Enhancing adhesion of ceramic particles by deposition of polymer using supercritical CO₂

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

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August, 2019
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Enhancing adhesion of ceramic particles by deposition of polymer using supercritical CO₂

be accepted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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Abstract

Ceramic particles do not have good adhesion characteristics. Adhesion is usually improved by the introduction of binders on the surface of these particles. However, conventional methods to coat ceramic particles rely on the use of toxic liquid chemicals. Potential candidates to substitute these chemicals include supercritical fluids which are commonly used in many industrial applications. Among its applications, supercritical carbon dioxide (scCO₂) stands out as one of the most promising options. ScCO₂ has a wide range of applications in industry, spanning from woodwork to pharmaceuticals. As a substitute to traditional chemicals used in industrial applications, scCO₂ usually has major advantages because of its non-toxicity, non-flammability, low-cost, and recyclability. Moreover, its supercritical qualities (extremely low surface tension, high diffusivity, and liquid-like density) give scCO₂ unrivaled performance when compared to traditional chemicals.

Coating particles using supercritical carbon dioxide is commonly used in industry to alter the substrate’s chemical and physical properties. Due to its economic, environmental and physical benefits, scCO₂ based coating is a very sought-after method. Despite their wide usage in industry, most processes currently used to coat particles are multi-step procedures and often complicated procedures. A different issue is that bare ceramic particles suffer from low adhesion potential. Thus, to address both these issues, an easy one-step method using Poly(vinylidene fluoride) to coat small LiCoO₂ ceramic particles with the assistance of supercritical carbon dioxide is proposed.
Three parameters for the process were optimized: temperature, pressure, and dissolution time. The optimal parameters for the process were determined to be 140 °C, 150 bar and 6 hours. Visual evidence of coating was obtained using Scanning Electron Microscopy. The presence of fluorine presence on the surface of the ceramic particles, which is indicative of the polymer, was verified using Energy Dispersive X-ray Spectroscopy. Fourier Transformed Infrared Spectroscopy and X-ray Diffraction were employed as tools to check for chemical integrity of the polymer. To confirm that adhesion was improved, pellets were manufactured with coated ceramic powders and were tested under compression using a universal mechanical testing system. Results show that the pellets made from powders coated under optimal conditions were not only uniformly coated but were also stronger when compared to pellets of products coated under non-optimal conditions and sub-critical conditions.
To My Dear Father

In memoriam
Acknowledgments

I would like to thank, first and foremost, my advisor Dr. Dev Chidambaram for the opportunity to pursue my graduate degree under his mentorship. His guidance through my two years as a MERlab student was always very helpful and encouraging. I would also like to give special thanks to Dr. Denis Phares for believing in my work and for always providing invaluable scientific advice. My deepest gratitude also extends to members of my committee, Dr. Dhanesh Chandra and Dr. Feifei Fan, for helping me through my graduate journey as a student and as a researcher. Without the support from this body of experts, I would have not been able to accomplish this work.

This research was supported by Dragonfly Energy Corporation. Without the resources provided by Dragonfly this project would have never been possible. Many thanks to the Chemical and Materials Engineering department for providing with a Teaching Assistant position and to the Nevada Wolf shop for the Graduate Assistant position. I’ll forever be grateful.

My special gratitude also extends to Zach Karmiol, for his countless hours of helping and mentoring me with several different characterization tools. I thank Kodi Summers and Jeremy Moon for all their tireless assistance with SEM/EDS, and Luis Caneiro for his amazing help with the compression experiments. To all MERlab members, current and
past, I feel deep appreciation for always feeling welcome by everyone and always being able to get assistance, no matter how trivial a project might have seemed.

I cannot imagine being able to achieve what I have achieved if it weren’t for both of my families, my Brazilian and my American halves. Mãe, eu te amo mais do que palavras podem descrever. Obrigado pelo amor infinito que todo dia eu sinto. Vó Tereza e Vô Márcio, eu amo muito vocês, obrigado por tudo. To mom and dad, I don’t think a word exists in the universe that expresses how grateful I am to have you both in my life; thank you for the infinite love and support you have always given me. I thank my girlfriend Lauren for being my partner, understanding me, encouraging me and withstanding my countless days going through the arduous trenches of graduate learning. I love you. I thank my Brothers, Sisters, late Grandparents, Uncles, Aunts, Cousins, Brothers-in-law, Friends and extended family; I would have not gotten this far if I didn’t have this amazing support system.

My last, but most important, fragment of appreciation goes to my very dearly loved father. I am who I am today thanks to the amazing guiding light, my true north, he represents to me. I can only hope to become one fourth of the man he once was. Onde quer que você esteja, saiba que essa conquista não é so minha, é nossa! Till we meet again!
# Table of contents

Abstract .......................................................................................................................... i
Acknowledgments .......................................................................................................... iv
List of tables .................................................................................................................... viii
List of Figures ................................................................................................................ x

Chapter 1: Introduction .................................................................................................... 1
  1.1 Ceramics’ properties ............................................................................................... 1
  1.2 Supercritical fluids ............................................................................................... 1
    1.2.1 Applications of Supercritical Fluids .............................................................. 2
  1.3 Supercritical Carbon Dioxide (scCO₂) ................................................................. 6
    1.3.1 Polymer solubility in ScCO₂ ....................................................................... 7
    1.3.2 Particle coating with Polymers in scCO₂ ..................................................... 8

Chapter 2: Experimental ................................................................................................. 13
  2.1 Sample preparation ............................................................................................... 13
  2.2 Sample characterization ....................................................................................... 16
    2.2.1 Scanning Electron Microscopy & Energy Dispersive X-Ray Spectroscopy ... 16
    2.2.2 Fourier Transformed Infrared Spectroscopy ................................................. 17
    2.2.3 X-ray Diffraction ......................................................................................... 18
  2.3 Compressive Strength Testing .............................................................................. 19

Chapter 3: Results and Discussion ................................................................................ 22
  3.1 Effect of temperature, pressure and dissolution time .......................................... 22
    3.1.1 Temperature influence on coating ............................................................... 22
    3.1.2 Pressure influence on coating .................................................................... 34
    3.1.3 Dissolution time influence ......................................................................... 42
    3.1.4 Samples prepared under sub-critical conditions ....................................... 47
  3.2 Chemical integrity of materials post-treatment ...................................................... 48
  3.3 Strength testing of composite pellets ..................................................................... 50

Chapter 4: Conclusions and Future Work ....................................................................... 55

Scholarly Work .............................................................................................................. 57
References.......................................................................................................................58
Appendix A: Copyright permission for Fig. 1.................................................................63
List of tables

Table 1: Summary of main processes that utilize scCO₂ to coat particles in industry. ..... 11
Table 2: Summary of parameters for temperature optimization experiments. ...............23
Table 3: Summary of parameters for pressure optimization studies.............................35
Table 4: Summary of parameters for dissolution time experiments..........................43
List of Figures

Fig. 1: Example of wood impregnation using supercritical carbon dioxide. The piece on the left side is bare while the three on the right have been impregnated using furfural under different conditions. This is a good example of the effusion abilities of supercritical fluids. This figure copyrights permissions were conceded by Extratex [8]. .................................................................3

Fig. 2: Phase diagram for Carbon dioxide. Critical point for CO₂ is relatively mild at 31.1 °C and 73.8 bar. This figure was modified from the article by Budisa et al [18]. .................................................................5

Fig. 3: Schematic representation of the RESS process. In this process SCF is pumped into a high-pressure chamber containing a solute. The solution is then sprayed through a nozzle into a substrate of interest. RESS is the most common process that utilizes scCO₂. This figure was adapted from an article by Parhi et al. [50]. .........................9

