CO_2 SELECTIVE CERAMIC MEMBRANE FOR WATER-GAS SHIFT REACTION WITH CONCOMITANT FOR THE RECOVERY OF CO_2

Quarterly Report for the Period July 2002- September 2002

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Technical Summary

In this quarter we focus on the membrane synthesis via interphase impregnation and slip casting. The slip casting method shows very promising. A well-organized hydrotalcite layer has been deposited on the porous ceramic substrate. Under SEM examination, few defects were recognized. In addition, its particle size in the range of ~500Å is comparable to our existing Al_2O_3 membrane with 100Å pore size. This membrane could be qualified for post-treatment with CVD/I to seal the opening to become a CO_2-affinity membrane. On the other hand, the hydrotalcite membrane prepared via impregnation requires further refinement. After 4th impregnation defects in the range of 0.2 micron were observed under SEM examination, likely due to the incomplete coverage. In the next quarter, we will improve the in-situ technique to overcome this problem.

1. Hydrotalcite Membrane Synthesis via Impregnation

As discussed in the previous quarterly report, hydrotalcite crystals (or gel) formed immediately after the combination of the Al/Mg chlorides with carbonate. Moreover, the precipitate thus formed is rather large in size, such as in the micron range. Thus, to deposit the hydrotalcite into the porous structure of the ceramic substrate as described in Figure 1, we propose the interphase contact approach. It is hoped that the precipitate can be deposited within the porous structure to form constriction with hydrotalcite crystals. In this section, we present the experimental results obtained during this quarter. The experimental condition we selected is pH=10 to form the precipitate in-situ. Then, the impregnated membrane is autoclaved at 150°C for 4 hours to insure the transformation of the precipitate into hydrotalcite crystals. Although our results thus far have indicated the formation of crystals without autoclaving, we continue the autoclaving practice for the time being to eliminate the uncertainty associated with this parameter.

Several trials have been performed for the preparation of the membranes via impregnation. Figures 3&4 present the SEM photomicrograph of the top surface from 1st- and 2nd in-situ deposition. Figure 5 presents the SEM photomicrograph from the sample with the 4th deposition. Between each impregnation, the membrane is subject to autoclaving, water rinsing, and drying. It appears that hydrotalcite does not cover the substrate completely based upon the SEM pictures of the top surface. However, the incomplete top surface coverage does not necessarily suggest the lack of the constriction formed by the crystal. Unfortunately there is no easy way for us to determine the presence of the constriction within the porous structure. Due to the incomplete coverage in the 1st impregnation, we continued the impregnation for three additional depositions. The He and N_2 permeances at room temperature after each impregnation were determined to gauge the degree of coverage (or the opening remained). Table 1 lists the permeance obtained throughout this exercise. Evidently the permeance levels off after the 3rd impregnation, more importantly, 85% permeance was reduced. However, the selectivity after the 3rd impregnation remains low, 1.8, indicating that defects may exist to dilute the Knudsen selectivity we usually obtain in the range of 2.1 or above. Further the SEM photograph after the 4th impregnation (shown in Figures 5a and 5b) is consistent with our speculation that defects remain to dilute the Knudsen selectivity. It appears that the defect shown in Figures 5a and 5b is resulted from the incomplete coverage left from the in-situ impregnation. The defect in the dimension of about 0.2 micron is not covered by the precipitate, most likely resulted from the lack of the reagents filled into this gap (for example an air pocket), during impregnation, and then no precipitate would form within the gap. The other possibility is that the membrane layer cracked after drying.

Although the layer defects exists in these parts, our experience thus far has demonstrated that the in-situ impregnation is a viable technique for the deposition of the hydrotalcite to existing porous ceramic membranes as substrate. The hydrotalcite membrane has been formed within the porous structure of the substrate based upon the SEM examination and the permeance measurement. However, defects remain to be eliminated. Two corrective actions will be incorporated in our next impregnation study:

- We may want to impregnate the reagent (i.e., carbonate) from both tube and shell sides to insure no air pocket or void between the interphase.
- Impregnation of the layer on the inner instead of the outer tubular surface. The outer layer deposition is more susceptible to layer cracked according to our experience.

2. Hydrotalcite Membrane Synthesis via Slip Casting

As described in Figure 2, slip casting of the hydrotalcite thin film is no different from the slip casting of existing mesoporous $A1_20_3$ membranes (with pore size in the range of 40Å to <0.2µ). The critical parameters for this approach include the slip with (i) a proper particle size, and (ii) appropriate rheology. Thus, a defect free thin film can be deposited on the surface of the membrane without defects after thermal annealing. Our goal here is to deposit a thin film of hydrotalcite with ~100Å pore size; then CVD/I technique can be applied to seal the opening in this range. According to our experience with Al_2O_3, the particle size required to form this range of pore size is in the neighborhood of 500 to 800Å as shown in Figure 6. Particles from the hydrotalcite gel are in fact smaller than this range and appear very uniform in size as shown in Figure 6. Based upon this observation, we believe that the hydrotalcite gel we prepare satisfies the first requirement in terms of the particle size.

As far as the rheology of the slip is concerned, we found that, without the modification of the viscosity of the sol, the layer quality was very poor. Our first attempt is to adapt the gel formula we use to prepare the Al_2O_3 thin film for our purpose. The result from this attempt appears very promising. The membranes with the 1, 2, and 3- layer casting have been prepared and well characterized. Each membrane was calcined at 400ºC before the characterization. Figures 7 & 8 show the membrane with one layer casting. The hydrotalcite evidently has covered most opening of the substrate. However, some uncovered defects were observed. Figures 9 & 10 show the membranes with the two-layer casting. The quality was improved significantly. It is clear that the particles formed by the gel are very uniformly and evenly deposited on the surface of the substrate. Figures 11 & 12 show the membrane with the 3-layer deposition. It appears that the layer quality is not improved; in fact, it shows some missing spots possibly due to its thickness. The permeance was measured for the 1, 2 and 3 layer membrane, which are presented in Table 2. About 50% permeance reduction was achieved with the 1-layer casting. The permeance after the 1st layer is not reduced noticeable, consistent with the observation from the SEM. Figure 13 shows the membrane prepared with two layers. However, this sample was calcined between the layers. Some micro crack was observed and its layer quality was not improved. Thus, we conclude from this study that the two-layer casting appears sufficient to prepare a uniform membrane. As shown in Table 2, the hydrotalcite membrane prepared with the 2-layer casting appears comparable to the existing 100Å membrane based upon the permeance. In the next quarter we will begin the characterization to determine its % of defect before we perform CVD.

As a final note to the slip casting approach, some big particles or agglomerates were found on the surface. A more careful handing of the material during ball milling is recommended for future material preparation.

3. Conclusions

- Hydrotalcite membranes prepared via in-situ impregnation have shown more than 85% reduction in the permeance after four depositions. After the 4th impregnation, the permeance becomes level off. However, major defects in the 0.2-micron size exist.
- Defects present in the membrane prepared via impregnation could be resulted from (i) incomplete coverage, i.e., not accessible by the reagents due to air pocket, or (ii) layer crack during drying. Strategy has been developed to correct these possible sources of problem.
- Hydrotalcite membranes prepared by slip casting have delivered an excellent layer after casting twice and then calcination at 400ºC. SEM examination demonstrates the well-organized deposition of uniform particles in the range of ~500Å. Further, its permeance is comparable with our existing $A1_20_3$ membranes with 100Å pore size. This membrane will be well characterized to qualify for the post treatment by CVD/I.

