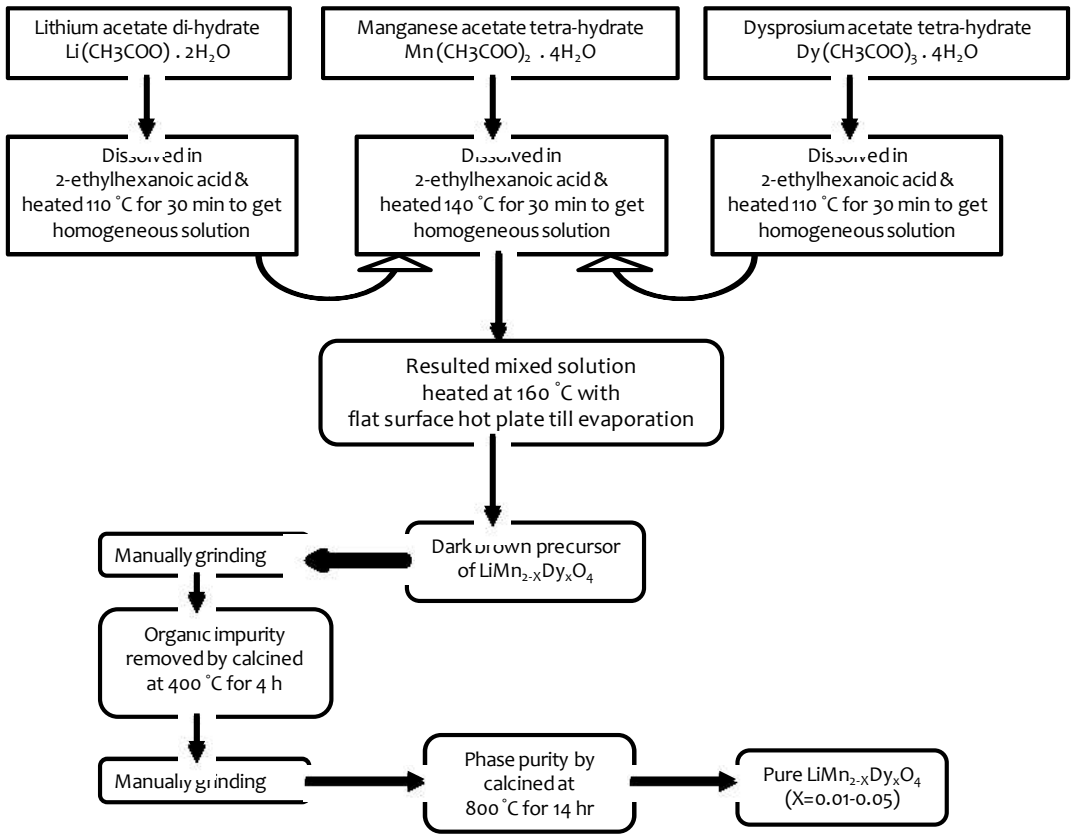

Figure 3.1: Schematic flow chart of dysprosium derivatives synthesis

3.3 PHYSICAL CHARACTERIZATION TECHNIQUES

After the synthesis of cathode materials, it becomes essential to analyze physical properties. The following physical characterization techniques are taken up which are briefed as.

3.3.1 X-ray Diffraction Technique: The cubic spinel phase information for all the synthesized samples are recorded on Brucker D8 Advanced model. The calcined and manullay grinded powder sample is filled in circular cavity holder (diameter = 50 mm and depth = 2 mm) and upper surface made smoothed flat using clean flat surface glass slide. The two theta angle (2θ) is scanned from 10° to 80° with scanned speed ~1° per minute in locked coupled mode. The x-ray beam originated from Cu source (average λ =1.5418 Å) is incident on sample surface. The diffracted x-ray beam from structural planes is detected by scintillation detector (NaI) attached with goniometry of X-ray machine.

The diffracted beam of x-ray from crystal planes is governed by the Bragg's law of diffraction [Kittel, 1996]. The schematic of Bragg's condition is represented in Figure 3.2 (a). The highest diffracted x-ray intensity is corresponds to plan (1 1 1) for spinel cubic structure for $LiMn_2O_4$ (LMO) and $LiMn_{1.95}RE_{0.05}O_4$ (LMO-RE05).