Fig. 4: Parr Instrument’s 1 L stirred batch reactor. Coating experiments took place inside reactor for a fixed amount of time. Reactor controller is located on the right-hand side of the photograph. The reactor controller was responsible for monitoring the temperature and pressure inside the reactor, as well as controlling the heating and stirring. .................................................................13

Fig. 5: Recorded parameters from one of the coating experiments. As the reactor was heated to the desired temperature, the pressure followed until both plateaued at the final conditions. Dissolution time was defined as the time at which the temperature was kept within 10% of the final temperature. .................................................................15

Fig. 6: Hitachi S-4700 II Field Emission Electron Microscope and Oxford Instruments Energy Dispersive X-Ray Spectroscopy unit attached. SEM was used to characterize the surface morphology of samples and EDS was used to ensure fluorine was present. .................................................................17

Fig. 7: Thermo Scientific Nicolet iN10 MX Fourier Transformed Infrared Spectrometer (a). Close up of the Ge tip ATR probe (b). This equipment was used to ensure that the chemical composition remained intact post-scCO₂ treatment. .........................18

Fig. 8: Rigaku SmartLab X-Ray diffractometer used to check on the chemical integrity of the powder product post-treatment under scCO₂. Bragg-Brentano mode was used to characterize the powder from 10° to 90°. .................................................................19

Fig. 9: Carver 4350 Benchtop Hydraulic press along with MTI 10 mm hardened stainless steel die set. Pellet samples were prepared at 13 MPa for 3 minutes. An example is shown on the right hand side of a resultant pellet. .................................................................20
Fig. 10: Instron 8872 Servohydraulic Testing System (a). Close up view of the loading cell along with the compressive testing apparatus (b). The pellet samples were compressed at a 0.03 \( \text{sec}^{-1} \) loading rate.

Fig. 11: SEM micrograph of Sample 1 done at 4500X magnification. PVDF particles are present in the sample. No extensive coating was observed at these conditions.

Fig. 12: (a) SEM micrograph taken at 250X magnification along with EDS fluorine map (b). From the fluorine map on the bottom, it was observed that most of the PVDF was present in large chunks throughout the sample.

Fig. 13: SEM micrograph of Sample 2 taken at 2500X magnification. Though, few particles were coated, most particles did not appear to receive any coating. This result was consistent with Sample 1.

Fig. 14: (a) SEM micrograph taken at 250X magnification. (b) EDS fluorine map of Sample 2. Fluorine is present throughout the whole sample but mostly is distinct chunks. This is evidence that the coating was not well distributed.

Fig. 15: SEM micrograph of Sample 3 taken at 4000X magnification. No PVDF particles are visible within this sample.

Fig. 16: SEM micrographs of Sample 4. No PVDF particles were detected in this sample either, which was evidence that the PVDF had melted and created the clusters observed after dissolutions were done.

Fig. 17: EDS colored map of Sample 3. Red dots represent fluorine counts, and green dots represent cobalt counts. Fluorine particles are surrounded by cobalt particles which reinforces the hypothesis that the PVDF melted and re-solidified in Samples 3 and 4.

Fig. 18: SEM micrographs of Sample 5 taken at 4500X magnification. This sample showed decent coating extent with some chunks of PVDF throughout. Little to no difference was observed in Sample 5 compared to Samples 1 and 2. 140 °C was chosen as the optimal temperature.

Fig. 19: (a) SEM micrograph of Sample 5 taken at 250X magnification. (b) EDS fluorine map of Sample 5. Sample 5 showed similar pattern compared Samples 1 and 2, with fluorine counts spread out and chunks as well.

Fig. 20: SEM micrograph of Sample 6 done at 2500X magnification. Large agglomerates of PVDF were identified throughout the sample and uniform coating was also observed along the sample. This result was akin to that of sample 5.

Fig. 21: (a) SEM micrograph of Sample 6 taken at 250X magnification. (b) EDS fluorine map of Sample 6. Despite a 10 bar pressure increase compared to the previous sample, no major differences in the extent of coating were observed.

Fig. 22: SEM micrograph of Sample 7 under 4500X magnification. Improvement was observed regarding the extent of coating compared to Sample 6. The only parameter modified from the previous experiment was pressure.
Fig. 23: (a) SEM micrograph of Sample 7 taken at 250X magnification. (b) EDS fluorine map of Sample 7. This map show that the fluorine distribution throughout the sample was improved, despite still presenting the large PVDF agglomerates. 39
Fig. 24: SEM micrograph of Sample 8 at 4000X magnification. PVDF nanospheres are clearly identified on the ceramic particles generating a uniform coating. 40
Fig. 25: EDS map of Sample 8. Well distributed fluorine as well as large agglomerates of PVDF are seen in the SEM micrograph (a) and respective EDS fluorine map (b). However, the magnified SEM view in (c) and respective EDS fluorine map (d) confirms the presence of well distributed fluorine at the particles' surfaces. 41
Fig. 26: SEM micrographs captured at 2500X magnification. Samples prepared under dissolution time of 24 (a), 12 (b), and 6 hours (c) showed very little difference in regard to the final coating. All samples were coated very uniformly. 42
Fig. 27: (a) SEM micrograph of Sample 11 taken at 250X magnification. (b) EDS fluorine mapping of sample 11. All three samples prepared for the dissolution time experiments displayed comparable coating. 43
Fig. 28: Amalgamation of SEM micrographs captured at 2500X magnification of the optimal samples. The repeatability of the optimal samples was excellent. Almost all particles in both samples were coated uniformly with a layer of PVDF nanospheres. 44
Fig. 29: Compilation of SEM micrographs of samples produced under sub-critical conditions. Though some small coating was observed in scattered particles, most of them did not receive any coating. This data fragment indicated that the coating on optimal particles was mostly a product of scCO₂ solvation of PVDF. 45
Fig. 30: ATR-FTIR spectra of (a) pure LiCoO₂ pre-treatment under scCO₂, (b) pure PVDF pre-treatment under scCO₂ and (c) composite powder post-treatment under scCO₂. 46
Fig. 31: XRD pattern of optimal powder material between the range of 2θ = 10° to 90°. Peaks indicating the presence of LiCoO₂ suggested that the material had not undergone chemical significant degradation. 47
Fig. 32: Compression Stress-Strain curves for samples prepared under optimal conditions. Their mechanic behavior was very similar, with samples yielding around the same point. This result reinforces the idea the coating method was accurate and repeatable. 48
Fig. 33: Compressive Stress-Strain graphs. (a) Sample prepared under optimized conditions vs. non-optimal conditions. (b) Sample prepared under optimized conditions vs. sub-critical conditions. (c) PVDF pellet vs. sample prepared under optimized conditions. 49
Fig. 34: Photograph taken after the production of an optimal sample. Powder was stuck inside all walls of the reactor. This phenomenon was not observed in samples prepared under most other conditions.

Fig. 35: Compressive stress strain curve for one of the samples prepared under optimal conditions. The orange line represents the 5% yield offset which was calculated based on ASTM D695-15 standard.
Chapter 1: Introduction

1.1 Ceramics’ properties

Ceramics are widely used for many different types of applications in industry. Specifically, tape casting, green body manufacturing, and slip casting are some of the applications in which ceramics are used [1–3]. Such applications normally require that the ceramic particles adhere cohesively to make larger structures. However, bare ceramic particles do not possess high adhesion capabilities [4]. Therefore, to ensure that the combined formation remains adhered together, the employment of binders (such as polymers) is usually necessary. Conventional methods utilized for coating ceramic particles with binders frequently use chemicals (such as organic solvents) which impose great risks to human health as well as the environment. The use of different types of solvents is a possible solution to circumvent this issue. Among the possible substitutes, supercritical fluids emerge as one of the best options. Over the next two sections, further details will be given as to why supercritical fluids make good substitutes for traditional chemicals used in ceramic coating.