4. Future Work

In the next quarter, we will continue the membrane synthesis via both impregnation and slip casting. For impregnation, we will attempt to avoid the void pocket during the impregnation. For slip casting, we will perform the defect analysis and then CVD/I to seal the residual opening to form a CO_2-affinity ceramic membrane.

Table 1 Permeance vs. No. of In-situ Crystalization
(Permeance: m^3/m^2/hr/bar at 25°C)

No. of Crystalization	He Permeance	N2 Permeance	Selectivity
0	148.0	82.5	1.79
1st	48.2	24.5	1.97
2nd	28.8	15.1	1.91
3rd	16.5	9.1	1.80
4th	19.1	10.5	1.82

Table 2 Permeance of Membranes prepared via Slip Casting

Sample ID	He Permeance [m^3/m^2/hr/bar]	N2 Permeance [m^3/m^2/hr/bar]	Selectivity
HT 94-02 -1 layer	69.85	33.54	2.08
HT 94-02 -2 layer	65.54	33.74	1.90
HT 94-02 -3 layer	64.81	35.41	1.83
Control M & P 100Å	87	40	2.18

Figure 1 Hydrotalciate Membrane Synthesis via Impregnation

STEP	PURPOSE
1. Interphase contact of reactants	Formation of precipitates as precursors
2. Aging via autoclaving	Enhancing crystal stability and crystallinity
3. Rinsing	Removing impurities

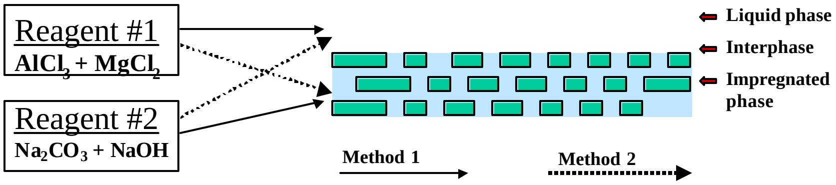
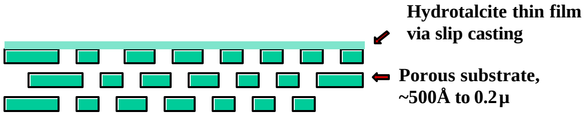


Figure 2 Hydrotalcite Membrane Synthesis via Slip Casting

- Composition of slip, particularly binder/HT ratio.
- Particle size to form porous thin film suitable for CVD backpatching



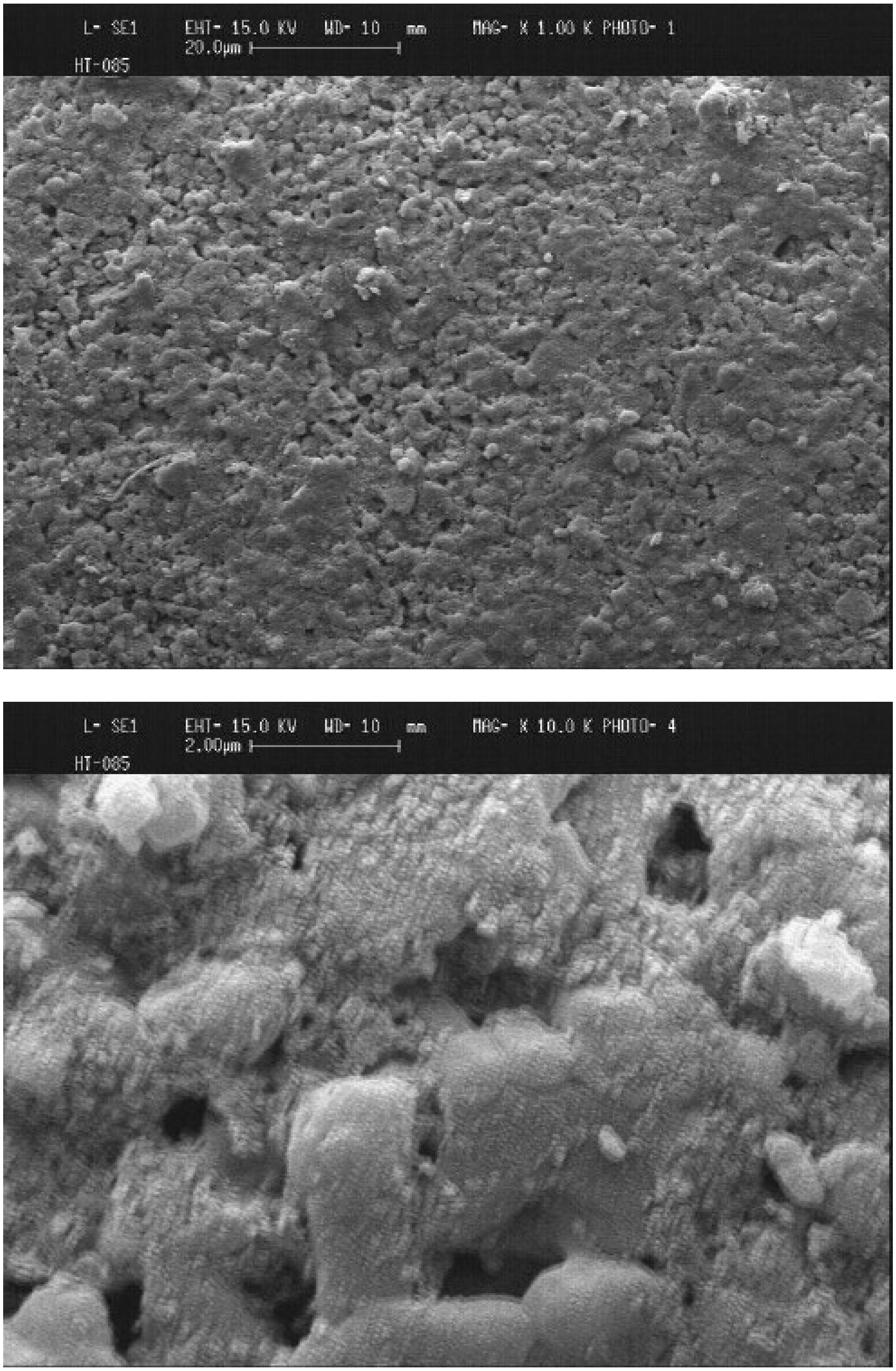


Figure 3 SEM photomicrograph for hydrotalcite membrane prepared Via impregnation: 1st deposition (Top: 1K mag, Bottom: 10K mag)