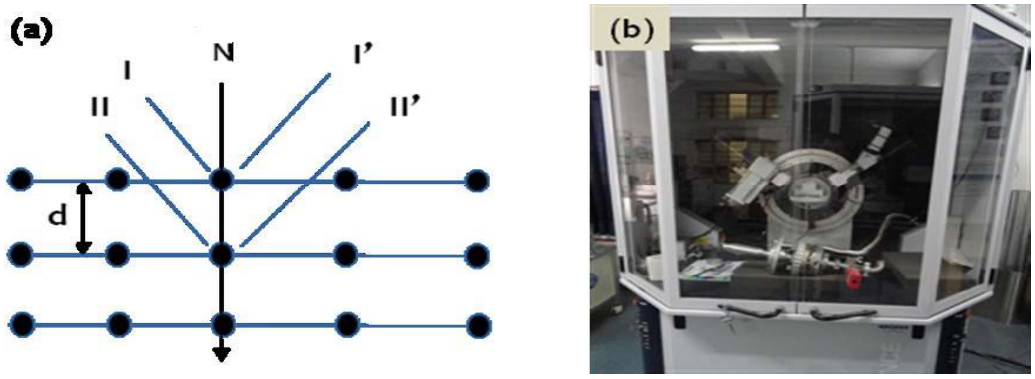

Figure 3.2: (a) Bragg's condition and (B) Bruker Axe XRD instrument

The path difference between incident x-rays (I and II) and diffracted x-rays (I′ and II′) for constructive interference is given by Bragg's condition as equation (3.1)

$$2 * d * \sin\theta = n * \lambda \ldots\ldots\ldots\ldots (3.1)$$

Where d – Spacing between two atomic layers (Å)

θ – Angle of x-ray incident beam with normal to plan (in degree)

n - Order of diffraction (here n=1, for first order)

λ - X-ray wavelength (here, Cu (k_α) = 1.5418 Å)

For the cubic spinel crystal system, the relation between lattice constant, a, and inter planner spacing, d, is given by eq. (3.2)

$$d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} \ldots\ldots\ldots\ldots (3.2)$$

Where (h k l) is plane miller indices. Here, miller indices for plane is taken as (1 1 1) to cubic spinel system. For the cubic system, all the basis vectors (**a**, **b** and **c**) have equal in magnitude. i.e a=b=c. Using these condition, the lattice constant (a) is calculated by equation (3.3).

$$a = d * \sqrt{3} \qquad .....(3.3)$$

Now, using equation (3.1) and equation (3.3), the lattice constant in angstrom unit (Å) is given by equation (3.4)

$$a = \frac{\sqrt{3} * \lambda}{2 * \sin\theta} ....(3.4)$$

3.3.2 Scanning Electron Microscopy and Elemental Detection Techniques: The surface morphology and elemental analysis are carried out on SEM EVO special edition, Bruker instrument. The powder sample is spread on adhesive silver tape and attached on stub (sample hoder). After that, the sample is made conducting by coating with gold-palladium target in SC7620 Mini sputter coater manufactured by Quorum Technology, United Kingdom. The operating parameters for coating are as time period: 120 second, plasma current: 8-10 mA and chamber pressure: below 0.04-0.06 mbar [SC7620, 2011].

To record SEM graphics, the high energy (EHT: 20 kV) focused electron beam current, 80 pA, incident on sample surface. The electrons beam interact with surface atoms and emit secondary electrons, backscattered electrons, bremsstrahlung radiation, augur electrons and characteristic x- ray photons. The secondary electrons and backscattered electrons are detected with Everhart-Thornley detector and 4Q-BSD/Scintillate detector respectively. The surface morphology of sample is produced by scanning small surface area with focused electron beam. The electron intensity is used to produce image by automated in built software [EVO, 2008].

The characteristic x-ray of different elements is analysed on EDX detector, Oxford Instreuments, attached as additional assembly with SEM EVO special edition. The recorded information are converted into an energy spectrum by automated in built software (INCA). The EDX system's INCA software is used to analyze the energy spectrum in order to determine the abundance of specific element. The EDX has limitation on detection of low atomic number (Z< 14) [EVO, 2008, INCA, 2006]

3.3.3 Tunneling Electron Microscopy Technique: The high resolution transmission electron microscopy (HRTEM) measurements were performed on Tecnai G2 instrument by FEI with an accelerating voltage of 200 kV. The selected area diffraction pattern (SAED) is also recorded for selected samples.