1.2 Supercritical fluids

Supercritical fluids (SCF) were first discovered by French scientist Charles Cagniard de la Tour in 1822. One of de la Tour’s interests was acoustics research. In one of his experiments he placed a flint sphere inside a Papin’s digester partly packed with liquid. As he rolled the unit, a splashing noise was produced every time the flint sphere passed through
the liquid-vapor interface. De la Tour noted that the splashing noise stopped above a certain temperature when he heated the system well beyond the boiling point of the fluid [5]. This experiment marked the discovery of the supercritical phase.

A SCF is any substance in which the temperature and pressure are kept above its critical point. Critical point is defined as the end point of the liquid-vapor equilibrium line of a substance above which liquid and vapor phases are indistinguishable. Pure SCF have liquid-like densities that are easily adjusted with changes in pressure and temperature. Furthermore, SCF possess very high, gas-like diffusivities. Moreover, their viscosity is extremely low, and their surface tension is nearly nonexistent. They can effuse through solids like gases, and dissolve substances like liquids. Such qualities make SCF an attractive choice for many practical applications in industry and research.

1.2.1 Applications of Supercritical Fluids

Based on its unique properties (e.g. high diffusivity, low viscosity, low surface tension, and variable density), supercritical fluids are used in a wide range of processes. SCF are usually utilized in processes where mass transfer, chemical reactions, and phase transitions are required [6]. Herein, its main applications will be briefly reviewed.
1.2.1.1 Extraction/impregnation of substances from/into solids

SCF’s penetrating abilities through solids make them an excellent choice for extraction of substances from solids. A very well-known example is caffeine extraction from coffee beans and tea leaves. In this case the moist substrate is loaded into a reactor and the supercritical fluid (usually supercritical carbon dioxide) runs through the reactor extracting the caffeine. The SCF is able to effuse through the beans and dissolve the caffeine contained within. The mixture of SCF and caffeine is later separated downstream. The rate at which the SCF is run, the temperature, and the pressure at which the process is conducted all play a role in how much caffeine is recovered downstream [7].

Fig. 1: Example of wood impregnation using supercritical carbon dioxide. The piece on the left side is bare while the three on the right have been impregnated using furfural under different conditions. This is a good example of the effusion abilities of supercritical fluids. This figure copyrights permissions were conceded by Extratex [8].

Though most of the research efforts on the effusion abilities of the SCF concentrate on the removal of substances from solids, the same process can be used to impregnate solid
substrates. Conventional use of this technique is found in the wood, leather, and textile fibers industry. Fig. 1 portrays a good example of wood pieces that were impregnated with furfural under different conditions using supercritical carbon dioxide. In these cases, SCF molecules rapidly diffuse through the pores of the substrate carrying along fungicides, polymers, and dyes. This process can protect, color or modify a substrate using SCF impregnation [6,9–11]. The advantages of using supercritical fluids (especially carbon dioxide) as opposed to conventional organic solvents for extraction/impregnation are that they do not impose a high risk to human health nor are they large environmental pollutants. Most organic solvents pose some risk to human health as well as the environment [12,13].

1.2.1.2 Production of chemicals using SCF

Using SCF as a medium for chemical reactions has been reported for the past few decades. SCF, especially supercritical CO₂, are not easily oxidized; they are also inert to free radicals, and are easily recycled [6,14]. Such qualities make SCF good reaction medium. Perhaps, the most prominent area in which SCF are utilized as reaction medium is polymerization. Fast reaction kinetics facilitated by high diffusivity as well as liquid-like solvation ability make SCF good substitutes for organic solvents, which are traditionally used for polymerization reactions. Large companies such as Mitsubishi and DuPont have developed and commercialized methods that utilize supercritical polymerization [6,15]. Other known instances where reactions take place in supercritical media include hydrogenation reactions, hydrothermal biomass gasification, and oxidation in supercritical water [6,16,17].
1.2.1.3 Phase changes in Supercritical fluids

Supercritical fluids are commonly used for phase transformation processes because their density can be easily tuned with small changes in temperature and pressure. Most of the research and industrial applications in this area utilize CO\textsubscript{2} as the medium due to its relatively mild critical point (31.1 °C, 73.8 bar) exemplified in Fig. 2. Furthermore, carbon dioxide is a non-toxic, non-flammable, and easily recyclable solvent [9].

![Phase diagram for Carbon dioxide](image)

Fig. 2: Phase diagram for Carbon dioxide. Critical point for CO\textsubscript{2} is relatively mild at 31.1 °C and 73.8 bar. This figure was modified from the article by Budisa et al [18].
Phase transition processes take advantage of two attributes of SCF. First is their solvation ability, which allows the supercritical fluid to act like a solvent and transport the solute. Second is SCF’s easy compressibility, which is in part responsible for precipitation of solutes onto substrates [19]. For the remainder of this introduction, phase transition processes will be further explained with special focus on processes that utilize supercritical carbon dioxide (scCO₂) as a solvent.

1.3 Supercritical Carbon Dioxide (scCO₂)

Though the negative effects carbon dioxide has on the environment as the leading greenhouse gas effect gas are well-known and well-documented, CO₂ has major economic value in scCO₂ applications [20–35]. Environmental concerns arising from the use of chlorofluorocarbons (CFCs) in the chemical industry sparked the search for substitute agents for their applications. Up until the early 1990s CFCs were ubiquitously used in applications such as refrigeration, aerosols, and standard solvents for many commercial processes [22,36]. Once the negative impacts that CFCs had on the environment (especially the ozone-depletion potential) were fully understood, an industry-wide effort led to the development of several replacements. Since then, scCO₂ rose as one of the most prominent substitutes, with a wide variety of applications [37]. Despite the adverse effects of CO₂ regarding climate change being already known, its advantages such as non-toxicity, non-flammability, and easy recyclability outweigh the cons. Besides, additional CO₂ is not generated for use as scCO₂, rather it is captured from other processes (such as combustion) for use.
Many applications have exploited the potential of scCO$_2$. In particular, coating of particles has received fair amount of attention since the 1990s [14,19,38–40]. Particles in industry are typically coated for degradation protection and adhesion improvement, among other things [19,41,42]. Moreover, particle coating using scCO$_2$ distinguishes itself due to a few factors: 1) traditional particle coating is usually carried out using organic solvents, which are usually toxic to human health (as well as flammable, hard to recycle, and cost inefficient); 2) the supercritical qualities of scCO$_2$ (described in section 1.2 Supercritical fluids) make it a better suited than organic solvents for particulate coating; 3) ScCO$_2$ is non-toxic, non-flammable, easy to recycle, and abundant, 4) and scCO$_2$ can dissolve several different types of polymers. Therefore, the use of scCO$_2$ to coat particles is much more advantageous in economic and environmental terms.

### 1.3.1 Polymer solubility in ScCO$_2$

Pioneering works of DeSimone et al. and McHugh et al., where they were able to successfully dissolve hydrofluorocarbons and perfluoropolymers (respectively) in scCO$_2$ [37,43], showed that it was possible to substitute the traditional organic solvents and CFCs with scCO$_2$ in a very efficient manner. In a different study, McHugh and co-workers were able to determine the solubility of poly(vinylidene fluoride) (PVDF) in scCO$_2$ and other SCF using the cloud-point method [44]. They concluded that PVDF is soluble in scCO$_2$, though at extreme pressures only. They also determined that chain length and architecture play a role in lowering or increasing the solubility of such polymers. Since then, the process
has evolved to encompass a wide variety of polymers in a vast range of applications, including particle coating.