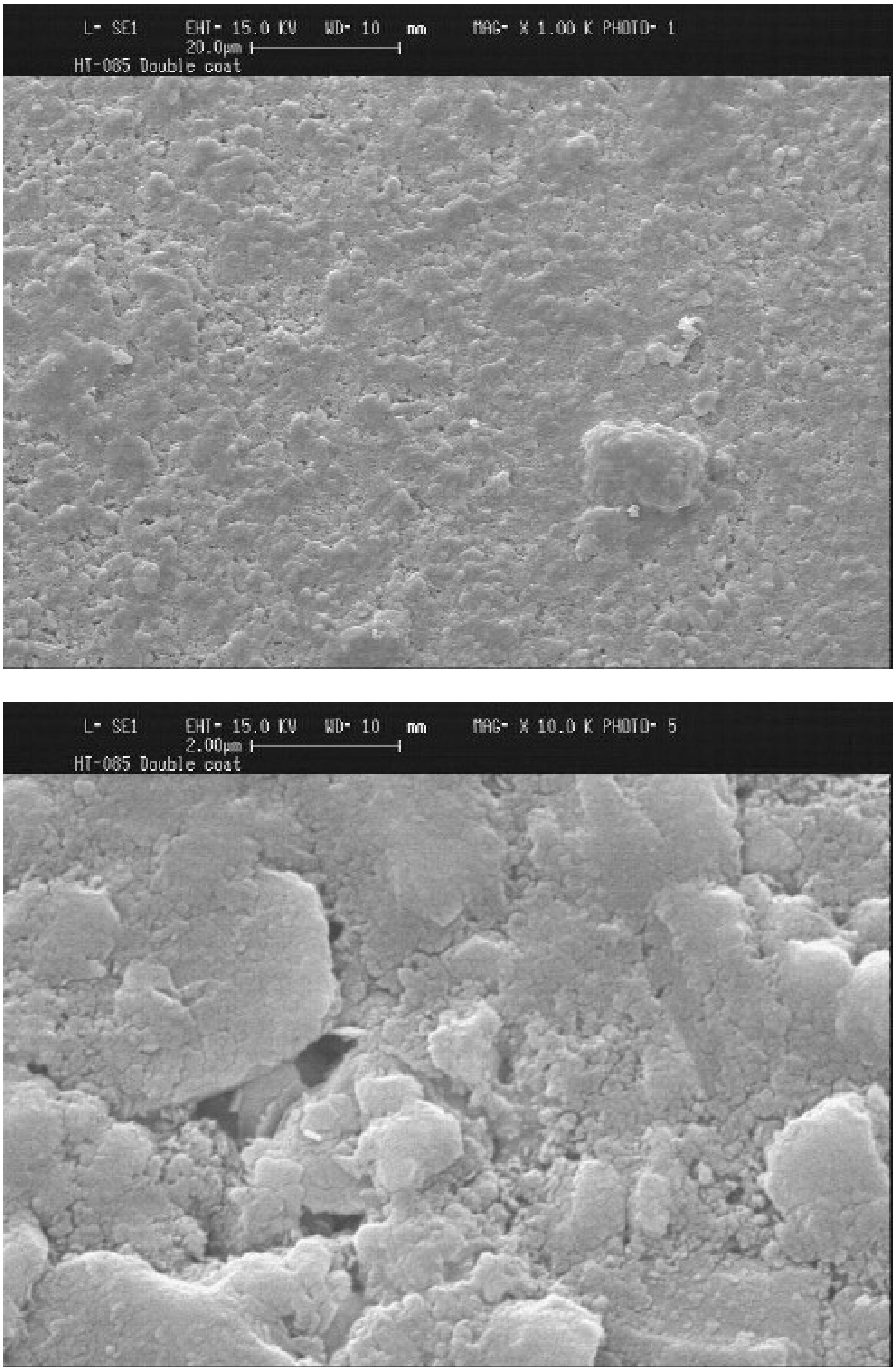


Figure 4 SEM photomicrograph of hydrotalcite membrane prepared via impregnation: 2nd deposition (Top: 1K mag, bottom: 10K mag).

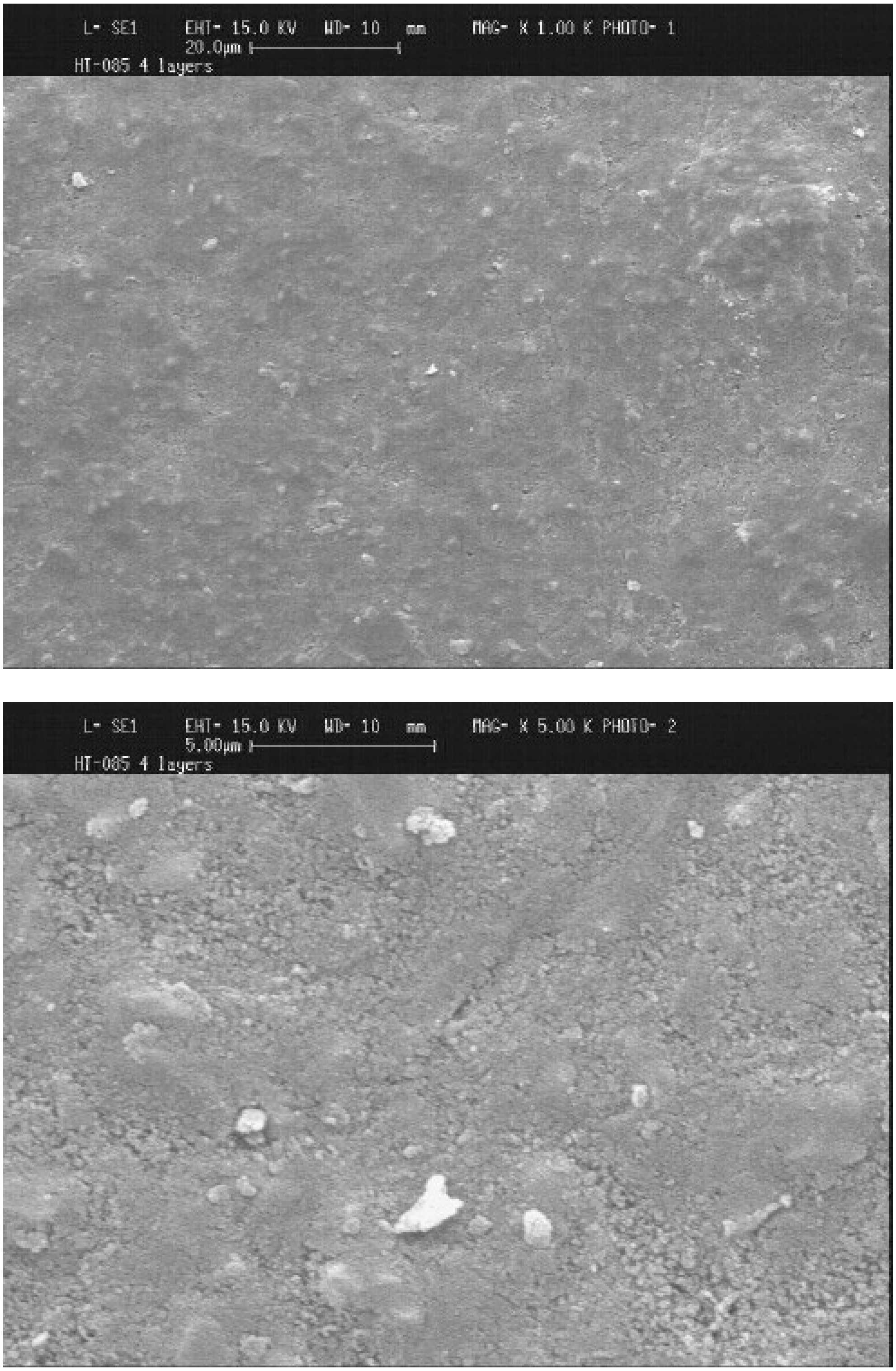


Figure 5a SEM photomicrograph of hydrotalcite membranes prepared from impregnation (4 times). Magnification: 1K top, 5K bottom.