3.3.4 Raman Spectrum: The selected samples are characterized for metal-oxygen bond strength. Raman spectra are obtained with a STR 500 spectrophotometer, Airix Japan. The excitation source was an air cooled diode laser source operating at 532 nm and measurements were performed with an incident laser power of 10 mW. The sample is in powder form.

3.3.5 Thermo-gravimetric Technique: The thermal stability of synthesized samples were analyzed on TGA 4000, PerkinElmer. Generally, 30-40 mg sample weight is taken to conduct thermo-gravimetric (TG) data recording. The thermal data was recorded from room (normally 30 °C) temperature to 800 °C with constant heating and cooling rate 10° per min. The heat flow and weight loss are recorded with temperature and time in controlled N_2 atmosphere at flow rate (20 ml per minute). The weight loss in terms of percentage with respect to temperature is plotted to analyze the thermal stability. The data are analyzed on Pyris software, version 10.1 (2009), supplied by PerkinElmer.

3.3.6 BET Specific Surface Area Technique: The BET surface area analysis is performed in AutoSorb (iQ3), Quantunchrome Instrument, USA. The 300 mg sample weight is degassed in H_2 atmosphere at 300 ^oC for 2 hr prior to record the adsorption and desorption data. The 20 points data are recorded in each adsorption and desorption process under N_2 atmosphere [Autosorb, 2016].

3.4 ELECTROCHEMICAL CHARACTERIZATION TECHNIQUES

Once the physical phase identification and particle size are assessed, then next step is to evaluate battery parameters such as open circuit potential, charge-discharge capacity, rate performance, cyclability, internal impedance, etc. To assess all these battery parameters, the fabrication of cathode from synthesized material is essential. After fabrication of cathode, the battery parts are assembled in inert atmosphere (Argon gas) and characterized using different techniques such as cyclic voltammetry, galvanostatic charge-discharge performance, rate performance, AC impedance spectroscopy etc. The cathode fabrication, cell assembling process and characterization techniques are presented in following sub sections.

3.4.1 Cathode Fabrication and Swagelok Cell Assembly: The cathode fabrication includes the slurry preparation, slurry coating on conducting metal foil and drying the wet slurry, cutting the cathode in desired geometry and size. The swagelok cell is assembled by sequential bringing together the different parts of battery.

3.4.1.1 Slurry Preparation: The schematic of slurry preparation process is shown in Figure 3.3. The cathode powder, carbon black and poly (vinylidene fluoride), PVDF, are taken in weight ratio of 0.8:0.1:0.1. First of all, the PVDF (20 mg) is poured into 1-methyl-2-pyrrolidinone, (NMP), solvent (600 µl) and stirred on magnetic stirrer continuously at 600 RPM for ~ 1 h to obtain homogeneous solution of PVDF. The dry mixed (cathode powder: carbon black :: 160 mg : 20 mg) solid phase is poured slowly - slowly into homogeneous PVDF solution. This procedure completes in about ~ 1 h. After pouring of dry mixture, the resultant is put for continuous stirring at 900 RPM for ~4 h to obtain desired viscous slurry.