### 1.3.2 Particle coating with Polymers in scCO$_2$

Several reports have proposed improved methods for coating different types of substrate with polymers [45–49]. For instance, Ratcharak et al. successfully presented a method in which Thermoplastic starch/poly(butylene adipate-co-terephthalate) mixture was coated with a hydrophobic layer of poly(trifluoroethyl methacrylate) in scCO$_2$ using the RESS method [45]. In another instance, Esmaeili et al. combined in situ polymerization with particle coating where they successfully coated aluminum nanoparticles using scCO$_2$ [46]. Another important application of scCO$_2$ is the coating of ceramic particles with polymers due to their poor adhesion abilities [47–49]. Processes such as Rapid Expansion of Supercritical Solution (RESS), Supercritical Anti-Solvent (SAS), and Gas Anti-Solvent (GAS) (amongst others) were all tailored for scCO$_2$ particle coating. These processes will be explained in more detail over the next sub-sections.

#### 1.3.2.1 RESS method

The RESS method was the first to be developed for the encapsulation of small particles in industry. It is now the most commonly used scCO$_2$ method in industry [39]. This method consists of a few different steps: 1) ScCO$_2$ is pumped into a high-pressure extraction vessel containing a polymer. 2) After the polymer is fully dissolved by the SCF, the supercritical solution exits the vessel. 3) The supercritical solution is then throttled through a capillary
nozzle into a low-pressure vessel containing the substrate of interest. The fast depressurization leads to nucleation of the solute onto the substrate; thus, leading to a surface coating. It should be noted that many parameters (temperature, pressure, nozzle geometry, etc.) play a role on the quality of the final coating [38–40]. Common applications for this method include pharmaceutical production, food processing, and surface protection. Fig. 3 shows a schematic representation of the RESS method.

![Schematic representation of the RESS process.](image)

**Fig. 3**: Schematic representation of the RESS process. In this process SCF is pumped into a high-pressure chamber containing a solute. The solution is then sprayed through a nozzle into a substrate of interest. RESS is the most common process that utilizes scCO₂. This figure was adapted from an article by Parhi et al. [50].

One major advantage of using the RESS method for coating particles is the fact that no cosolvents are needed for this process. However, its disadvantages lie in the fact that this process can become complicated. It takes more than one vessel to carry out this process, and the nozzle geometry plays a role on how the particles get coated. Combining both facts, RESS can sometimes be not entirely straightforward.
1.3.2.2 SAS method

The SAS method works with an opposite principle as compared to RESS. In SAS, instead of the SCF being used as a solvent, it works as an anti-solvent. In this process a conventional organic solution containing the polymer of interest is sprayed though a nozzle into a vessel filled with SCF. Such polymer is insoluble in the SCF, which leads to precipitation of the polymer from the organic solvent [51,52].

A few reports have been published on particle-coating utilizing the SAS method[51–53]. Wang and co-workers reported a method in which they coated silica particles with poly(lactide-co-glycolide) (PLGA). They discovered that the polymer-to-substrate ratio and polymer concentration in the solvent are critical parameters for the operation of this process [52]. Advantages of this process are that it can be operated under much lower pressure, and polymer-containing solutions can be more concentrated [39]. On the other hand, this method utilizes toxic organic solvents which usually contaminate the final product [39]. Moreover, similarly to RESS, SAS is complex because many variables must be taken into account for proper operation, such as temperature, pressure, liquid solvent compatibility, polymer concentration, etc. On top of that, this process also requires more than one vessel for operation.

1.3.2.3 Gas method

The GAS method is similar to the SAS method in a sense that it utilizes the SCF as an anti-solvent agent. However, instead of being sprayed though a nozzle all at once into the solution containing the polymer, the SCF is sprayed gradually until the target saturation is
achieved [39,40]. This method provides very fine control over the morphology of coating, as the speed at which the SCF is sprayed dictates the outcome [39]. Just like SAS, this method contains multiple variables that need to be adjusted for proper operation. Table 1 summarizes all three methods (RESS, SAS, and GAS), including their respective advantages and disadvantages.

Table 1: Summary of main processes that utilize scCO₂ to coat particles in industry.

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>RESS</td>
<td>No liquid solvents are needed for operation</td>
<td>Multiple vessels are needed for operation; Nozzle can impose unwanted complications</td>
</tr>
<tr>
<td>SAS</td>
<td>Can be operated at lower pressure; polymer can be very concentrated in liquid solution</td>
<td>Multiple vessels are needed for operation; use of toxic organic solvents</td>
</tr>
<tr>
<td>GAS</td>
<td>Coating morphology can be finely tuned based on speed of depressurization</td>
<td>Multiple vessels are needed for operation; use of toxic organic solvents</td>
</tr>
</tbody>
</table>

Though many reports concentrate on the coating of small particles using the aforementioned methods, very few studies focus on simple methods that do not involve multi-stage processes and the use of toxic organic solvents. Thus, the motivation of this study derives from the concept of improving the adhesion properties of ceramic particles using a simple one-step method that utilizes a non-toxic solvent. A simple, one-step process

"simple, one-step process"
for coating ceramic particles with polymer was created and optimized, using benchtop-scale versions of industrywide equipment for scCO\(_2\) coating. Chapter 2 of this thesis details the experimental process and equipment used to fabricate, characterize, mechanically test the composite material. Chapter 3 presents and discusses the results obtained from this study. Chapters 4 summarizes the main conclusions and recommendations for future research elucidated from the results of this study.
Chapter 2: Experimental

2.1 Sample preparation

A mass of ceramic LiCoO$_2$ particles (MTI Corp., Avg. diameter = 10μm) was weighed out to a value of 20.00 ± 0.01 g. That powder was then placed inside a 1 L stainless steel stirred batch reactor (Parr Instrument Company, 4520 series benchtop reactor) along with 2.22 ± 0.01 g of PVDF (Alfa Aesar, Mw = 400,000 g/mol). Fig. 4 shows the reactor in which the coating experiments took place.

Fig. 4: Parr Instrument’s 1 L stirred batch reactor. Coating experiments took place inside reactor for a fixed amount of time. Reactor controller is located on the right-hand side of the photograph. The reactor controller was responsible for monitoring the temperature and pressure inside the reactor, as well as controlling the heating and stirring.
The inlet of the reactor was connected to a CO₂ source provided by Praxair Gas (99.95% purity), while the outlet was connected to atmosphere though a needle valve. Once both powders were placed inside, the reactor was sealed. Both inlet and outlet were gently opened for 5 minutes to allow CO₂ to purge the reactor of any retained moisture and oxygen. After the purge step was complete, the outlet of the reactor was closed and subsequently filled with CO₂ until it reached 45 ± 3 bar. The speed at which the reactor was filled with CO₂ was of utmost importance as it dictated the height of the final pressure (i.e. the final pressure was higher if the CO₂ inlet was opened quickly and vice-versa). Heating was set at a rate of 1.5 °C/min to avoid overshoot and stirring was set at 500 rpm. Both parameters were controlled via a controller reactor (Parr Instruments Co., 4848 Reactor controller). Temperature, pressure, and dissolution time were optimized for the process though no experiments were performed above 225 °C and 160 bar for safety reasons, as this was upper limit for safe operation of the reactor suggested by the manufacturer. Fig. 5 shows the recorded temperature and pressure inside the reactor during one of the coating experiments.
Fig. 5: Recorded parameters from one of the coating experiments. As the reactor was heated to the desired temperature, the pressure increased until both plateaued at the final conditions. Dissolution time was defined as the time at which the temperature was kept within 10% of the final temperature.