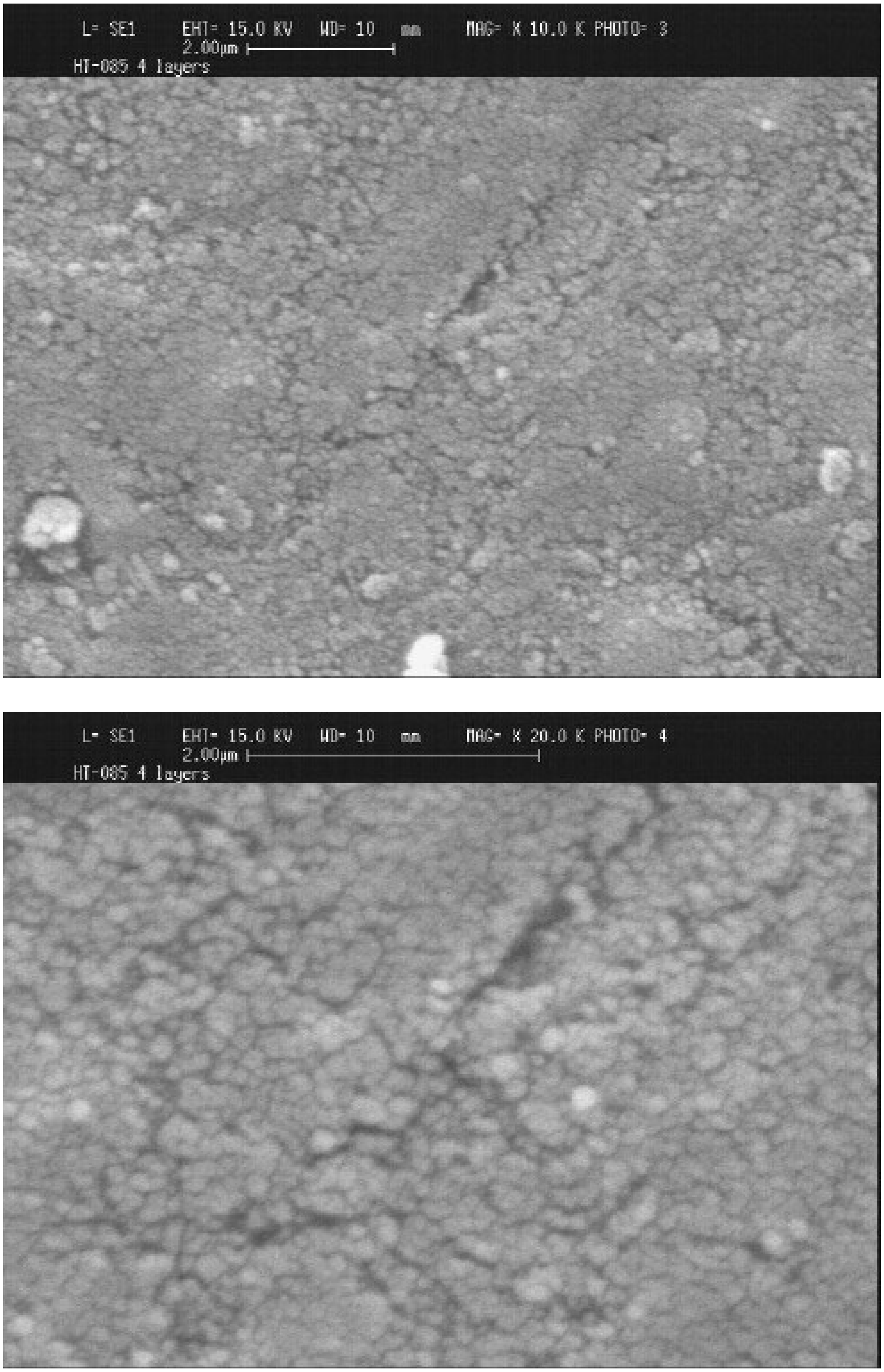


Figure 5b SEM photomicrograph of hydrotalcite membranes prepared from impregnation (4 times). Magnification: 10K top, 20K bottom.

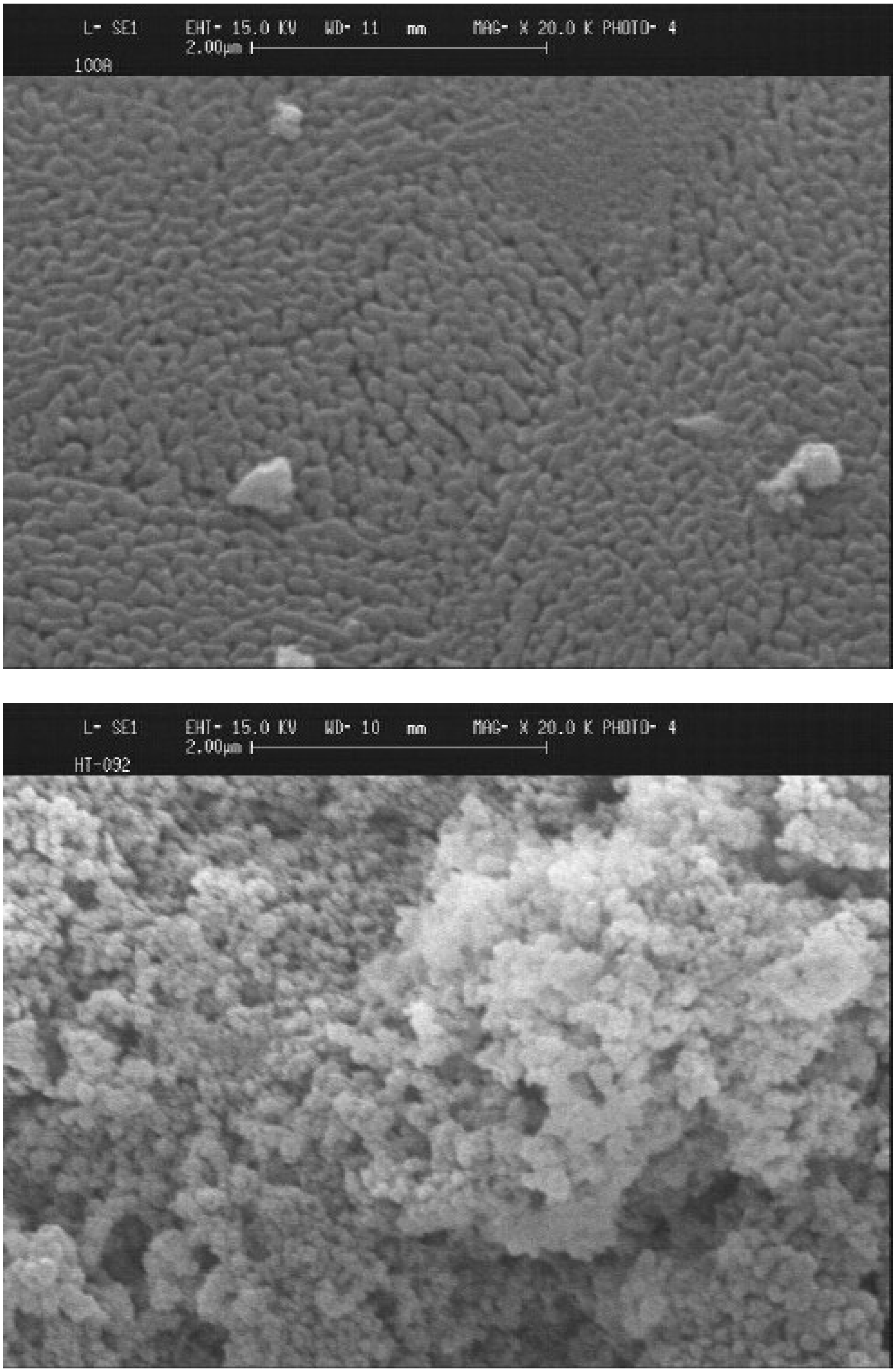


Figure 6 Particle size comparison between M&P's commercial ceramic membrane with 100Å pore size (top) vs hydrotalcite gel prepared by us (bottom).