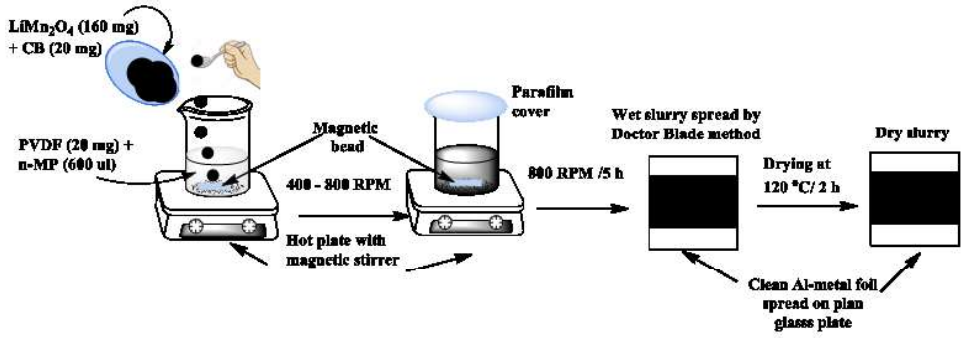

Figure 3.3: Schematic of slurry preparation process

3.4.1.2 *Slurry spreading and drying:* The prepared viscous slurry is spread uniformly on clean scrubbed surface of thin, 0.025 mm, Al-metal foil backed by glass substrate by using Doctor blade method. The wet coating thickness of slurry is about ~ 400 µm. The coated slurry is put into oven at 120 °C for overnight to dry. The wet of dry electrode (8 mm diameter) is in range 6 - 9 mg. The weight of cathode material was calculated after subtracting the Al-metal foil weight 3.50 mg. The weight of active material was in range 3.4- 4.0 mg. The specific capacity was calculated by considering only spinel phase purity.

3.4.1.3 *Cathode cutting:* The cathode is cut using sharp edge punch of 8 mm diameter. The selected electrode, Figure 3.4 (a), is prepared using already 8 mm diameter cut cleaned surface Al metal foil. rom uniform spread and dry slurry, the 8mm cathodes are cut and after 8 mm diameter cut open geometry is shown in Figure 3.4 (b). The viscous slurry is poured onto it using controlled volume pipette and spread using blunt edge clean stainless steel pin. After that, it is put for dry in same oven. The excessive slurry mass loading is resulted into crack formation as shown in Figure 3.4 (c).

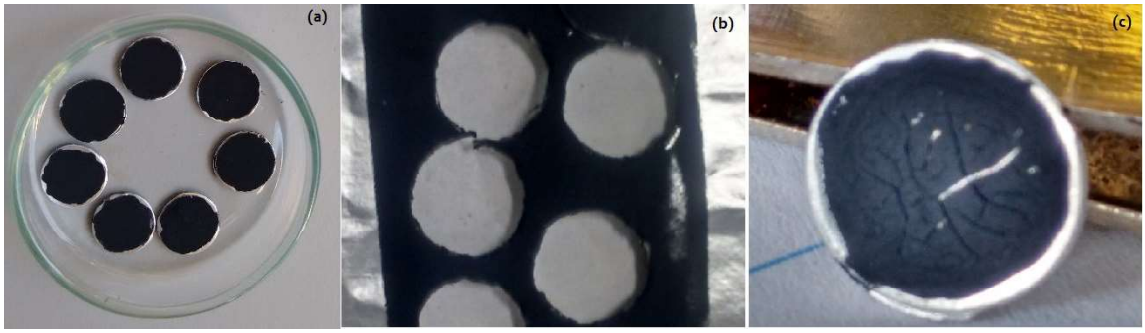

Figure 3.4: (a) Fabricated cathode on 8 mm cut from Al foil (b) After 8 mm diameter cut open geometry and (c) Cracks developed on cathode

3.4.1.4 Swagelok cell assembling: The flow chart for battery assembling is shown in Figure 3.5. Once the cathode is fabricated, then two or three electrode swagelok battery/cell is assembled in Ar- atmosphere inside M'Bruna Glove box, Germany. The concentration of H_2O and O_2 are < 1 PPM and < 4PPM, respectively.