Once experiments concluded, the reactor was slowly depressurized to ambient pressure in order to avoid major loss of material. The reactor was then opened, and the sample inside was recovered and stored in airtight containers until they were characterized and mechanically tested.
2.2 Sample characterization

2.2.1 Scanning Electron Microscopy & Energy Dispersive X-Ray Spectroscopy

Visual verification of surface coating as well as surface morphology analysis were studied using Scanning Electron Microscopy (SEM) with a Hitachi S-4700 II microscope. Additionally, an attached Energy Dispersive X-Ray Spectroscopy (Oxford Instruments) unit was used to check for the presence or absence of fluorine on post-treated samples. An accelerating voltage of 20 kV and a working distance of 12 mm were set for both SEM imaging and EDS processing. EDS data was processed using Oxford’s software INCA. The equipment setup is represented in Fig. 6.
Fig. 6: Hitachi S-4700 II Field Emission Electron Microscope and Oxford Instruments Energy Dispersive X-Ray Spectroscopy unit attached. SEM was used to characterize the surface morphology of samples and EDS was used to ensure fluorine was present.

2.2.2 Fourier Transformed Infrared Spectroscopy

Attenuated Total Reflectance Fourier Transformed Infrared Spectroscopy (ATR-FTIR) analysis was conducted using a Thermo Scientific Nicolet iN10 MX to confirm that the chemical composition of the composite samples was kept intact after treatment under scCO$_2$. Enough powder to cover the whole ATR tip from each sample was mounted onto
a glass slide. A Ge tip crystal was used as the ATR probe with a 45° contact angle and 2 cm\(^{-1}\) resolution. Data was processed using Thermo Scientific’s OMINIC Picta software package. The equipment is displayed in Fig. 7.

Fig. 7: Thermo Scientific Nicolet iN10 MX Fourier Transformed Infrared Spectrometer (a). Close up of the Ge tip ATR probe (b). This equipment was used to ensure that the chemical composition remained intact post-scCO\(_2\) treatment.

2.2.3 X-ray Diffraction

Some samples were investigated using X-ray diffraction (XRD) with a Rigaku SmartLab X-ray diffractometer using CuK\(\alpha\) radiation. Powder samples were analyzed using Bragg-Brentano focusing. All patterns were collected over the range of 2\(\theta\) = 10.000° to 90.000° with a step size of 0.016°. Rigaku PDXL2 analysis software and JCPDS cards were used in assessing the XRD data. Fig. 8 shows the X-ray diffractometer.
Fig. 8: Rigaku SmartLab X-Ray diffractometer used to check on the chemical integrity of the powder product post-treatment under scCO₂. Bragg-Brentano mode was used to characterize the powder from 10° to 90°.

2.3 Compressive Strength Testing

Small amounts of each sample (450 ± 10 mg) were compressed into small disks at room temperature inside a 10 mm hardened stainless steel die set (MTI Corp.) under 13 MPa using a manual hydraulic press (Carver, Inc., 4350 Benchtop Laboratory Pellet Press) for 3 minutes each. The resulting pellets measured ca. 1.8 mm in thickness. An image of the hydraulic press/die set along with an example of a manufactured pellet is shown in Fig. 9.
Fig. 9: Carver 4350 Benchtop Hydraulic press along with MTI 10 mm hardened stainless steel die set. Pellet samples were prepared at 13 MPa for 3 minutes. An example is shown on the right hand side of a resultant pellet.

Once the pellets were made, their strength was measured by compression method using a Servohydraulic Fatigue testing system (Instron, 8872 Fatigues testing system). The loading rate was set at 0.03 mm · sec$^{-1}$ for all samples. Each sample was compressed until it failed.

Fig. 10 shows the testing apparatus used to in the compressive strength studies.
Fig. 10: Instron 8872 Servohydraulic Testing System (a). Close up view of the loading cell along with the compressive testing apparatus (b). The pellet samples were compressed at a $0.03 \cdot \text{sec}^{-1}$ loading rate.
Chapter 3: Results and Discussion

3.1 Effect of temperature, pressure and dissolution time

In contrast to most studies on coating of particles using scCO$_2$, neither rapid expansion of SCF (RESS) nor SCF antisolvent (SAS) methods were used. Instead, the focus was on creating a simple one-step process. Pressure and temperature safety limitations were imposed due to the operating limits of the reactor (160 bar and 225 °C). Therefore, none of the experiments were conducted above that threshold.

3.1.1 Temperature influence on coating

Temperature at which the process was conducted was the first parameter to be optimized. All experiments were carried out between 130 °C and 225 °C. Though CO$_2$ becomes supercritical at 31.1 °C, the bottom temperature limit was set at 130 °C because preliminary experiments showed that getting above the critical pressure with final temperatures below this temperature was very hard to accomplish, regardless of how fast the CO$_2$ inlet valve was opened. Therefore, in order to make sure CO$_2$ became supercritical, all subsequent experiments were carried at or above 130 °C. Table 2 shows all the temperature experiments that were carried out, with the respective pressure achieved, and dissolution time.
Table 2: Summary of parameters for temperature optimization experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Dissolution time (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>130</td>
<td>80</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>160</td>
<td>80</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>190</td>
<td>105</td>
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</tr>
<tr>
<td>4</td>
<td>170</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>140</td>
<td>80</td>
<td>6</td>
</tr>
</tbody>
</table>

In order to assess the extent to which particles were coated, samples were checked under SEM and further confirmed with EDS. Following sub-sections describe each sample based on SEM and EDS observations.

3.1.1.1 Sample 1 (130 °C, 80 bar, 6 hours)

The pressure at which this sample was made was barely above the critical point. Fig. 11 shows the SEM micrograph of the sample. It was observed that PVDF nanospheres were clearly present, though most particles did not seem to have a good layer of coating. The lack of coating can be explained by the fact that this was done at barely-above supercritical pressure. Therefore, the scCO₂ did not present good solvation power.
To confirm PVDF was present in the mixture, EDS was used to track the presence of fluorine. Fig. 12 shows the EDS map taken at a lower magnification and it shows the clear presence of fluorine throughout the sample. It was also observed that fluorine was mostly present in large chunks by themselves, and not where the LiCoO$_2$ particles were, confirming the same observation made by the SEM micrographs.
Fig. 12: (a) SEM micrograph taken at 250X magnification along with EDS fluorine map (b). From the fluorine map on the bottom, it was observed that most of the PVDF was present in large chunks throughout the sample.
3.1.1.2 Sample 2 (160 °C, 80 bar, 6 hours)

Pressure was kept constant for this sample compared to Sample 1. The temperature was raised by 30 °C to 160 °C. The increase in temperature did not seem to affect the extent of coating on the ceramic particles very much. Fig. 13 shows one of the SEM micrographs taken from Sample 2. Though there were sporadic coated particles throughout this sample, most particles did not appear to be coated very well.

![SEM micrograph of Sample 2 taken at 2500X magnification. Though, few particles were coated, most particles did not appear to receive any coating. This result was consistent with Sample 1.](image)
The EDS map for this sample looked very similar to Sample 1. A large amount of fluorine was present as agglomerates and not on the same locations as the LiCoO$_2$ particles. Fig. 14 shows the EDS map taken from Sample 2 at a lower magnification.