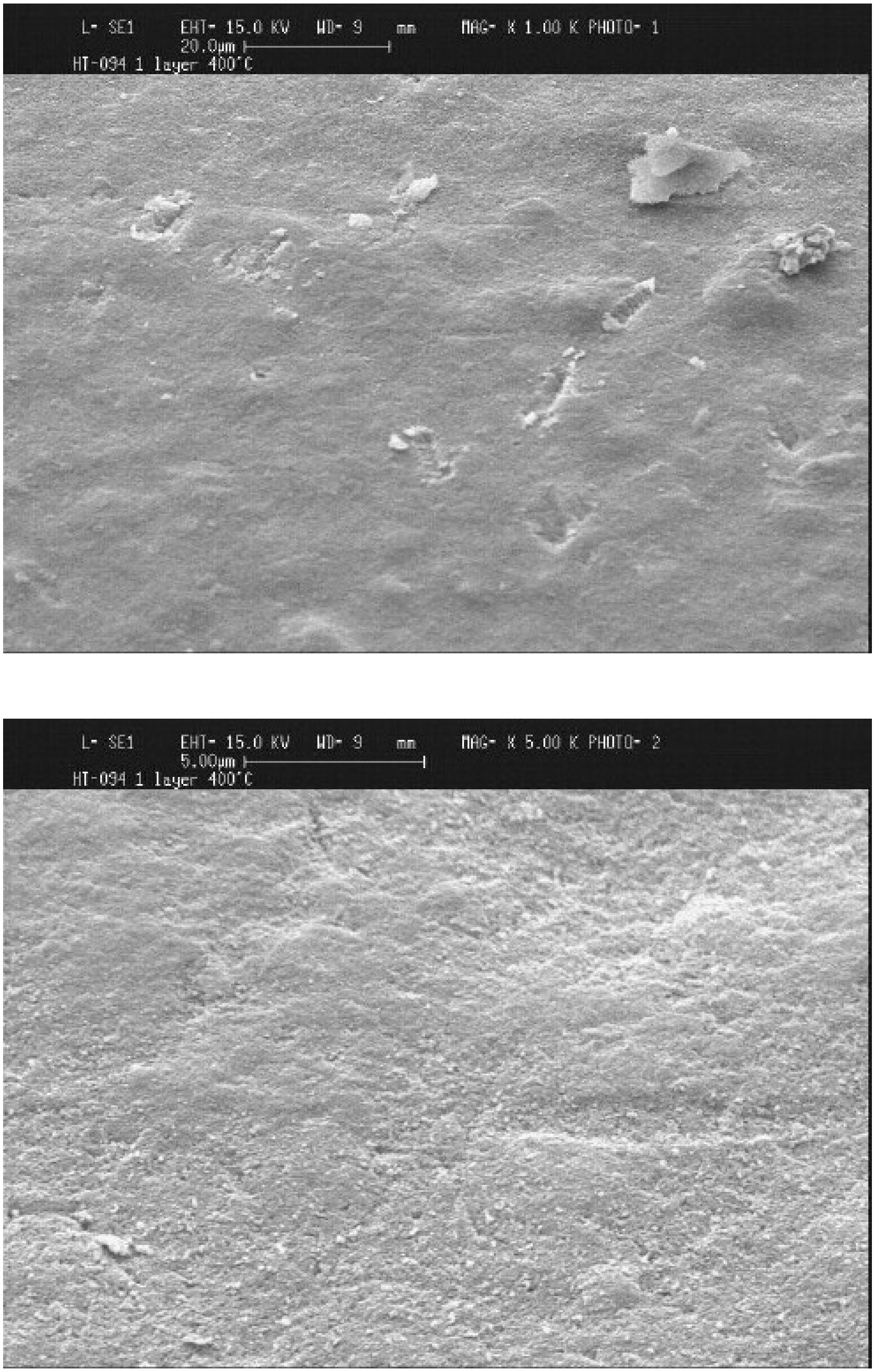


Figure 7 SEM photomicrograph of hydrotalcite membrane prepared from Slip casting: one layer casting and then calcined at 400ºC (Top: 1 K mag, Bottom: 5K)