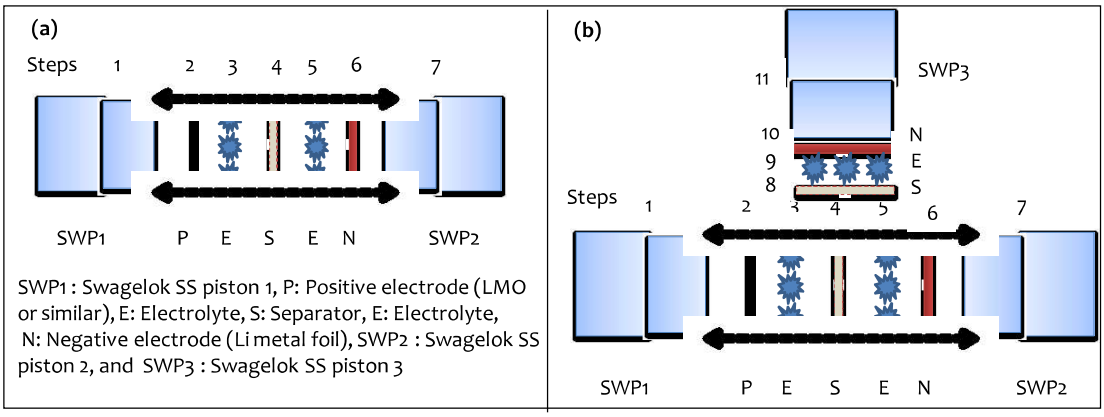

Figure 3.5: Flow chart of cell assembling (a) Two electrode and (b) Three electrode

3.4.2 Cyclic Voltammetry Technique:

The cyclic voltammetry (CV) is carried out on CHI600 Instrument and Landt instrument, USA, to obtain the oxidation and reduction potential of cathode materials. The two or three cycles of CV are run on three electrode assembled swagelok battery. The open circuit potential (OCP) of assembled cell normally is found in 3.7 - 3.9 V. The CV was performed in OCP to 4.5 V potential windows with scan speed 0.01 mV per second.

3.4.3 Galvanostatic Charge and Discharge Technique: The galvano-static charge-discharge technique is executed to measure the charge-discharge capacity of assembled two electrode battery using BTS8 Series 8 channel battery Analyzer, MTI corporation, and Landt Instrument, USA. The constant current corresponds to different C-rates (C/10, C/5, C/2, C) for charging and discharging are applied in software with limiting parameters as potential 4.2 V and current 10 mA. After each cycle, the two minute pause step is given prior to next cycling. The cycling study is carried out upto 5 cycles or other cycles to assess degradation in the charge-discharge capacity with cyclability. The data analysis is done using Battery Testing System Data Analyzer (BTSDA) software version 7.0.56 [BST8].

The specific capacity of cathode material is calculated by considering the spinel phase purity. The single electron per Li-ion is transferred during the lithiation/delithiation process. The reaction mechanism is considered in faradic nature. The theoretical specific capacity of spinel phase cathode material is calculated using below formula:

$$\text{Specific Capacity (mAhg}^{-1}) = \frac{\text{No. of Charge (mAh/mole)}}{\text{Cathode Molecular Weight (g/mole)}} \qquad \text{……..(3.5)}$$

The rate of charging and discharging is defined on the basis of number of hour required to fully charge and discharge of cell with calculated capacity. It provides the value of current at which the charging and discharging is taking place. For example, a battery has capacity 1000mAh, then, the C rate is defined as equation (3.6) i.e.

$$\text{C –rate (mA)} = \text{Capacity (mAh)/ no. of hours} \quad \text{…… (3.6)}$$

i.e. 1 C means the full capacity of battery will be discharge in 1 h and C/10 means that the full capacity of battery will be discharge in 10 h.

3.4.4 Rate Performance and Cyclability: The technique is similar to galvano-static charge-discharge technique except number of cycles is more i.e. cycles 10, 40, 50 at different C-rates [BST8].

3.4.5 Electrochemical Impedance Spectroscopy: The three electrodes Swagelok cell is assembled by using reference electrode (Li-metal), working electrode (fabricated cathode) and counter electrode (Li-metal). The AC impedance technique is run by applying 5 mV AC signal over open circuit potential on CHI 600 electrochemical work station. The frequency is scanned from mHz/Hz to 0.1/1.0 MHz. This technique is used to measure total internal impedance of cell. The fractional contribution of different resistive factor; ohmic resistance, charge-transfer resistance, double layer capacitance, Warburg resistance etc; can also evaluate using AC impedance technique and an associated simulating software.

3.5 CLOSING REMARKS

The detail about analytical grade reagents and procedure for cathode material synthesis via organic sol-gel method have discussed. The different physical characterization techniques, such as XRD, SEM, EDX, TGA and Raman spectroscopy, and their basic principles have talked about. The electrochemical characterization techniques such as CV, galvano-static charge-discharge capacity, rate performance, cyclability, and alternating current impedance spectroscopy, have presented. The cathode fabrication and a Swagelok cell assembling procedure have stated.