Fig. 14: (a) SEM micrograph taken at 250X magnification. (b) EDS fluorine map of Sample 2. Fluorine is present throughout the whole sample but mostly is distinct chunks. This is evidence that the coating was not well distributed.
Though fluorine was observed throughout the whole sample, it was largely present in congregate
classes which were also observed in SEM. Both Samples 1 and 2 indicate that either the
temperature at which samples were coated did not seem to influence the outcome of the
coating much, or both these temperatures were significantly off the range for optimal
coating formation.

3.1.1.3 Sample 3 (190 °C, 105 bar, 6 hours)

Temperature was increased 30 °C to 190 °C in Sample 3. Though the pressure was significantly higher compared to Samples 1 and 2, this condition did not influence the coating outcome. Upon SEM analysis, no evidence of PVDF particles was found within this sample. Fig. 15 shows the SEM micrograph of sample 3, in which only bare LiCoO₂ particles were observed. Furthermore, after the experiment was finished, large agglomerates of powder were glued to the reactor’s walls, phenomenon which was not observed in the first two samples. Based on qualitative sticking evidence, as well as the lack of PVDF particles observed in the SEM micrograph, it was hypothesized that the PVDF had melted inside the reactor, re-solidified once temperature was brought down which lead to the creation of the clusters. Thus, the pressure at which this experiment was carried was irrelevant.
3.1.1.4 Sample 4 (170 °C, 60 bar, 6 hours)

In order to try to avoid the melting issue, for the next prepared sample (Sample 4) the temperature was lowered 20 °C to 170 °C. However, similar to Sample 3, PVDF was not found in Sample 4 based on the SEM micrographs (Fig. 16). Furthermore, the same phenomenon observed in Sample 3, in which large chunks got stuck on the reactor’s walls, also took place in for Sample 4. Thus, based on the SEM evidence along with the qualitative observation of sticking, it was surmised that PVDF in Sample 4 had also melted. Though pressure for this sample was set at sub-critical conditions at 60 bar, it still melted.
Thus, pressure had no effect on this process once PVDF got above its melting temperature, regardless whether or not the process was carried out under supercritical conditions.

Fig. 16: SEM micrographs of Sample 4. No PVDF particles were detected in this sample either, which was evidence that the PVDF had melted and created the clusters observed after dissolutions were done.
Fig. 17: EDS colored map of Sample 3. Red dots represent fluorine counts, and green dots represent cobalt counts. Fluorine particles are surrounded by cobalt particles which reinforces the hypothesis that the PVDF melted and re-solidified in Samples 3 and 4.

Adding to the SEM and visual evidences that PVDF melting was the causing factor for the formation of the clusters, EDS data from Sample 3 showed that fluorine was present inside of one of these clusters. Fig. 17 shows that fluorine was detected behind a few ceramic particles. The red dots represent the fluorine counts, while they are surrounded by counts of cobalt which are represented by the green dots. Moreover, literature confirms that the melting temperature of PVDF varies between 155 °C and 170 °C, depending on the phase, chain length, and chain characteristics [54,55].
3.1.1.5 Sample 5 (140 °C, 80 bar, 6 hours)

Once it was determined that temperatures above 170 °C were unfit for this process, one more experiment was carried to determine the optimal temperature. A temperature of 140 °C was chosen for Sample 5. The experiment was repeated once using the same parameters as Samples 1 and 2 except for the temperature. Fig. 18 shows the SEM micrograph of Sample 5. The same aspect was observed as was seen in Samples 1 and 2, where fine coating was visualized throughout the whole sample, yet major chunks were still present.

Fig. 18: SEM micrographs of Sample 5 taken at 4500X magnification. This sample showed decent coating extent with some chunks of PVDF throughout. Little to no difference was observed in Sample 5 compared to Samples 1 and 2. 140 °C was chosen as the optimal temperature.
Fig. 19a shows an SEM micrograph of Sample 5, with the respective EDS fluorine map (Fig. 19b). The EDS map for Sample 5 appeared very similar to that of Samples 1 and 2. Fluorine counts were apparent throughout the whole map, with scattered chunks of fluorine.

Fig. 19: (a) SEM micrograph of Sample 5 taken at 250X magnification. (b) EDS fluorine map of Sample 5. Sample 5 showed similar pattern compared to Samples 1 and 2, with fluorine counts spread out and chunks as well.
In order to determine the optimal temperature for this process, extent of coating was disregarded as it appeared that temperature did not play a big role on the coating outcome. Overall, samples made at 130 °C, 140 °C, and 160 °C seemed to show little to no difference regarding their extent of coating. Such observation was consistent with literature. Dinoia and co-workers demonstrated that temperature does not significantly affect the solubility of PVDF in scCO₂. Only in certain cases, temperature plays an effect on its solubility [44]. Thus, the temperature was set at 140 °C for the coating process for a couple of reasons:

1) Compared to 130 °C, supercritical pressures were achieved much easier at 140 °C. 130 °C proved to be not a repeatable mark based on preliminary experiments, where some got above supercritical while other experiments didn’t.

2) At 160 °C mark, the process was running too close to the melting temperature of PVDF, so there was risk that the behavior observed in Samples 3 and 4 could reoccur.

3) Even if melting were not to happen consistently at 160 °C, from an energetic standpoint coating at a lower temperature is less expensive. Therefore, taking in account convenience, physical, and energetic factors, the temperature was fixed at 140 °C for all remaining samples.

3.1.2 Pressure influence on coating

After temperature studies were concluded, the effect that pressure had on the extent of coating was investigated. Samples were prepared under three different points between the
supercritical point (73.8 bar) and the pressure safety limit (160 bar). Temperature was kept at 140 °C and dissolution time was maintained at 12 hours for all experiments. Table 3 summarizes the parameters at which the pressure optimization studies were conducted.

Table 3: Summary of parameters for pressure optimization studies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Dissolution time (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>90</td>
<td>140</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>120</td>
<td>140</td>
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</tr>
<tr>
<td>8</td>
<td>150</td>
<td>140</td>
<td>12</td>
</tr>
</tbody>
</table>

Similar to the temperature optimization experiments, the extent of coating was analyzed via SEM and EDS data. The following sub-sections expand on each sample mentioned in Table 3.

3.1.2.1 Sample 6 (90 bar, 140 °C, 12 hours)

The first sample produced for the pressure studies was done at 10 pressure units above Sample 5 at 90 bar. Despite the small increment in pressure, the resulting coating of Sample 6 was comparable to that of Sample 5. Fig. 20 shows the SEM micrograph of Sample 6, in which a large cluster of PVDF particles can be observed in the middle.
Fig. 20: SEM micrograph of Sample 6 done at 2500X magnification. Large agglomerates of PVDF were identified throughout the sample and uniform coating was also observed along the sample. This result was akin to that of sample 5.

EDS data of Sample 6 confirmed the presence of large conglomerates of PVDF throughout the whole sample. Fig. 21 shows the map of Sample 6 taken at a lower magnification along with the fluorine count map. Though faint counts of fluorine are present in the whole sample, the distinctive chunks are clearly seen in the map. Thus, the mere 10 bar increase in pressure did not seem to have a large impact on the result coating in Sample 6.
Fig. 21: (a) SEM micrograph of Sample 6 taken at 250X magnification. (b) EDS fluorine map of Sample 6. Despite a 10 bar pressure increase compared to the previous sample, no major differences in the extent of coating were observed.
3.1.2.2 Sample 7 (120 bar, 140 °C, 12 hours)

While keeping the other two parameters constant, pressure was increased to 120 bar and the coating experiment took place. Subsequent SEM analysis showed a noticeable improvement in coating. Though coating was not uniform in all particles, the number of coated particles showed vast improvement. Fig. 22 shows the SEM micrograph of Sample 7.