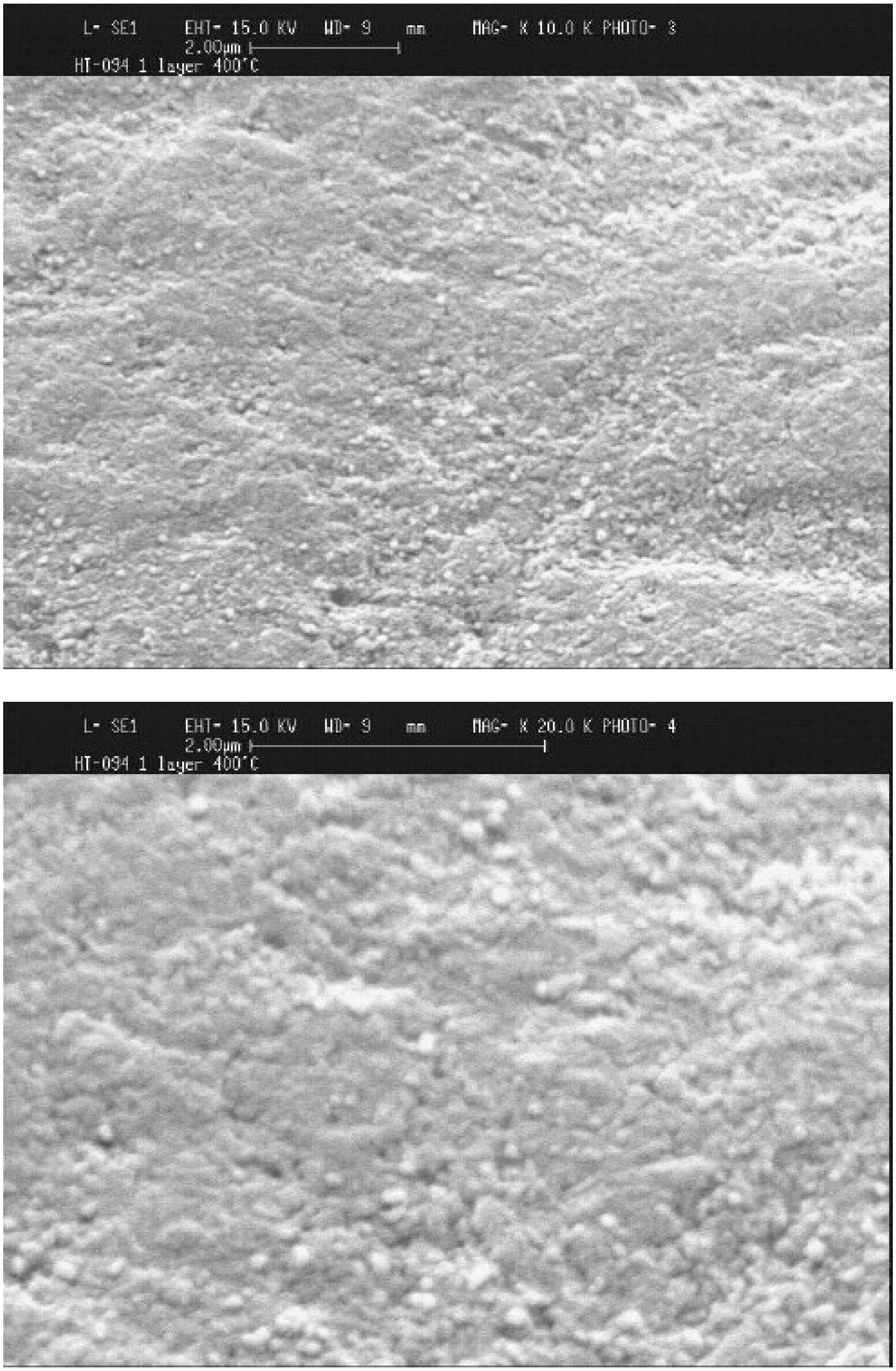


Figure 8 SEM photomicrograph of hydrotalcite membrane prepared from slip casting: one layer casting and then calcined at 400ºC (Top: 10 K mag, Bottom: 20K)

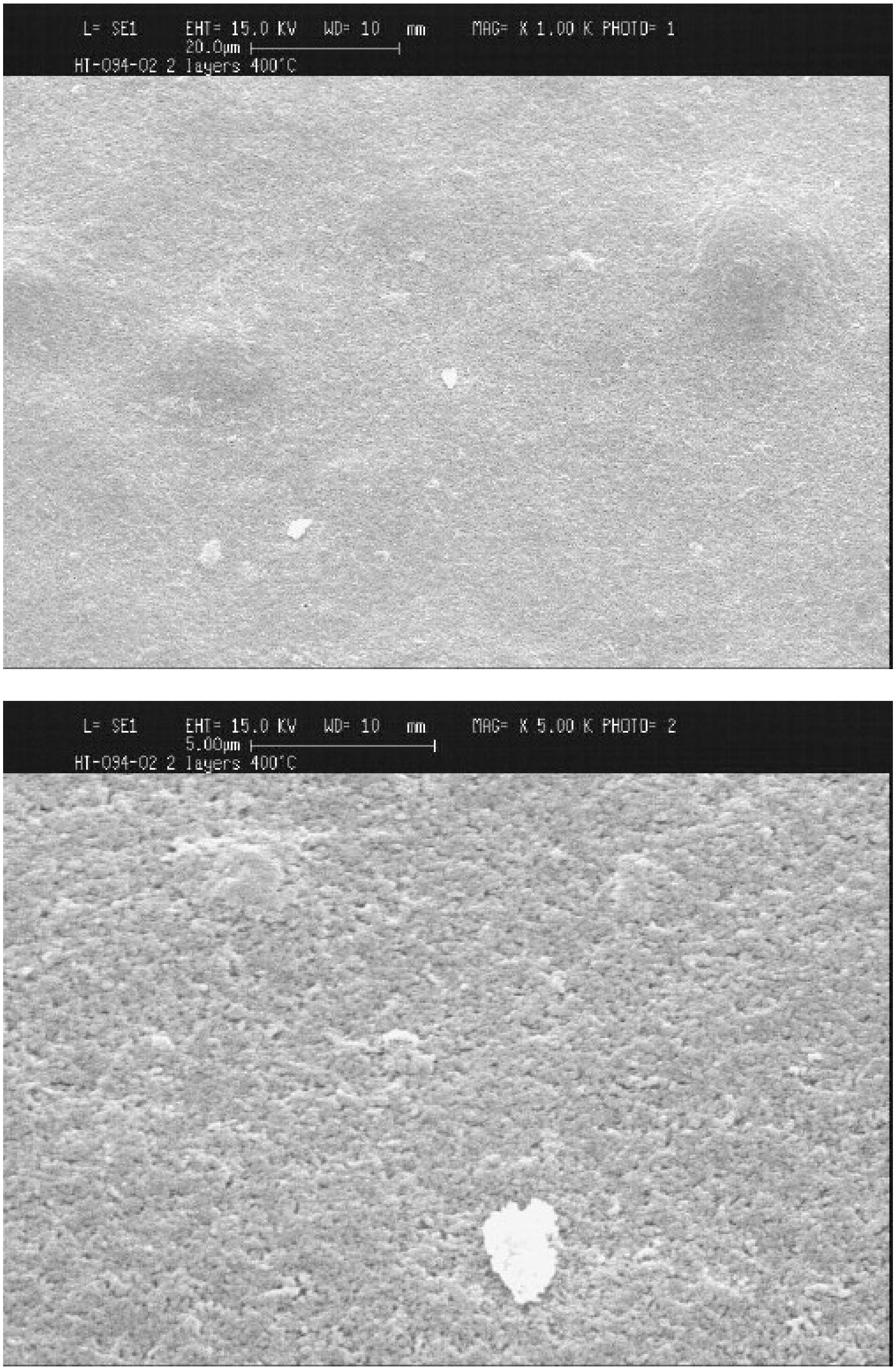


Figure 9 SEM photomicrograph of hydrotalcite membrane prepared from slip casting: two-layer casting and then calcined at 400ºC (Top: 1 K mag, Bottom: 5K mag)

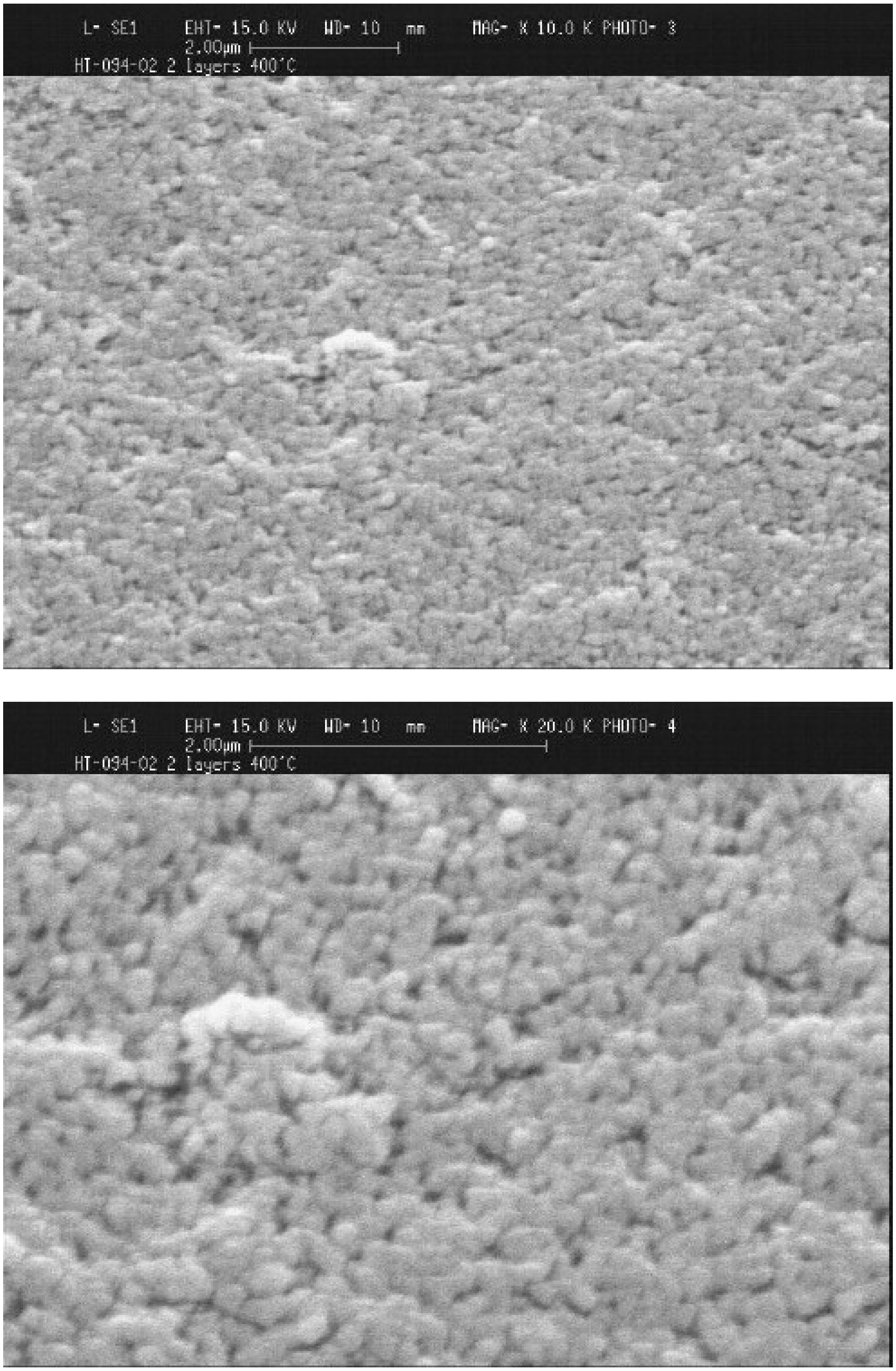


Figure 10 SEM photomicrograph of hydrotalcite membrane prepared from slip casting: two-layer casting and then calcined at 400ºC (Top: 10 K mag, Bottom: 20K mag)

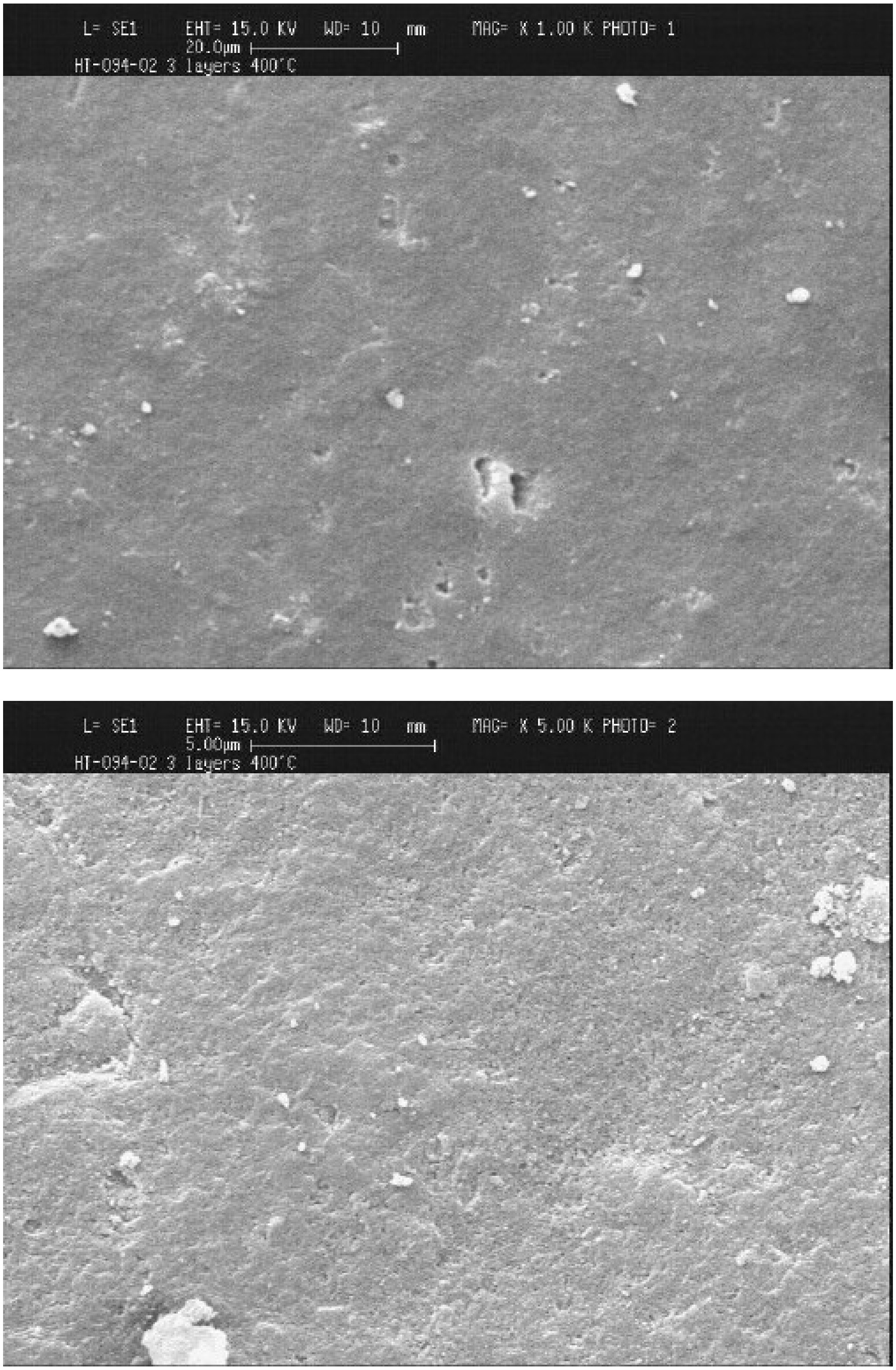


Figure 11 SEM photomicrograph of hydrotalcite membrane prepared from slip casting: three-layer casting and then calcined at 400ºC (Top: 1 K mag, Bottom: 5K mag)