Fig. 22: SEM micrograph of Sample 7 under 4500X magnification. Improvement was observed regarding the extent of coating compared to Sample 6. The only parameter modified from the previous experiment was pressure.
Adding to the SEM indication that coating was improved from Sample 6, EDS data showed that fluorine counts were more dispersed within the sample when. However, the large agglomerates were still present. Fig. 23 shows the fluorine EDS map of Sample 7.

Fig. 23: (a) SEM micrograph of Sample 7 taken at 250X magnification. (b) EDS fluorine map of Sample 7. This map show that the fluorine distribution throughout the sample was improved, despite still presenting the large PVDF agglomerates.
3.1.2.3 Sample 8 (150 bar, 140 °C, 12 hours)

Pressure was increased another 30 bar to 150 bar for Sample 8. The increment in pressure seemed to have a positive effect on the coating. SEM analysis of Sample 8 showed that a more uniform coating was achieved by increasing the pressure. Fig. 24 displays a SEM micrograph of Sample 8, where most ceramic particles seen show uniform coating on PVDF nanospheres.

![SEM micrograph of Sample 8](image)

**Fig. 24:** SEM micrograph of Sample 8 at 4000X magnification. PVDF nanospheres are clearly identified on the ceramic particles generating a uniform coating.

Though SEM showed clear evidence of improved uniformity of coating in Sample 8, EDS mapping demonstrated similar behavior as Sample 7 regarding the distribution of agglomerates (Fig. 25a and b). Due to the nature of this process — meaning that both
coating agent and substrate start and end the process in the same vessel — any PVDF that did not dissolve in scCO$_2$ and subsequently precipitate onto the surface of a particle ends up just loose in the main bulk. Furthermore, the complete solubility of PVDF in scCO$_2$ is only achievable at extremely high pressures [44,56]. Therefore, the large chunks were an expected consequence of this method. In order to avoid their formation, this process would have had to be carried out at a much higher pressure.

Fig. 25: EDS map of Sample 8. Well distributed fluorine as well as large agglomerates of PVDF are seen in the SEM micrograph (a) and respective EDS fluorine map (b). However, the magnified SEM view in (c) and respective EDS fluorine map (d) confirms the presence of well distributed fluorine at the particles' surfaces.
Notably, in Fig. 25c and d the magnified EDS fluorine maps for Sample 8 showed drastic improvement in the uniformity and extent of surface coating as compared to Samples 6 and 7. The SEM evidence combined with EDS mapping of the ceramics’ surfaces demonstrated that higher pressure resulted in better coating. This observation was in agreement with prior works [41,45]. In most cases, the higher the pressure a process is conducted, the higher the solubility of the polymer in scCO₂. Even though PVDF is barely soluble in the pressure ranges at which this process performed, coating was still achieved, as evidenced by SEM and EDS. Glebov et al. developed a process utilizing RESS to coat metal particles with PVDF at pressures close this process. They observed that although PVDF is barely soluble in these pressure ranges, coating of small particles was still achieved [41]. Their observations were consistent with the results achieved by the pressure experiments. Along these lines, Ratcharek et al. determined that the pressure at which their coating experiment took place had a direct impact on the final coating morphology of the substrate [45]. That observation was also consistent with the pressure experiments. And despite the fact that both of their processes were based on RESS method, the same behavior transpired for the pressure experiments. Therefore, the optimal pressure was set at 150 bar.

### 3.1.3 Dissolution time influence

After temperature and pressure were determined for the process, the last parameter needed to be optimized was dissolution time. Samples were prepared at 24, 12 and 6 hours while keeping the temperature and pressure under optimal conditions. Table 4 gives a summary of the parameters for the dissolutions time experiments.
Table 4: Summary of parameters for dissolution time experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dissolution time (Hours)</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
</tr>
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<tbody>
<tr>
<td>9</td>
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</tr>
<tr>
<td>11</td>
<td>6</td>
<td>150</td>
<td>140</td>
</tr>
</tbody>
</table>

Little to no difference was noted on the Samples 9 through 11. Fig. 26 shows the SEM micrographs of Sample 9, 10, and 11 respectively. The results from the three samples were nearly identical in regard to extent of coating.
Fig. 26: SEM micrographs captured at 2500X magnification. Samples prepared under dissolution time of 24 (a), 12 (b), and 6 hours (c) showed very little difference in regard to the final coating. All samples were coated very uniformly.
EDS mapping for all three samples appeared very similar. Once again, the coating on the surfaces was very well distributed. Fig. 27 shows the EDS map of sample 11.

Fig. 27: (a) SEM micrograph of Sample 11 taken at 250X magnification. (b) EDS fluorine mapping of sample 11. All three samples prepared for the dissolution time experiments displayed comparable coating.
Since no noticeable difference was seen between Samples 9 - 11, it was surmised that dissolution time did not have an appreciable impact on the degree of coating. Thus, the optimal time for coating was fixed at 6 hours. 6 hours was also the minimum amount time it took for the reactors’ inside temperature to plateau at 140 °C. All succeeding experiments were conducted at 6 hours as the same result was achieved in a shorter time period. Finally, after all parameters were optimized, the coating process was repeated twice at the optimal values (140 °C, 150 bar and 6 hour dissolution). Fig. 28 is an amalgamation of some SEM micrographs of the two optimal samples.

Fig. 28: Amalgamation of SEM micrographs captured at 2500X magnification of the optimal samples. The repetability of the optimal samples was excellent. Almost all particles in both samples were coated uniformly with a layer of PVDF nanospheres.
Based on the micrographs of the optimized samples, repeatable coverage was certainly achieved. Most particles were coated with uniform layers of PVDF nanospheres. These results reinforced that such parameters were optimal for this process.

### 3.1.4 Samples prepared under sub-critical conditions

Lastly, three samples were prepared under sub-critical conditions at 65 bar while keeping same optimal temperature and dissolution time. The purpose was to ensure that all the coating that took place was primarily due to the supercritical nature of CO₂ rather than just convective currents inside the reactor generated by the stirring. Based on the SEM micrographs in Fig. 29, all three samples prepared under sub-critical conditions show little to no surface coating. Hence, the coating observed on the samples prepared under optimal conditions was mostly a product of scCO₂-assisted coating.
3.2 Chemical integrity of materials post-treatment

To confirm that the PVDF samples did not undergo any changes in composition, ATR-FTIR analysis was employed. Fig. 30 shows the spectra of materials pre- and post-treatment. The spectrum for pure LiCoO$_2$ (Fig. 30a) displays only one peak at 580 cm$^{-1}$ assigned to the O-Co-O stretching vibration [57]. The spectrum for PVDF (Fig. 30b) is in close match to literature showing all main features corresponding to $\alpha$-PVDF phase [58]. All peaks corresponding to both $\alpha$-PVDF and LiCoO$_2$ are seen on the spectra from the coated samples (Fig. 30c); hence chemical composition was kept intact post-treatment.
Wang et al. has reported a similar method for checking for chemical integrity using FTIR in which they coated Silica nanoparticles with Eudragit polymer [51].

![ATR-FTIR spectra](image)

**Fig. 30:** ATR-FTIR spectra of (a) pure LiCoO$_2$ pre-treatment under scCO$_2$, (b) pure PVDF pre-treatment under scCO$_2$ and (c) composite powder post-treatment under scCO$_2$.

In addition to FTIR, XRD was also conducted on the resulting powders in order to cross-check for chemical integrity. Fig. 31 shows the spectra of one of the optimized samples. The peaks for the optimized samples are very consistent with LiCoO$_2$ (JCPDS 44-0145). Other samples were also analyzed using XRD to check for their chemical composition, and their spectrum looked identical to that of Fig. 31. Therefore, based on both XRD and FTIR spectra, it was surmised that the samples had not undergone chemical decomposition.
Fig. 31: XRD pattern of optimal powder material between the range of $2\theta = 10^\circ$ to $90^\circ$. Peaks indicating the presence of LiCoO$_2$ suggested that the material had not undergone chemical significant degradation.