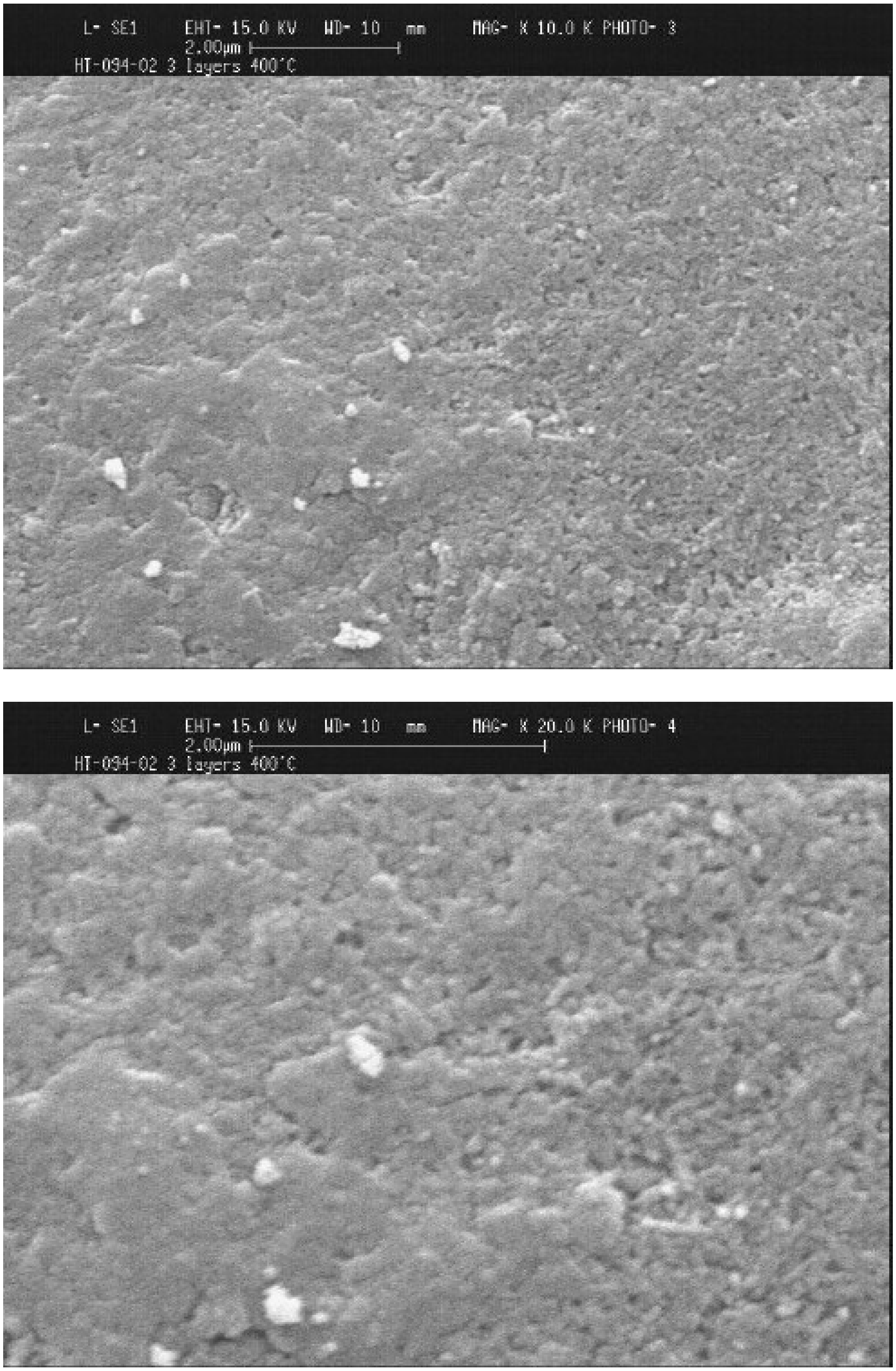


Figure 12 SEM photomicrograph of hydrotalcite membrane prepared from slip casting: three layer casting and then calcined at 400ºC (Top: 10 K mag, Bottom: 20K mag)

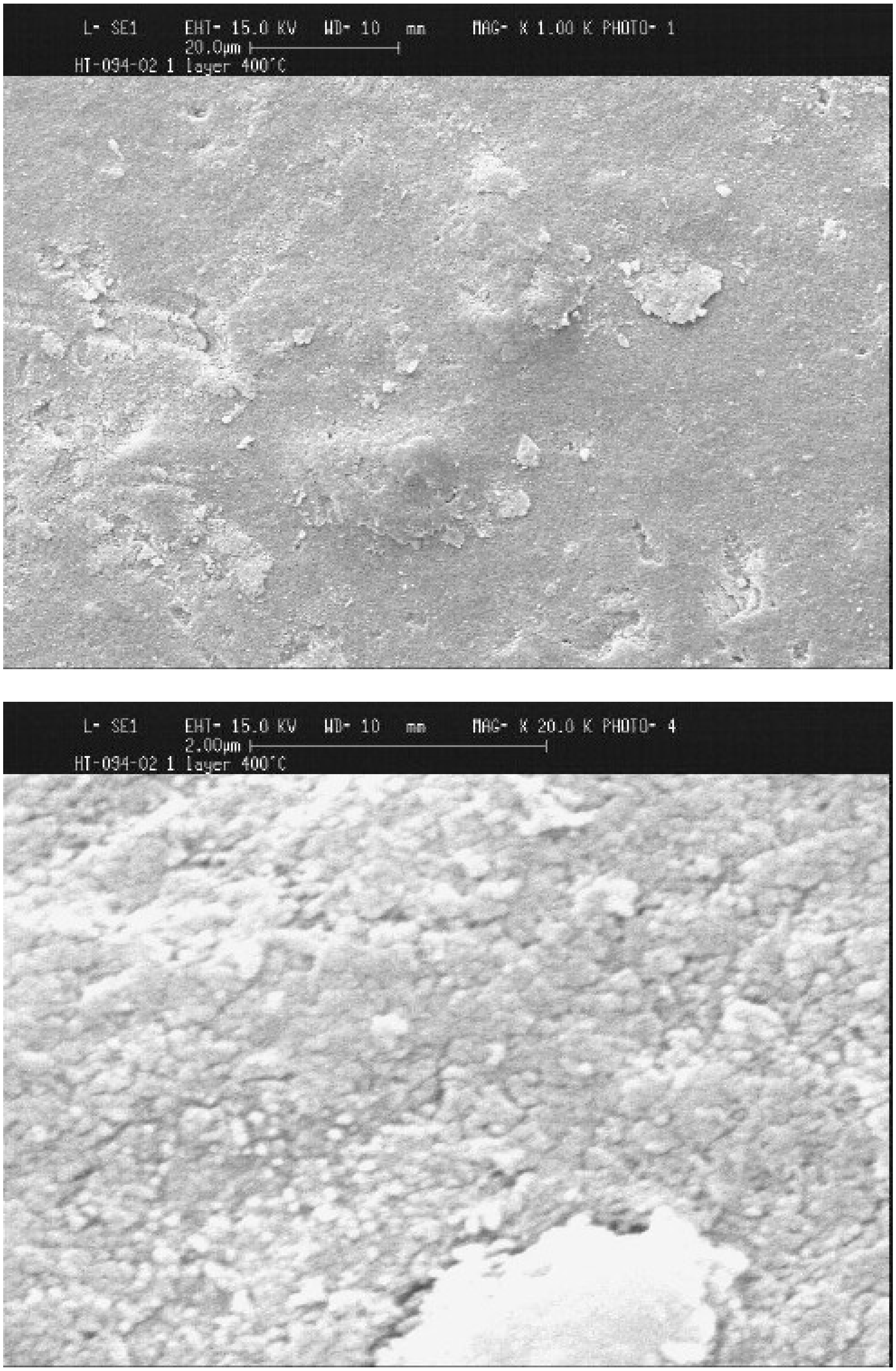


Figure 13 SEM photomicrograph of hydrotalcite membrane prepared from slip casting: one layer casting, calcined at 400ºC, another layer casting and calcined at 400ºC. (Top: 1 K mag, Bottom: 20K)