3.3 Strength testing of composite pellets

In contrast to most literature, the coating process did not utilize the RESS method or in situ polymerization. Thus, any polymer particle that was not attached to a ceramic substrate was still present in the final bulk. This means that in order to validate whether the SEM/EDS assessments regarding the extent of coating of the ceramic particles were accurate, a means of confirmation was warranted. The hypothesis was that if individual particles were more uniformly coated, the yield strength of the compressed pellet would be
higher as compared to samples where the particles were not as well coated. Because PVDF would provide a higher inter-particle bonding strength (as opposed to bare particle interactions), the adherence of the powder would be increased if uniform coating was achieved. Three pellets from each sample were made as described in Section 2.3 and each pellet was then tested. All the following data is an average from the three pellets from each sample. According to Fig. 32, all samples prepared at optimal conditions showed excellent repeatability, yielding around the same point. This result adds to the SEM/EDS evidence that repeatable coating was achieved.

![Compression Stress-Strain curves for samples prepared under optimal conditions. Their mechanic behavior was very similar, with samples yielding around the same point. This result reinforces the idea the coating method was accurate and repeatable.](image)

Fig. 32: Compression Stress-Strain curves for samples prepared under optimal conditions. Their mechanic behavior was very similar, with samples yielding around the same point. This result reinforces the idea the coating method was accurate and repeatable.
Fig. 33: Compressive Stress-Strain graphs. (a) Sample prepared under optimized conditions vs. non-optimal conditions. (b) Sample prepared under optimized conditions
vs. sub-critical conditions. (c) PVDF pellet vs. sample prepared under optimized conditions.

According to Fig. 33a, a significant increase in compressive yield on samples prepared at optimal conditions compared to samples prepared at non-optimal conditions was observed. Moreover, when compared to samples prepared under sub-critical conditions, samples prepared under optimal conditions displayed considerable improvement in compressive yield (Fig. 33b). Both results support the hypothesis that the optimal samples were more evenly coated as compared to the non-optimal and sub-critical samples. Furthermore, visual inspection for adhesion improvement showed that powder adhered inside all walls of the reactor from optimal conditions (Fig. 34), a phenomenon which was not observed in samples prepared under most other conditions.

Fig. 34: Photograph taken after the production of an optimal sample. Powder was stuck inside all walls of the reactor. This phenomenon was not observed in samples prepared under most other conditions.
Lastly, PVDF pellets were made under the same conditions for comparison, and the compressive yield of the optimized material was found to be closer to that of PVDF as seen in Fig. 33c. No ceramic-only control pellets were manufactured due to the difficulty of keeping them intact without adding a binder. This methodology for compressive yield testing has been commonly reported before [49,59]. For all samples, the yield point was calculated using ASTM D695-15 standard with a 5% yield offset. Fig. 35 shows the determination of the yield point based on the 5% offset for one of the samples prepared under optimal conditions. From the compressive yield strength results, along with the SEM/EDS analysis, it can be concluded that the method created for optimization and coating of LiCoO$_2$ with PVDF using scCO$_2$ in one vessel was successful.

![Compressive stress strain curve](image)

Fig. 35: Compressive stress strain curve for one of the samples prepared under optimal conditions. The orange line represents the 5% yield offset which was calculated based on ASTM D695-15 standard.
Chapter 4: Conclusions and Future Work

The results reported in this work show that a successful method for coating LiCoO$_2$ particles with PVDF was achieved through a simple one-step process using scCO$_2$-assisted dissolution. This process was optimized with respect to temperature, pressure, and dissolution time. Temperature at which this process was carried out and dissolution time were found to have minor impact on the outcome of the coating of the particles. Whereas the pressure at which the process was carried out seemed to have a direct impact on the extent of coating of the particles. Optimal parameters were found to be 140 °C, at 150 bar for 6 hours. As observed from the SEM micrographs, LiCoO$_2$ particles were coated with a uniform layer of PVDF nanospheres. EDS further confirmed the presence of fluorine on the surface of the ceramic particles and ATR-FTIR confirmed that PVDF was not degraded during the process, and XRD confirmed that the composite material was also intact. Finally, compressive strength testing added to the SEM/EDS evidence of optimal coating, with samples prepared at optimal conditions showing compelling evidence of improvement in compressive yield and adherence relative to samples prepared at non-optimal conditions and samples prepared at sub-critical conditions. SEM micrographs of samples prepared at optimal conditions were almost indistinguishable. This fact, along with the very similar stress strain curves, attest to the legitimacy of the process that was developed and optimized.
Future Work

This process has many pathways for future development and improvement. First, this process was designed around a relatively low-pressure threshold imposed by the safety limitations of the reactor. Extensive literature indicates that most polymers (including PVDF) are more soluble in scCO$_2$ at much higher pressures. Therefore, repeating the same one-step process at much higher pressures (inside a reactor designed to withstand pressures of at least one order of magnitude higher) than optimal pressure would logically yield better coating results. However, the advantage of running a process at lower temperature and pressure is that it takes significant less amount of energy to carry out such process. Accordingly, an interesting avenue worth pursuing would be a different optimization investigation, in which energy consumption with regards to desired coating outcome was subject to a cost-benefit analysis. Secondly, the use other types of polymers and supercritical fluids for this process is warranted. Several reports show coating of particles using other families of polymers and disparate kinds of SCF. As such, exploring a variety of polymers classes and different SCF would most certainly yield different optimized parameters. Finally, varying the substrate size and morphology would almost surely impact the coating efficiency under given conditions. Smaller particle size means there is more surface area per unit mass, and therefore more nucleation sites for dissolved polymers in SCF to deposit. That in turn would mean more extensive coating. Similarly, varying the morphology of particles will influence the coating as well. More porous particles mean more surface area is available, while porosity might also impact the degree of penetration through the boundary layer.
Scholarly Work

Publication

G. Stehling Vieira Martins, D. Phares, D. Chidambaram, Enhancing adhesion of ceramics by coating with polymer using supercritical CO$_2$. (Submitted for peer-review journal).
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Objet : Re: Copyright permission for use of picture for Master’s thesis
Importance : Haute

Hello,

My apologies for reaching out again, but this is an extreme time sensitive matter. I first reached out to you Saturday, 13th of July and I still haven’t received a response. I am sorry if this is coming out as “pushy”, but I really need a response as soon as possible. Please refer to the threat below to check the regards of this inquiry. I look forward to hearing back from you soon! Thank you for your time again!

Respectfully,

Gabriel Martins
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https://outlook.office365.com/owa/?path=mail/inbox
Hello,

My name is Gabriel and I am a graduate student at the University of Nevada, Reno, located in Nevada, USA. I am a second year Master’s student in Materials Science and Engineering and I am currently writing my thesis about Supercritical Carbon Dioxide. In my thesis I have included a chapter sub-section which talks about impregnation using scCO2. With that being said, I noticed that on your website under the "Processes" tab, the sixth figure down is a good example of impregnation using scCO2. So, I was wondering if it would be a possibility for me to acquire copyrights for that picture for thesis publication regards strictly. My thesis once published will be publicly available for anyone free of cost. Therefore, I have no monetary gain from using that picture. Please let me know if that would be a possibility. I have attached the picture in case you have any questions which one I’m talking about. I look forward to hear back soon! Thank you so much for your time!

Respectfully,

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